Supporting Information for “Synthesis of a Novel Hybrid Metal Organic Salt and its Solid-State Transformation.”

Javier Martí-Rujas,* Massimo Cametti.

Contents

1. Experimental

Fig. S1. ORTEP view of the crystal structure of 1 after manually removing the water molecule in order to show the void space left (i.e., pocket). Using a 1.2 Å probe radius, grid spacing of 0.5 Å and considering the contact surface area the void volume corresponds to 1.9 % of the total unit cell volume.

Table. S1 List of all the symmetry operators observed in 1.

2. Single crystal X-ray structure of 2.

Fig. S2. (a) Crystal structure of salt 2 viewed along the b-axis; (b) detailed view of the dication showing the trifurcated weak intramolecular N–H···O hydrogen bonding (only one is showed); (c) view of two [ZnI₄]²⁻ dianions surrounded by K222–H₂⁺ dications. (d) C–H···I interactions observed in 2. Color code: Carbon: green; Nitrogen: blue; Oxygen: red; Nitrogen: grey; Hydrogen: light grey. Weak hydrogen bonding shown as dashed lines.

Table. S2 Relevant distances in molecular salts 1–4.

Fig. S3. Ball and stick model viewed along the a-axis of isostructural crystal structures 2, 3 and 4 (a), (b) and (c) respectively.

Fig. S4. Simulated PXRD pattern of 2 and experimental PXRD pattern of a sample obtained
after grinding K222 and ZnI₂ (1:2 molar ratio) in the presence of a drop of methanol.

**Fig. S5.** Experimental vs simulated from single crystal PXRD patterns of 3 measured at rt. The experimental pattern of the ZnBr₄²⁻ was crystallized from methanol. Clearly, both diffraction patterns show the same crystalline structure.

**Fig. S6.** Experimental PXRD of obtained after crystallization of K222 and ZnI₂ (1:2) in ethanol and simulated of 2 crystallized from methanol. Clearly, both diffraction patterns show the same crystalline structure.

**Fig. S7.** Experimental PXRD corresponding to the solid obtained when ZnI₂ was added into a solution of K222 (MeOH) warmed at 45°C. The diffraction pattern corresponds to that of 2.

**Fig. S8.** Experimental PXRD corresponding to the solid obtained when ZnBr₂ was added into a solution of K222 (MeOH) cooled at 0°C using ice bath. The diffraction pattern corresponds to that of 3.

**Fig. S9.** Experimental PXRD corresponding to the solid obtained when ZnCl₂ was added into a solution of K222 (MeOH) cooled at 0°C using ice bath. The diffraction pattern corresponds to that of 4.

**Fig. S10.** Figure showing the μ-O-based and μ-S clusters based on *ab initio* calculations on the adamantanoid dianion of formula [Zn₄(MeO)₆I₄]²⁻ and [Zn₄(MeS)₆I₄]²⁻ at the HF-3-21G level. The volumes and distances between opposite μ-O(S) atoms are 382.5 Å³ – 4.32 Å and 446.5 Å³ – 5.44 Å for the μ-O and μ-S clusters, respectively. An additional carbon on the alkoxide chain would probably lead to significant sterical clash with the apical I atoms.

**Fig. S11.** ¹H-NMR spectrum of a 2.5 mM solution of 1 in DMSO-d6:acetone-d6 2:1 mixture at 25°C.

**Fig. S12.** Portion of the ¹H-NMR spectrum of a 2.5 mM solution of 1 in DMSO-d6:acetone-d6 2:1 mixture at 25°C. Two groups of signals (labeled ● and ○) can be identified (at ppm δ = 3.60 s, 3.54 t and 2.58 t; δ = 3.79 t, 3.78 t and 3.69 s ) and they can be assigned to the cationic K222–H₂²⁺ of 1 in both its associated ion-pair and its solvated forms.
Fig. S13. $^1$H-NMR spectrum of a 2.5 mM solution of 2 in DMSO-d6:acetone-d6 2:1 mixture at 25°C and magnification of the 4.0-3.6 ppm region.

Fig. S14. Spectral comparison between an equimolar solution of 1 (top) and 2 (bottom) in DMSO-d6:acetone-d6 2:1 mixture at 25°C. Shift of the K222–H$_2^{2+}$ signals are highlighted by the black arrows.
1. Experimental

1.2 X-ray Diffraction Data

Single crystal X-ray diffraction data for 1, 2 and 3 were recorded with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with an Incoatec $\mu$S$_{\text{Cu}}$ microphocus X-ray source (CuK$_\alpha$ radiation, $\lambda = 1.54056$ Å) and with a CCD detector. The low temperature experiments were collected using a Bruker Oxford Cryosystem device. SHELXL$^1$ was used for structure solution and refinement. X-ray powder diffraction experiments were recorded on a Bruker D2 Phaser diffractometer ($\lambda = 1.54056$ Å). The 2θ scan range was 4.7° – 40° with a step size 0.02°. The exposure time was 2s. Simulated PXRD patterns were generated using Mercury Version 3.1 software program. Figures depicting the crystal packing were created using PyMol software.
**Fig. S1.** ORTEP view of the crystal structure of 1 after manually removing the water molecule in order to show the void space left (i.e., pocket). Using a 1.2 Å probe radius, grid spacing of 0.5 Å and considering the contact surface area the void volume corresponds to 1.9 % of the total unit cell volume.

**Table. S1** List of all the symmetry operators observed in 1.

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<th>Detailed Description</th>
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<td>3-fold rotation axis with direction [1, 1, 1] at x, x, x</td>
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<tr>
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<td>y,z,x</td>
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<td>3-fold rotation axis with direction [1, 1, 1] at x, x, x</td>
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<td>3-fold screw axis with direction [1, -1, 1] at x+5/6, -x+1/3, x with screw component [1/3, -1/3, 1/3]</td>
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<tr>
<td>5</td>
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2. Single crystal X-ray structure of 2.

In crystal 2, the K222 is doubly-protonated and adopts the endo-endo type conformation where the N atoms are directed towards the inner cavity of the macrocycle (Figure S1). The O atoms also point inwards the cavity where weak hydrogen bond interaction with the endo N+–H∙∙∙O group is observed. In 2, the nonbonding N∙∙∙N separation (6.340(1) Å) is shorter than that of the empty cryptand (6.871(4) Å). The [ZnI₄]²⁻ anions lying in the 3-fold crystallographic axis have tetrahedral coordination. Two [ZnI₄]²⁻ anions are positioned in a “head-to-head” fashion with intermolecular I∙∙∙I distance of 3.679(1) Å (Figure S1a and S1c). There is a disordered water molecule that is located between two symmetry related dications. Out of the mother liquors, the crystals of 2 are stable at room temperature in contact with air for several days.

Fig. S2. (a) Crystal structure of salt 2 viewed along the b-axis; (b) detailed view of the dication showing the trifurcated weak intramolecular N–H∙∙∙O hydrogen bonding (only one is showed); (c) view of two [ZnI₄]²⁻ dianions surrounded by K222–H₂⁺ dications. (d) C–H∙∙∙I interactions observed in 2. Color code: Carbon: green; Nitrogen: blue; Oxygen: red; Nitrogen: grey; Hydrogen: light grey. Weak hydrogen bonding shown as dashed lines.


Using the same protocol, we set up crystallization experiments using ZnBr₂ and ZnCl₂ instead of ZnI₂. Colorless plate-like crystals precipitated after 1 hour, however the solution was left over a week to allow crystallization to proceed. Single crystal X-ray diffraction showed that an isostructural [ZnBr₄]²⁻ complex (3) to the reported ZnCl₂ version (4),² had been obtained (R-3c).
and therefore, the molecular packing has been maintained in this class of hybrid metal-organic salts.

**Table. S2** Relevant distances in molecular salts 1–4.

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<td>4</td>
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<td>6.376(2)</td>
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<sup>a</sup> C⋯X = I, Br, Cl.

**Fig. S3.** Ball and stick model viewed along the <i>a</i>-axis of isostructural crystal structures 2, 3 and 4 (a), (b) and (c) respectively.
Fig. S4. Simulated PXRD pattern of 2 and experimental PXRD pattern of a sample obtained after grinding K222 and ZnI\(_2\) (1:2 molar ratio) in the presence of a drop of methanol.

Fig. S5. Experimental vs simulated from single crystal PXRD patterns of 3 measured at rt. The experimental pattern of the ZnBr\(_4^{2-}\) was crystallized from methanol. Clearly, both diffraction patterns show the same crystalline structure.
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checkCIF/PLATON (standard)

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. Please wait while processing .... CIF dictionary Interpreting this report

Datablock: 1

Bond precision: C-C = 0.0127 Å  Wavelength=1.5417 Å

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Click on the hyperlinks for more details of the test.

\textbf{Alert level B}

\text{PLAT222\_ALERT\_3\_B} Large Non-Solvent H Uiso(max)/Uiso(min) .. 8.0 Ratio

\textbf{Alert level C}

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\text{PLAT029\_ALERT\_3\_C} \_diffrn\_measured\_fraction\_theta\_full Low ....... 0.969
\text{PLAT041\_ALERT\_1\_C} Calc. and Reported SumFormula Strings Differ Please Check
\text{PLAT068\_ALERT\_1\_C} Reported F000 Differs from Calcd (or Missing)...
Please Check
\text{PLAT090\_ALERT\_3\_C} Poor Data / Parameter Ratio (Zmax > 18) ........ 9.41
\text{PLAT230\_ALERT\_2\_C} Hirshfeld Test Diff for C3 -- C4 .. 5.3
\text{PLAT245\_ALERT\_2\_C} U(iso) H101 Smaller than U(eq) N1 by ...
0.023 AngSq
\text{PLAT342\_ALERT\_3\_C} Low Bond Precision on C-C Bonds ............ 0.0127 Ang.

\textbf{Alert level G}

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Atom count from the \_atom\_site data: C24 H56 I4 N2 O12.3 Zn4

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From the CIF: \_chemical\_formula\_sum C24 H58 I4 N2 O12 Zn4

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atom Z*formula cif sites diff
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I 16.00 16.00 0.00
N 8.00 8.00 0.00
Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

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# start Validation Reply Form
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; PROBLEM: Large Non-Solvent H Uiso(max)/Uiso(min) .. 8.0 Ratio
 RESPONSE: ...

; # end Validation Reply Form
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the “special_details” fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (Acta Crystallographica, Journal of Applied)
Publication of your CIF in other journals

Please refer to the Notes for Authors of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock 1 - ellipsoid plot
**checkCIF/PLATON (standard)**

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The following ALERTS were generated. Each ALERT has the format

**test-name_ALERT_alert-type_alert-level**

Click on the hyperlinks for more details of the test.

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  - Absorption correction given as Multi-scan

- **PLAT041_ALERT_1_C** Calc. and Reported SumFormula Strings Differ
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- **PLAT068_ALERT_1_C** Reported F000 Differs from Calcd (or Missing)...
  - Please Check

- **PLAT094_ALERT_2_C** Ratio of Maximum / Minimum Residual Density .... 2.40

- **PLAT222_ALERT_3_C** Large Non-Solvent H Uiso(max)/Uiso(min) .. 6.5 Ratio

- **PLAT342_ALERT_3_C** Low Bond Precision on C-C Bonds ............ 0.0157 Ang.

- **FORMU01_ALERT_2_G** There is a discrepancy between the atom counts in the _chemical_formula_sum and the formula from the _atom_site*
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- **CELLZ01_ALERT_1_G** Difference between formula and atom_site contents detected.

- **CELLZ01_ALERT_1_G** WARNING: H atoms missing from atom site list. Is this intentional?
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  - From the CIF: _chemical_formula_sum C18 H40 I4 N2 O6.17 Zn
  - TEST: Compare cell contents of formula and atom_site data

- **PLAT002_ALERT_2_G** Number of Distance or Angle Restraints on AtSite
  - 4 Note

- **PLAT005_ALERT_5_G** No _iucr_refine_instructions_details in the CIF
  - Please Do!

- **PLAT072_ALERT_2_G** SHELXL First Parameter in WGHT Unusually Large. 0.10
PLAT083 ALERT 2 G SHELXL Second Parameter in WGHT Unusually Large. 170.68
PLAT152 ALERT 1 G The Supplied and Calc. Volume s.u. Differ by ...
4 Units
PLAT302 ALERT 4 G Anion/Solvent Disorder .............. Percentage =
6 Note
PLAT311 ALERT 2 G Isolated Disordered Oxygen Atom (No H's ?) ..... O7 Check
PLAT764 ALERT 4 G Overcomplete CIF Bond List Detected (Rep/Expd) .
1.13 Ratio
PLAT794 ALERT 5 G Tentative Bond Valency for Zn1 (II) ...... 2.02 Note
PLAT860 ALERT 3 G Number of Least-Squares Restraints ............ 2 Note

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
13 ALERT level G = General information/check it is not something unexpected

6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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PLATON version of 18/09/2013; check.def file version of 12/09/2013
Datablock 2 - ellipsoid plot

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. Please wait while processing ....

Datablock: 3

Bond precision: C-C = 0.0067 A  Wavelength=1.54178

Cell: a=11.0600(6)  b=11.0600(6)  c=78.221(5)

alpha=90  beta=90  gamma=120

Temperature: 100 K
<table>
<thead>
<tr>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>8286.4(12)</td>
</tr>
<tr>
<td>Space group</td>
<td>R -3 c</td>
</tr>
<tr>
<td>Hall group</td>
<td>-R 3 2&quot;c</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>2(C18 H38 N2 O6), 2(Br4 Zn), O ?</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C36 H76 Br8 N4 O13 Zn2</td>
</tr>
<tr>
<td>Mr</td>
<td>1542.99</td>
</tr>
<tr>
<td>Dx, g cm-3</td>
<td>1.855</td>
</tr>
<tr>
<td>Z</td>
<td>6</td>
</tr>
<tr>
<td>Mu (mm-1)</td>
<td>8.320</td>
</tr>
<tr>
<td>F000</td>
<td>4584.0</td>
</tr>
<tr>
<td>F000'</td>
<td>4541.18</td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>13,13,92</td>
</tr>
<tr>
<td>Nref</td>
<td>1632</td>
</tr>
<tr>
<td>Tmin,Tmax</td>
<td>0.576,0.716</td>
</tr>
<tr>
<td>Tmin'</td>
<td>0.296</td>
</tr>
<tr>
<td>Correction method= MULTI-SCAN</td>
<td></td>
</tr>
<tr>
<td>Data completeness= 0.994</td>
<td>Theta(max)= 66.390</td>
</tr>
<tr>
<td>R(reflections)= 0.0344( 1439)</td>
<td>wR2(reflections)= 0.1019( 1622)</td>
</tr>
<tr>
<td>S = 1.093</td>
<td>Npar= 100</td>
</tr>
</tbody>
</table>

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level. Click on the hyperlinks for more details of the test.

**Alert level B**

**PLAT306 ALERT 2 B** Isolated Oxygen Atom (H-atoms Missing ?) .......... O1S Check

**Alert level C**

**ABSTY02 ALERT 1 C** An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as Multi-scan

**CHEMW03 ALERT 2 C** The ratio of given/expected molecular weight as
calculated from the _atom_site* data lies outside
the range 0.99 <> 1.01
From the CIF: _cell_formula_units_Z  12
From the CIF: _chemical_formula_weight  781.53
TEST: Calculate formula weight from _atom_site*
atom  mass  num  sum
C  12.01  18.00  216.20
H  1.01  38.00  38.30
N  14.01  2.00  28.01
O  16.00  6.50  103.99
Zn  65.39  1.00  65.39
Br  79.90  4.00  319.62
Calculated formula weight  771.52

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in
_thechemical_formula_sum and the formula from the _atom_site*
data.
Atom count from _chemical_formula_sum: C18 H40 Br4 N2 O7
Zn1
Atom count from the _atom_site data:  C18 H38 Br4 N2 O6.5 Zn1
CELLZ01_ALERT_1_G Difference between formula and atom_site contents
detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
symmetry error - see SYMMG tests
From the CIF: _cell_formula_units_Z  12
From the CIF: _chemical_formula_sum  C18 H40 Br4 N2 O7 Zn
TEST: Compare cell contents of formula and atom_site data
atom  Z*formula  cif sites diff
C  216.00  216.00  0.00
H  480.00  456.00  24.00
Br  48.00  48.00  0.00
N  24.00  24.00  0.00
O  84.00  78.00  6.00
Zn  12.00  12.00  0.00

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite
4 Note
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF
Please Do !
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ............
0.50 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually
Large.  35.49
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...
4 Units
PLAT434_ALERT_2_G Short Inter HL...HL Contact  Br1  ..  Br1  ...
3.55 Ang.
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .
1.13 Ratio
PLAT794_ALERT_5_G Tentative Bond Valency for Zn3  (II) ..... 
1.94 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............
2 Note
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Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

# start Validation Reply Form
_vrf.PLAT306_test_trigonal
; PROBLEM: Isolated Oxygen Atom (H-atoms Missing ?) ....... O1S Check
RESPONSE: ...
;
# end Validation Reply Form

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Datablock 3 - ellipsoid plot