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

Javier Martí-Rujas,* Massimo Cametti.

Contents

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.

Fig. S6. Experimental PXRD of obtained after crystallization of K222 and ZnI_2 (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 ZnI_2 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 $ZnBr_2$ 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 $ZnCl_2$ 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 $[Zn_4(MeO)_6I_4]^{2-}$ and $[Zn_4(MeS)_6I_4]^{2-}$ at the HF-3-21G level. The volumes and distances between opposite μ-O(S) atoms 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. ^{1}H-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 ^{1}H-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–H_2^{2+} 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 IμS$_{Cu}$ microphocus X-ray source (CuK_α radiation, λ = 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 (λ = 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.

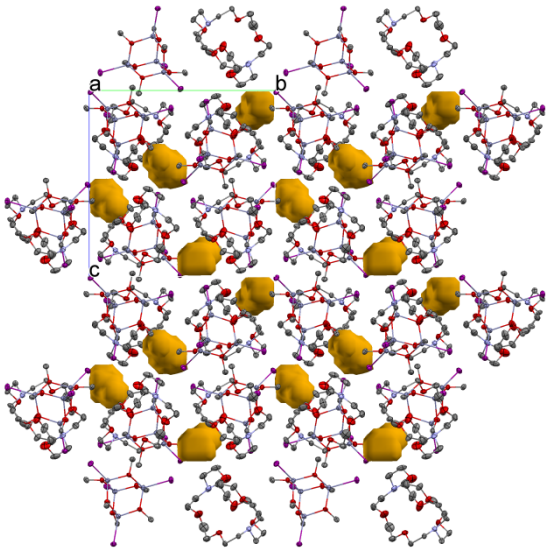

Fig. S1. ORTEP view of the crystal structure of **1** after manually removing the water molecule in order to show the void space left (i.e., pocket). Using a 1.2 Å probe radius, grid spacing of 0.5 Å and considering the contact surface area the void volume corresponds to 1.9 % of the total unit cell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

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

Number	Symm. Op.	Description	Detailed Description	Order	Type
1	x,y,z	Identity	Identity	1	1
2	z,x,y	Rotation axis (3-fold)	3-fold rotation axis with direction [1, 1, 1] at x, x, x	3	3
3	y,z,x	Rotation axis (3-fold)	3-fold rotation axis with direction [1, 1, 1] at x, x, x	3	3
4	1/2-y,-z,1/2+x	Screw axis (3-fold)	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]	3	3
5	1/2+z,1/2-x,-y	Rotation axis (3-fold)	3-fold rotation axis with direction [1, -1, 1] at x+1/2, -x, x	3	3
6	-y,1/2+z,1/2-x	Screw axis (3-fold)	3-fold screw axis with direction [1, -1, -1] at x+1/6, -x+1/6, -x with screw component [-1/3, 1/3, 1/3]	3	3
7	1/2-z,-x,1/2+y	Rotation axis (3-fold)	3-fold rotation axis with direction [1, -1, -1] at x+1/2, -x+1/2, -x	3	3
8	-z,1/2+x,1/2-y	Rotation axis (3-fold)	3-fold rotation axis with direction [1, 1, -1] at x, x+1/2, -x	3	3
9	1/2+y,1/2-z,-x	Screw axis (3-fold)	3-fold screw axis with direction [1, 1, -1] at x+1/3, x+1/6, -x with screw component [1/3, 1/3, -1/3]	3	3
10	1/2+x,1/2-y,-z	Screw axis (2-fold)	2-fold screw axis with direction [1, 0, 0] at x, 1/4, 0 with screw component [1/2, 0, 0]	2	2
11	-x,1/2+y,1/2-z	Screw axis (2-fold)	2-fold screw axis with direction [0, 1, 0] at 0, y, 1/4 with screw component [0, 1/2, 0]	2	2
12	1/2-x,-y,1/2+z	Screw axis (2-fold)	2-fold screw axis with direction [0, 0, 1] at 1/4, 0, z with screw component [0, 0, 1/2]	2	2

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 $[ZnI_4]^{2-}$ anions lying in the 3-fold crystallographic axis have tetrahedral coordination. Two $[ZnI_4]^{2-}$ 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.

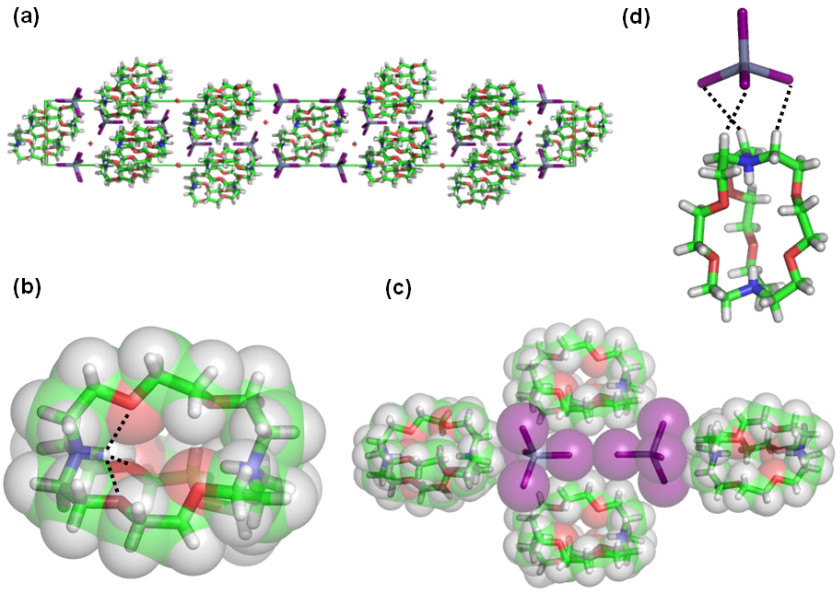

Fig. S2. (a) Crystal structure of salt **2** viewed along the *b*-axis; (b) detailed view of the dication showing the trifurcated weak intramolecular N–H···O hydrogen bonding (only one is showed); (c) view of two $[ZnI_4]^{2-}$ dianions surrounded by K222–H_2^{2+} dications. (d) C–H···I interactions observed in **2**. Color code: Carbon: green; Nitrogen: blue; Oxygen: red; Nitrogen: grey; Hydrogen: light grey. Weak hydrogen bonding shown as dashed lines.

3. Single crystal X-ray structure of 3.

Using the same protocol, we set up crystallization experiments using $ZnBr_2$ and $ZnCl_2$ instead of ZnI_2. 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 $[ZnBr_4]^{2-}$ complex (**3**) to the reported $ZnCl_2$ 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**.

Crystal	C–H···X[a] (Å)	Zn···Zn (Å)	N···N (Å)
1	4.009(9)	-	6.124(9)
2	3.95(1)	8.823(2)	6.34(1)
3	3.705(5)	8.317(1)	6.380(2)
4	3.770(2)	8.0269(8)	6.376(2)

[a] C···X = I, Br, Cl.

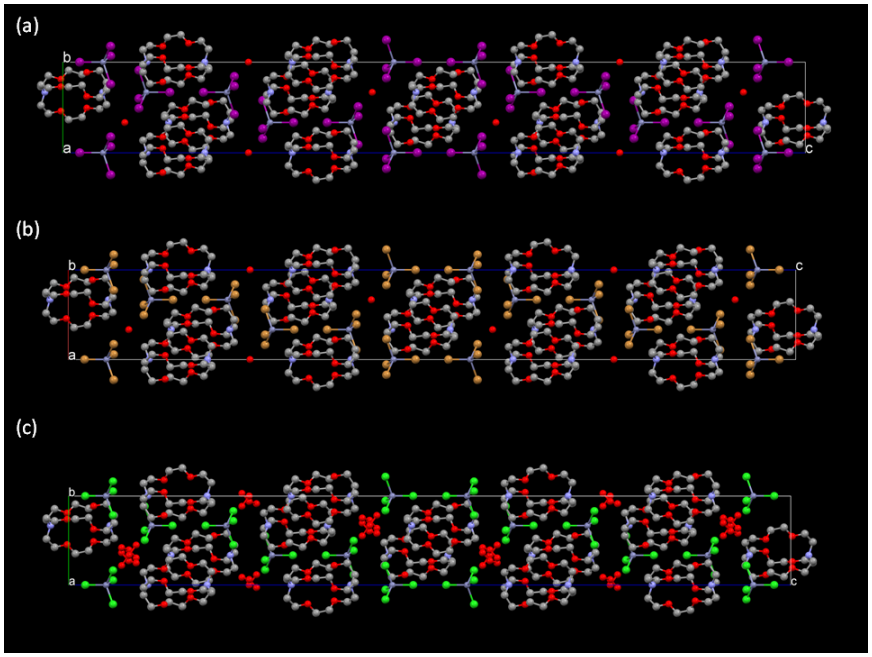

Fig. S3. Ball and stick model viewed along the *a*-axis of isostructural crystal structures **2**, **3** and **4** (a), (b) and (c) respectively.

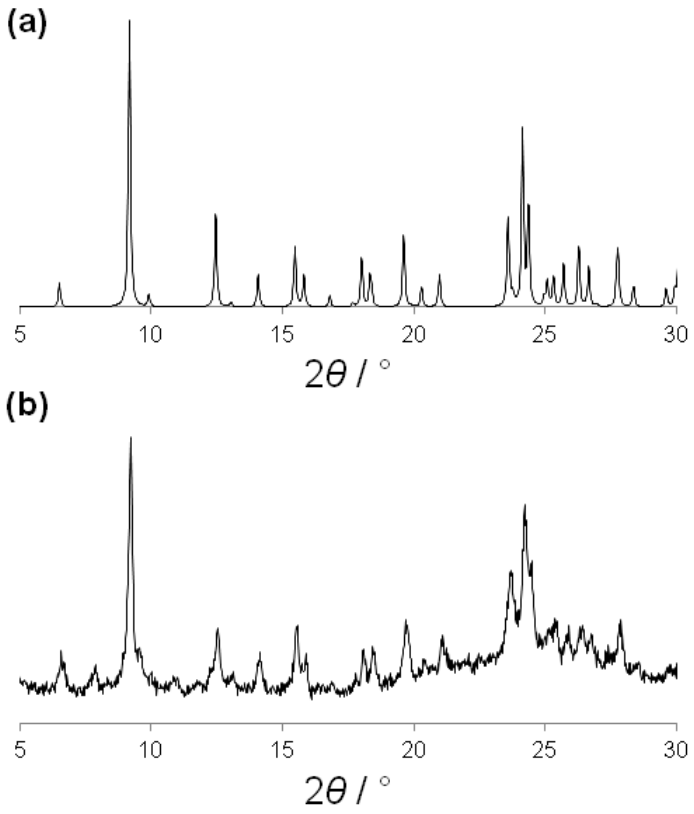

Fig. S4. Simulated PXRD pattern of **2** and experimental PXRD pattern of a sample obtained after grinding K222 and ZnI_2 (1:2 molar ratio) in the presence of a drop of methanol.

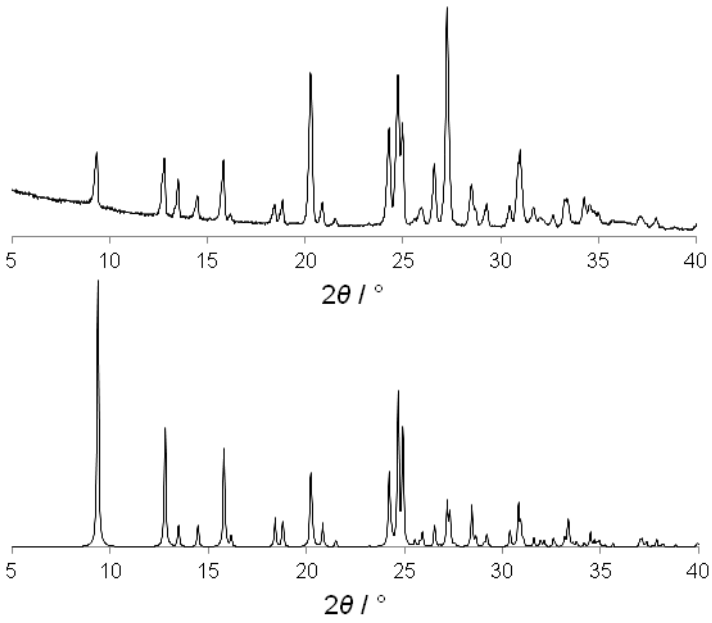

Fig. S5. Experimental vs simulated from single crystal PXRD patterns of **3** measured at rt. The experimental pattern of the $ZnBr_4^{2-}$ was crystallized from methanol. Clearly, both diffraction patterns show the same crystalline structure.

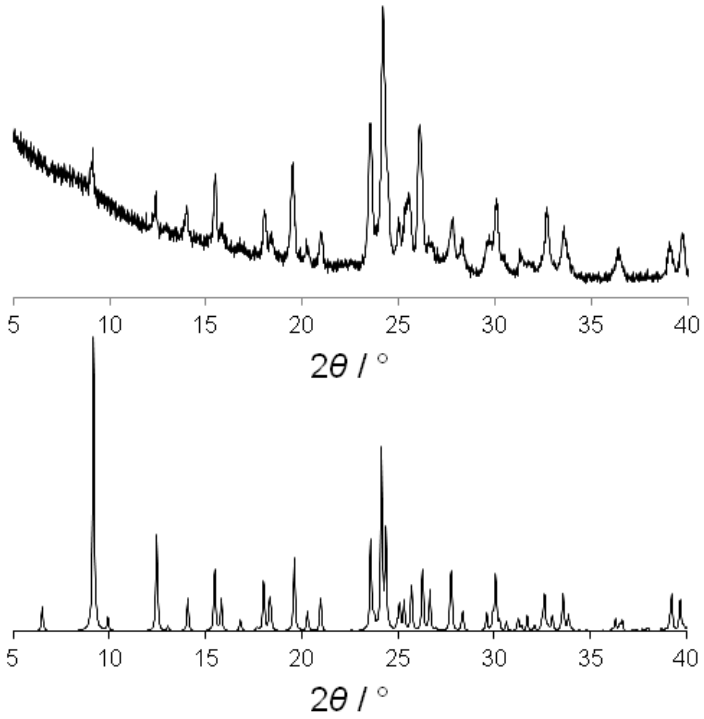

Fig. S6. Experimental PXRD of obtained after crystallization of K222 and ZnI_2 (1:2) in ethanol and simulated of **2** crystallized from methanol. Clearly, both diffraction patterns show the same crystalline structure.

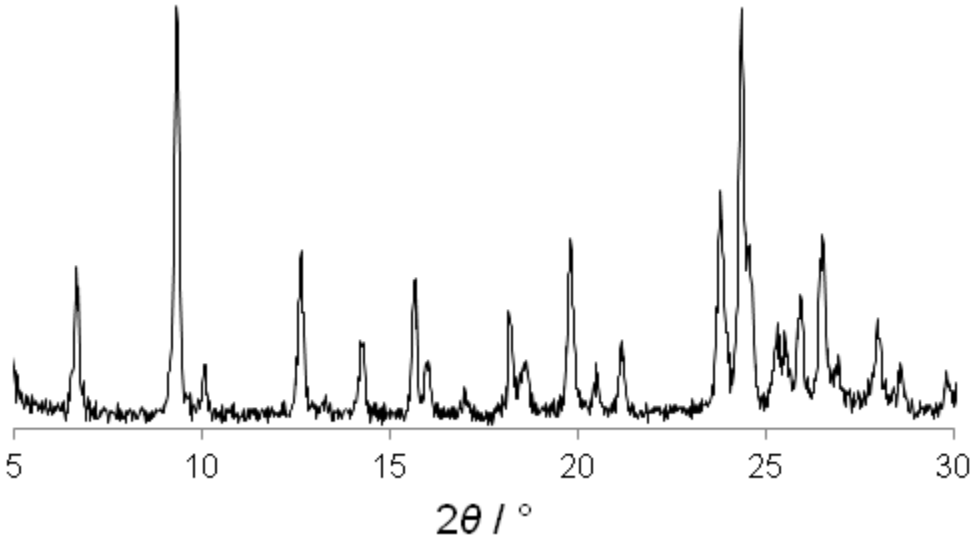

Fig. S7. Experimental PXRD corresponding to the solid obtained when ZnI_2 was added into a solution of K222 (MeOH) warmed at 45°C. The diffraction pattern corresponds to that of **2**.

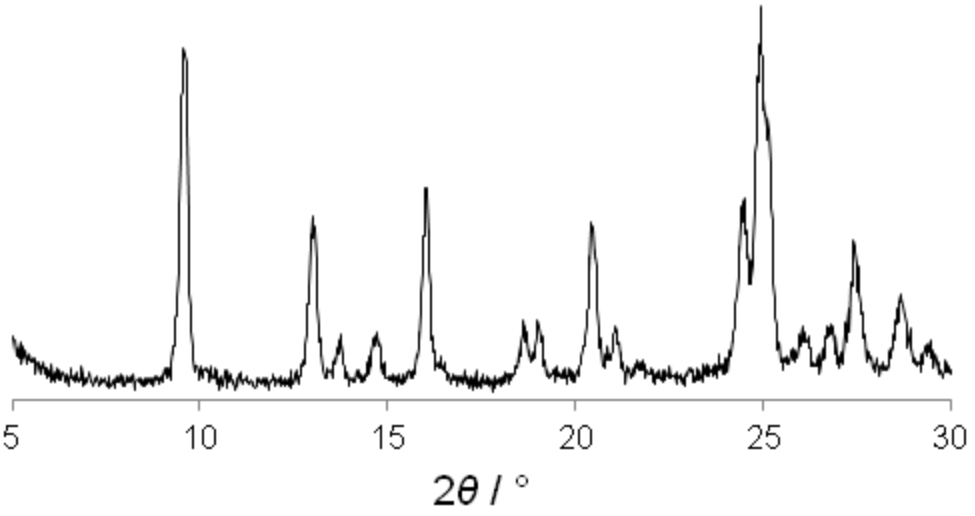

Fig. S8. Experimental PXRD corresponding to the solid obtained when $ZnBr_2$ was added into a solution of K222 (MeOH) cooled at 0°C using ice bath. The diffraction pattern corresponds to that of **3**.

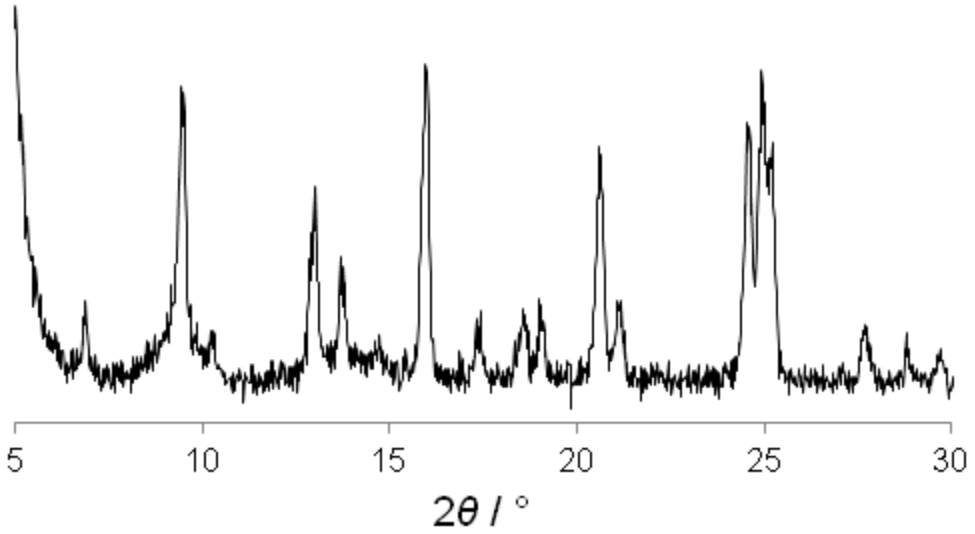

Fig. S9. Experimental PXRD corresponding to the solid obtained when $ZnCl_2$ was added into a solution of K222 (MeOH) cooled at 0°C using ice bath. The diffraction pattern corresponds to that of **4**.

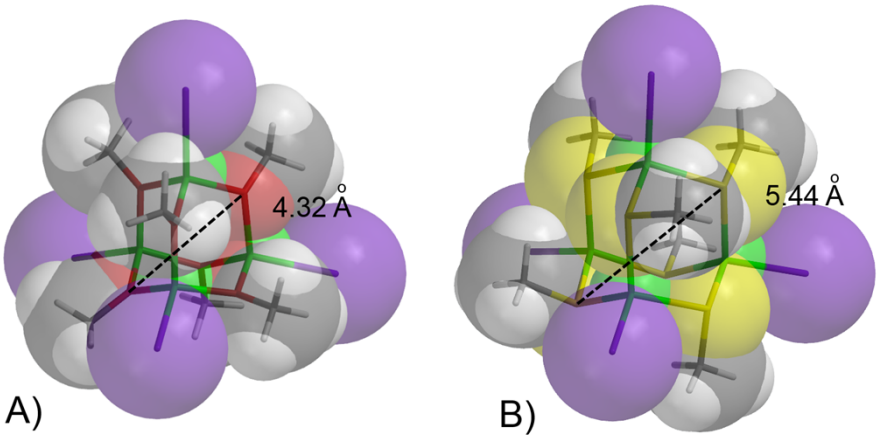

Fig. S10. Figure showing the μ-O-based and μ-S clusters based on *ab initio* calculations on the adamantanoid dianion of formula $[Zn_4(MeO)_6I_4]^{2-}$ and $[Zn_4(MeS)_6I_4]^{2-}$ at the HF-3-21G level. The volumes and distances between opposite μ-O(S) atoms 382.5 Å3 – 4.32 Å and 446.5 Å3 – 5.44 Å for 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.

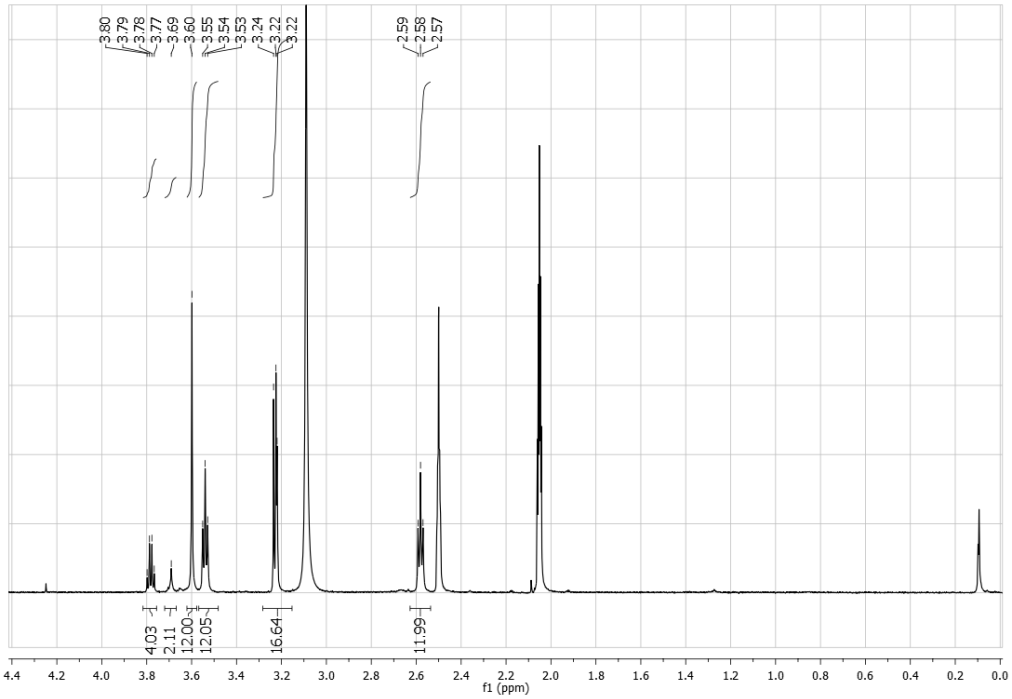

Fig. S11. [1]H-NMR spectrum of a 2.5 mM solution of **1** in DMSO-d6:acetone-d6 2:1 mixture at 25°C.

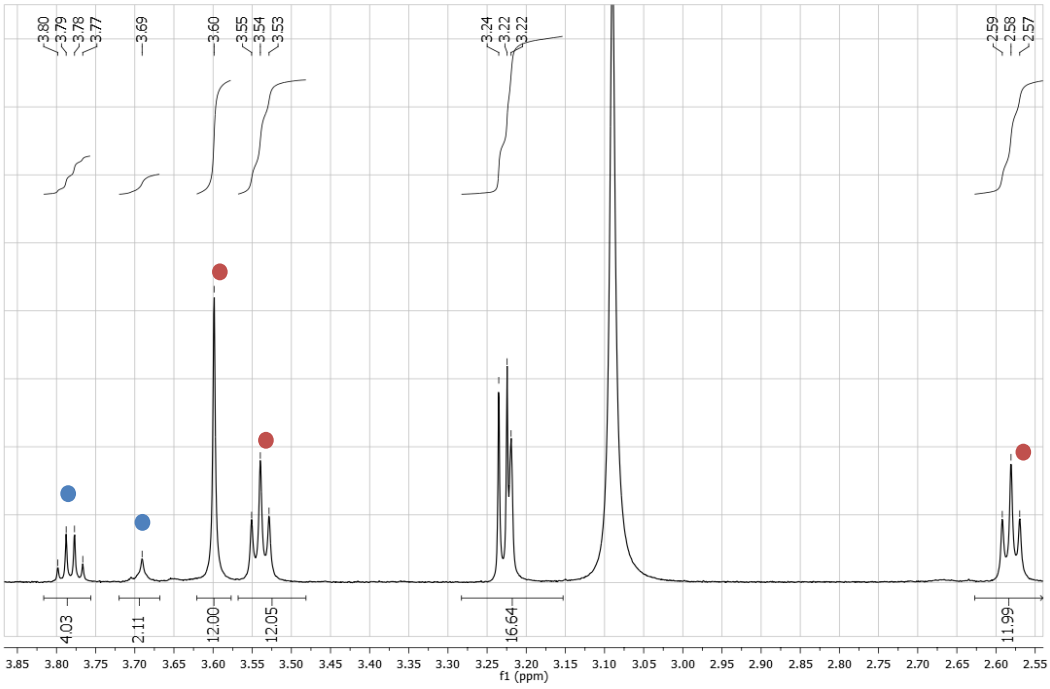

Fig. S12. Portion of the [1]H-NMR spectrum of a 2.5 mM solution of **1** in DMSO-d6:acetone-d6 2:1 mixture at 25°C. Two groups of signals (labeled ● and ●) can be identified (at ppm δ = 3.60 s, 3.54 t and 2.58 t; δ = 3.79 t, 3.78 t and 3.69 s) and they can be assigned to the cationic K222–H_2^{2+} of **1** in both its associated ion-pair and its solvated forms.

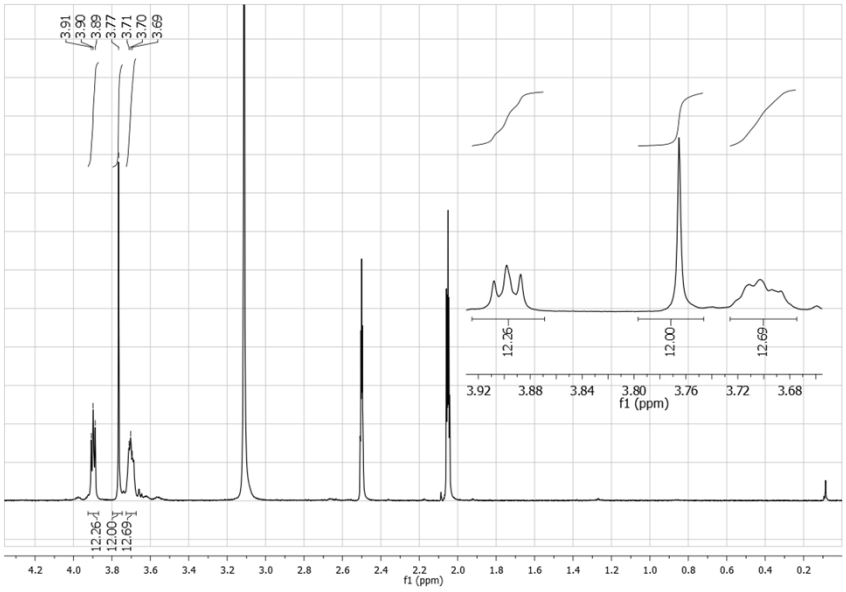

Fig. S13. ^{1}H-NMR spectrum of a 2.5 mM solution of **2** in DMSO-d6:acetone-d6 2:1 mixture at 25°C and magnification of the 4.0-3.6 ppm region.

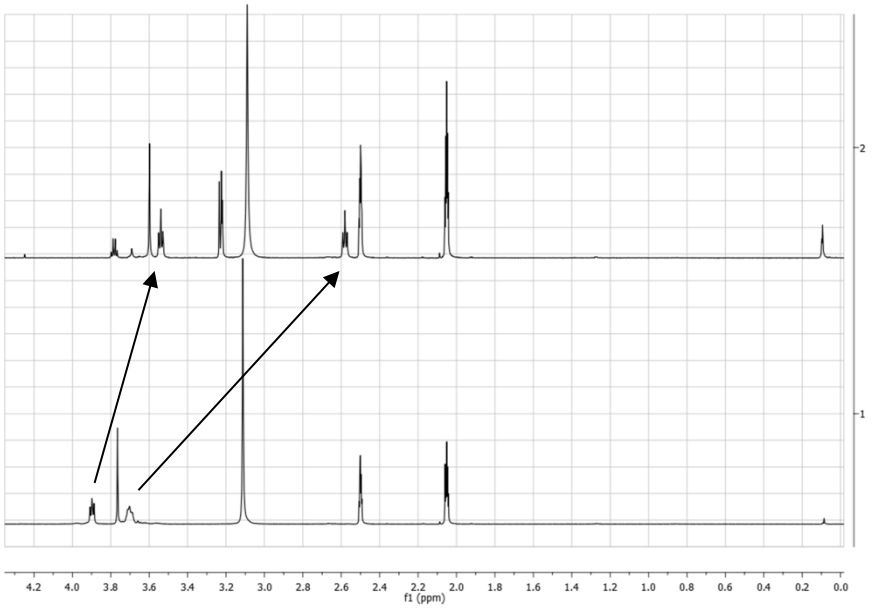

Fig. S14. Spectral comparison between an equimolar solution of **1** (top) and **2** (bottom) in DMSO-d6:acetone-d6 2:1 mixture at 25°C. Shift of the K222–H_2^{2+} signals are highlighted by the black arrows.

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 A Wavelength=1.54178

Cell: a=16.3228(18) b=16.3228(18) c=16.3228(18)

alpha=90 beta=90 gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	4349.0(14)	4348.9(8)
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Hall group	P 2ac 2ab 3	?
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Sum formula	C24 H56 I4 N2 O12.30 Zn4	C24 H58 I4 N2 O12 Zn4
Mr	1338.67	1335.80
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Z	4	4
Mu (mm-1)	25.223	25.215
F000	2577.6	2576.0
F000'	2554.58	
h,k,lmax	19,19,19	14,18,18
Nref	2502[1393]	2127
Tmin,Tmax	0.180,0.220	0.141,0.299

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Tmin'              0.025

Correction method= MULTI-SCAN

Data completeness= 1.53/0.85    Theta(max)= 65.460

R(reflections)= 0.0316( 1972)      wR2(reflections)= 0.0718( 2127)

S = 1.072              Npar= 148
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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.

Alert level B

PLAT222_ALERT_3_B Large Non-Solvent H Uiso(max)/Uiso(min) .. 8.0 Ratio

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
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low 0.969
PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ Please Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) 9.41
PLAT230_ALERT_2_C Hirshfeld Test Diff for C3 -- C4 .. 5.3 su
PLAT245_ALERT_2_C U(iso) H101 Smaller than U(eq) N1 by ... 0.023 AngSq
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0127 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C24 H58 I4 N2 O12 Zn4
Atom count from the _atom_site data: C24 H56 I4 N2 O12.3 Zn4
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 4
From the CIF: _chemical_formula_sum C24 H58 I4 N2 O12 Zn4
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	96.00	96.00	0.00
H	232.00	224.00	8.00
I	16.00	16.00	0.00
N	8.00	8.00	0.00

O 48.00 49.20 -1.20
Zn 16.00 16.00 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 !
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...
6 Units
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage =
100 Note
PLAT311_ALERT_2_G Isolated Disordered Oxygen Atom (No H's ?) .....
O1S Check
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....
2 Note
PLAT950_ALERT_5_G Reported and Calculated Hmax Values Differ by ..
5

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

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

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_PLAT222_test
;
PROBLEM: Large Non-Solvent    H    Uiso(max)/Uiso(min) ..       8.0 Ratio
RESPONSE: ...
;
# end Validation Reply Form
```

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*

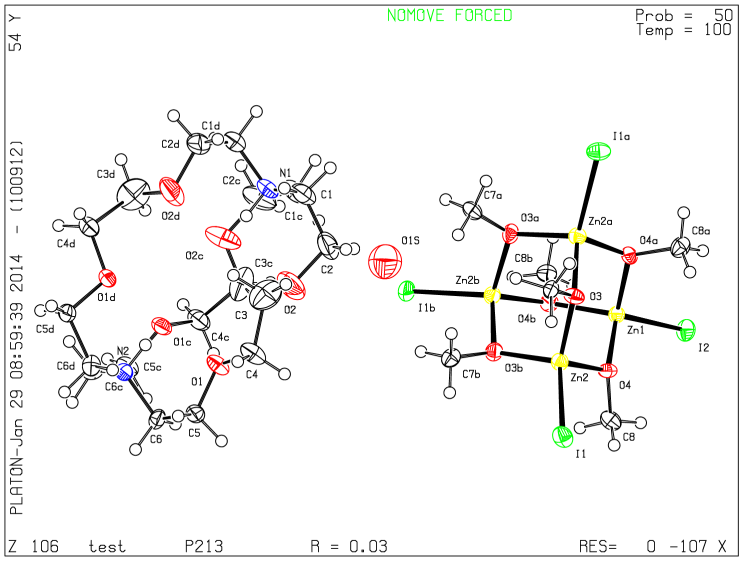
Crystallography, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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



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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: 2

Bond precision: C-C = 0.0157 A Wavelength=1.54178

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alpha=90 beta=90 gamma=120

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Hall group	-R 3 2"c	?
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F000'	5398.73	
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Nref	1804	1797
Tmin,Tmax	0.035,0.518	0.100,0.518

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Tmin'              0.006

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S = 1.127              Npar= 100
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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.

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
PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ Please Check
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.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site* data.
Atom count from _chemical_formula_sum:C18 H40 I4 N2 O6.17 Zn1
Atom count from the _atom_site data: C18 H38 I4 N2 O6.15 Zn1
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?
From the CIF: _cell_formula_units_Z 12
From the CIF: _chemical_formula_sum C18 H40 I4 N2 O6.17 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
I	48.00	48.00	0.00
N	24.00	24.00	0.00
O	74.04	73.80	0.24
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 !
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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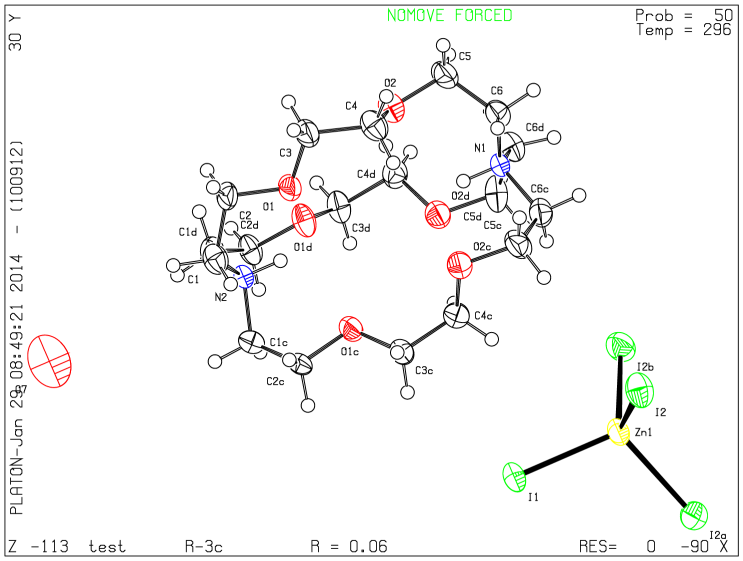
PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock 2 - ellipsoid plot



Download CIF editor (publCIF) from the IUCr
Download CIF editor (enCIFer) from the CCDC
Test a new CIF entry

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: 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

	Calculated	Reported
Volume	8286.4(12)	8286.4(8)
Space group	R -3 c	R-3c
Hall group	-R 3 2"c	?
Moiety formula	2(C18 H38 N2 O6), 2(Br4 Zn), O	?
Sum formula	C36 H76 Br8 N4 O13 Zn2	C18 H40 Br4 N2 O7 Zn
Mr	1542.99	781.53
Dx,g cm-3	1.855	1.879
Z	6	12
Mu (mm-1)	8.320	8.343
F000	4584.0	4656.0
F000'	4541.18	
h,k,lmax	13,13,92	13,13,92
Nref	1632	1622
Tmin,Tmax	0.576,0.716	0.388,0.731
Tmin'	0.296	

Correction method= MULTI-SCAN

Data completeness= 0.994 Theta(max)= 66.390

R(reflections)= 0.0344(1439) wR2(reflections)= 0.1019(1622)

S = 1.093 Npar= 100

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

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ Please Check
PLAT043_ALERT_1_C Calculated and Reported Mol. Weight Differ by .. 20.07 Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.08
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0067 Ang.

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_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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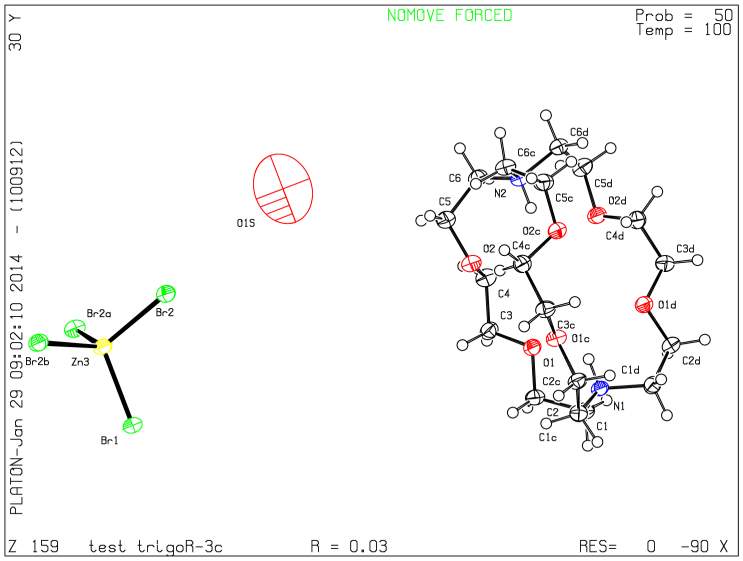
PLATON version of 18/09/2013; check.def file version of 12/09/2013

Datablock 3 - ellipsoid plot



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1 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
2 A. N. Chekhlov, *Russ. J. Coord. Chem*. 2007, **33**, 932.