# Supporting Information: Mechanochemical dehydrochlorination and chelation reaction in the solid state: from a molecular salt to a coordination complex†‡

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**Figure S5**. TGA plot corresponding to complex **2•2H$_2$O**. The observed weight loss corresponds to 5.6 % of the total weight of the solid.

**Figure S6**. View along the *b*- and *c*-axis of the voids generated after manually removing the included water molecules in **2•2H$_2$O.** A 1.2 probe radius was used to determine the contact surface area corresponding to the **6 %** of the unit cell (**419** Å$^3$) area using Mercury 3.1 software.

**Table S1**. Structural data corresponding to **1** and **2•2H$_2$O**.

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**Figure S8**. Calculated HOMO orbitals in the gas phase of bidentate ligand in **1**.

**Figure S9**. (a) Calculated HOMO orbitals in the gas phase of deprotonated bidentate ligand **L**. The absence of the two protons ($H^+$) in **L** shows the frontier orbitals spreading along the chelating -N-C-C-N- backbone. (b) Calculated HOMO orbitals in the gas phase corresponding to the ligand **L** after complexation.

**Figure S10**. The simulated XRPD of **1** and **2•2H$_2$O**. In the inset detailed view of the two reflections suitable to monitor the kinetics of the reaction.

## 1. Experimental Details

Commercial HPLC-grade solvents were used without further purification. All the reagents were commercially available and used without any further purification.

Synthesis by solution of **2•2H$_2$O**: 540 mg (1 mmol) L was solved in 15 mL methanol, then 170 mg (1 mmol) $CuCl_2$•$2H_2O$ was added and shaken until the contents were all dissolved. The flask was allowed to stand for about 1-2 days at room temperature. After the crystals were separated out by filtration, recrystallization gave green and block crystals. m.p. 107-109 ºC. IR (KBr), ν max / $cm^{-1}$: 3003 (w, ArH), 2836 (s, $CH_2$), 2955 (s, $CH_3$), 1610, 1513, 1464 (s, Ar), 1254, 1031 (s, O–C). 1H-NMR ($CDCl_3$, 300 MHz) δ: 1.517 (4H, s, $CH_2$), 4.117 (20H, m, $CH_2$, $OCH_3$), 7.227-7.572 (16H, m, ArH).

Crystallography: Powder X-ray analysis were collected at room temperature on Bruker D8 advance diffractometer using Cu Kα radiation (λ= 1.54056Å). Single crystals were mounted on a Rigaku saturn CCD area detector X-ray diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Intensity data were collected at 113 K. The CrystalClear software was used for data reduction and empirical absorption correction.[1] The structures were determined using direct methods and refined (based on F2 using all independent data) by full-matrix least-square methods (SHELXTL 97).[2] All non-hydrogen atoms were located from different Fourier maps and refined with isotropic displacement parameters.

Elemental analysis of **1**: Calc. C, 62.88; N, 4.31; H, 7.14 %. Found. C, 63.01; N, 4.45; H, 7.25 %

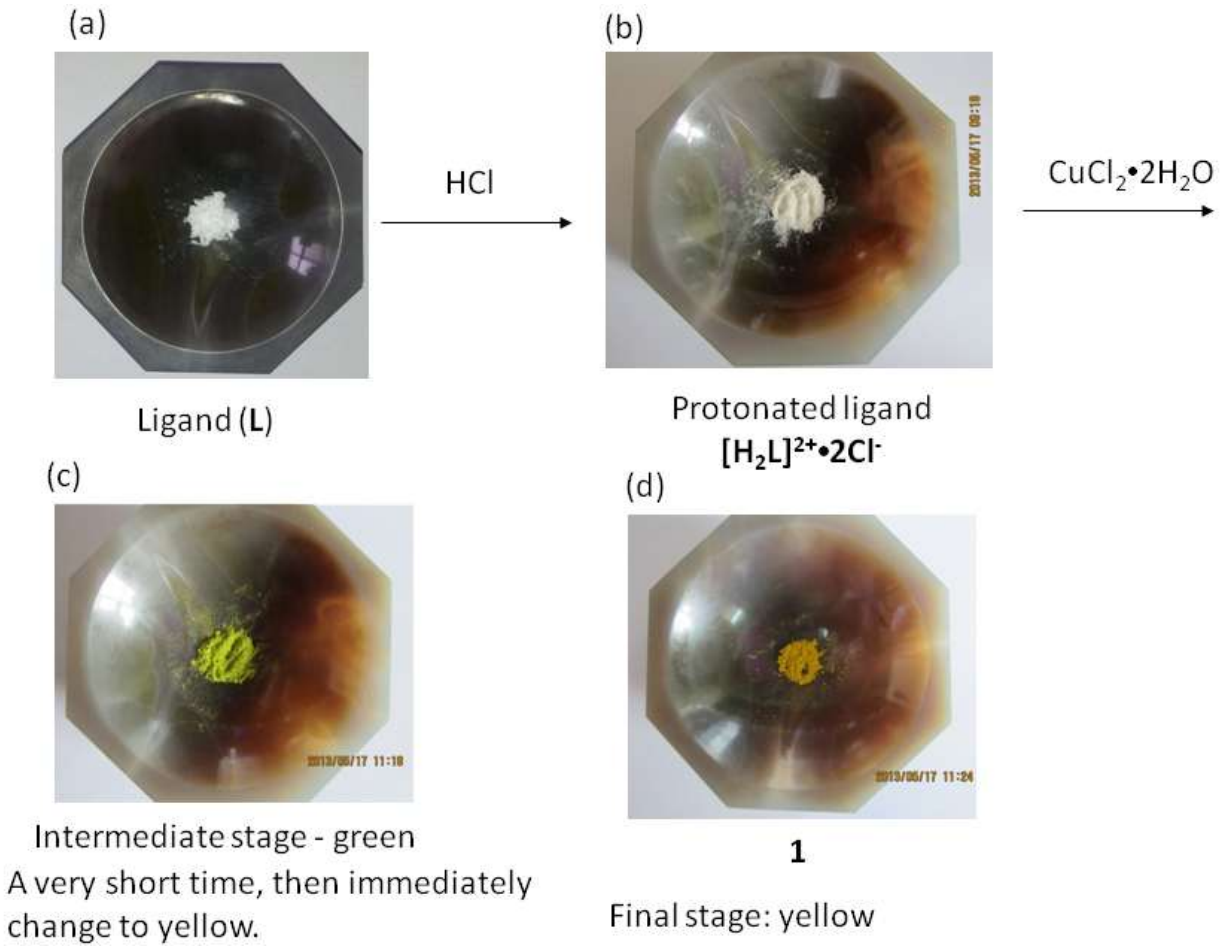



**Figure S1.** Protonation of ligand **L** by mechanochemical reaction upon addition of HCl. An intermediate green solid is observed in the formation of **1** (yellow/orange solid).

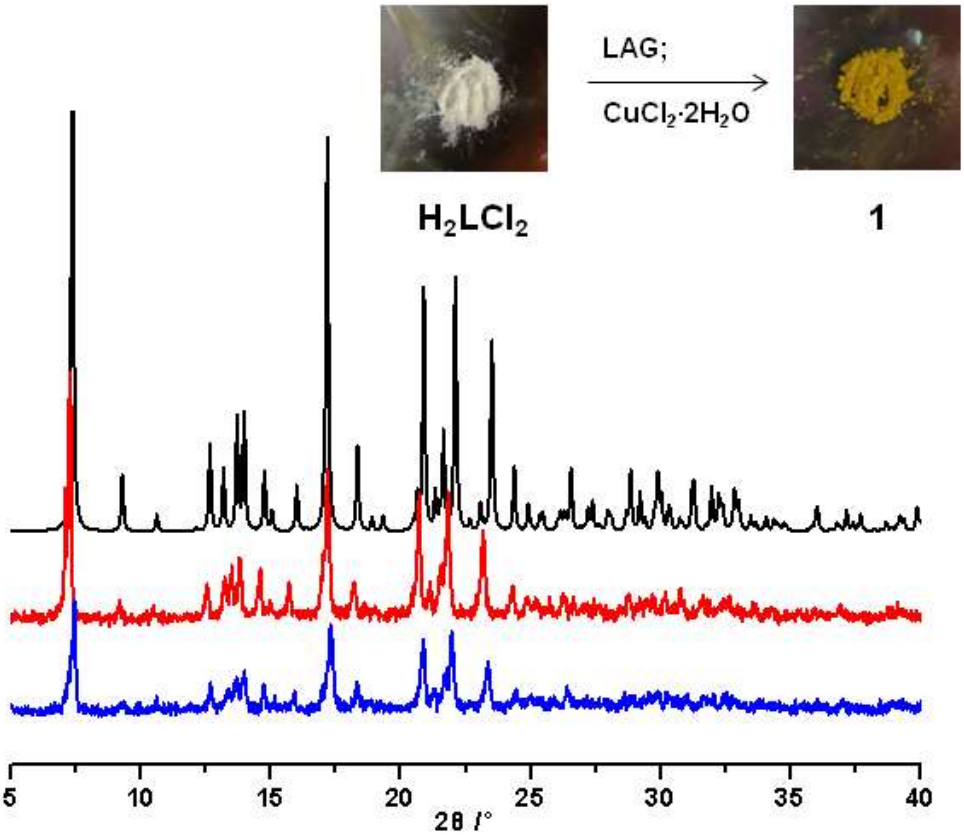
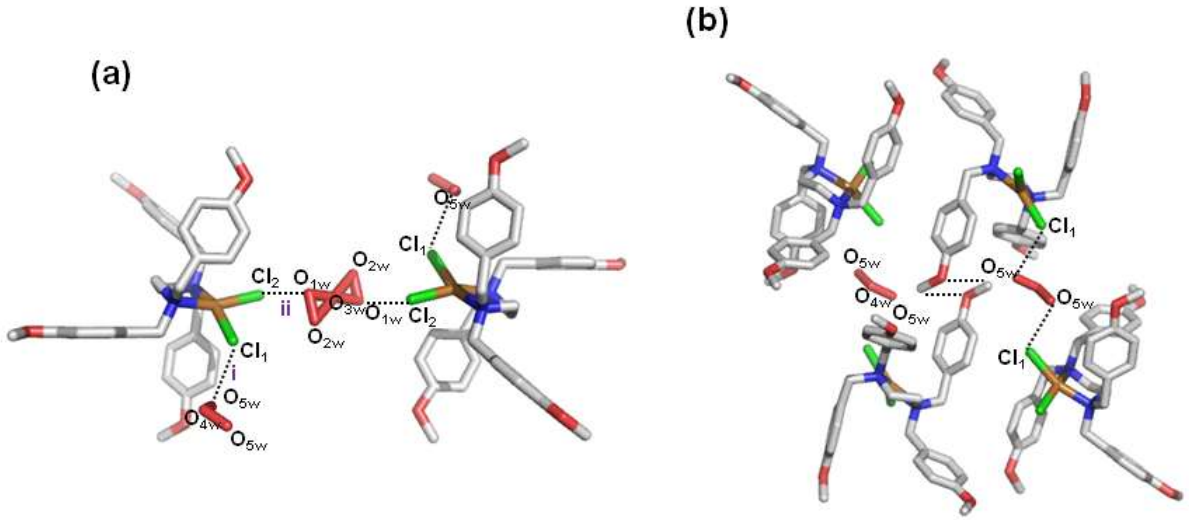
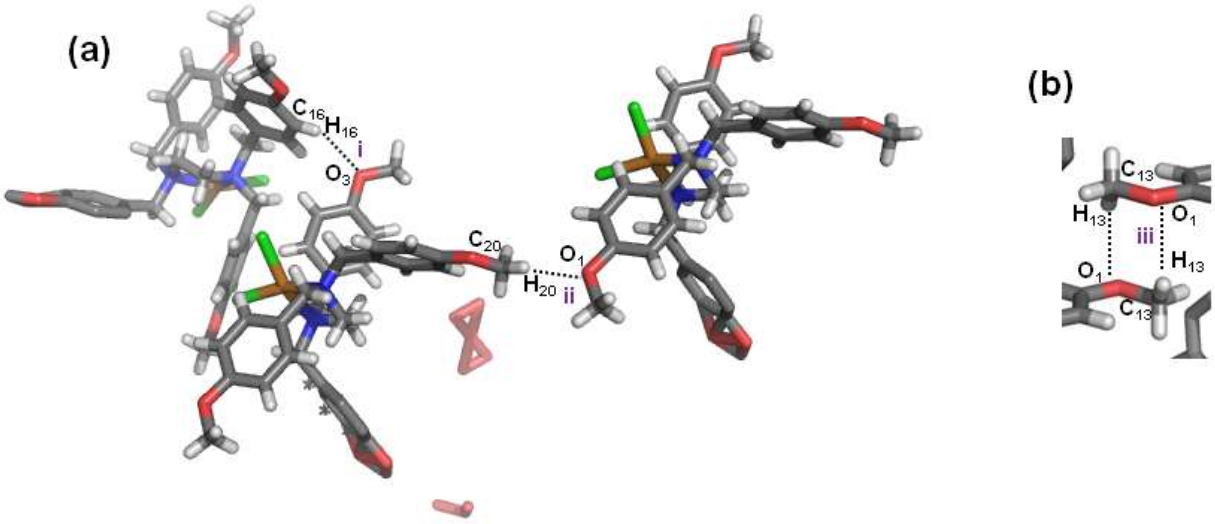



**Figure S2.** Comparison of XRPD patterns of **1** from simulated XRPD (top), solution synthesis (center) and solid-state synthesis (bottom).




| Contacts | Atoms | Distances (Å) |
|---|---|---|
| *i* | Cl1···O5w | 3.09(1) |
| *ii* | Cl2···O1w | 3.188(9) |

**Figure S3.** Crystal structure of **2•2$H_2O$.** (a) Display of the interactions between **ML** units and the Cl···O interaction with one of the two disordered water molecules. (b) View of the two water molecules interacting via Cl···O interactions with two **ML** units. Hydrogen atoms are omitted for clarity.




| Contacts | Atoms | Distances (Å) | Angles (°) |
|---|---|---|---|
| *i* | C16-H16···O3 | 3.394(4) | 136.61(2) |
| *ii* | C20-H20···O1 | 3.59(1) | 165.1(4) |
| *iii* | C13-H13···O1 | 3.453(7) | 133.7(3) |

**Figure S4.** Crystal structure of **2•2$H_2O$.** (a) View of the two **ML** interacting via C-H···O interactions involving the aromatic ring (i) and the methoxy groups (ii). (b) Display of the HB interactions between **ML** units forming dimers (iii).

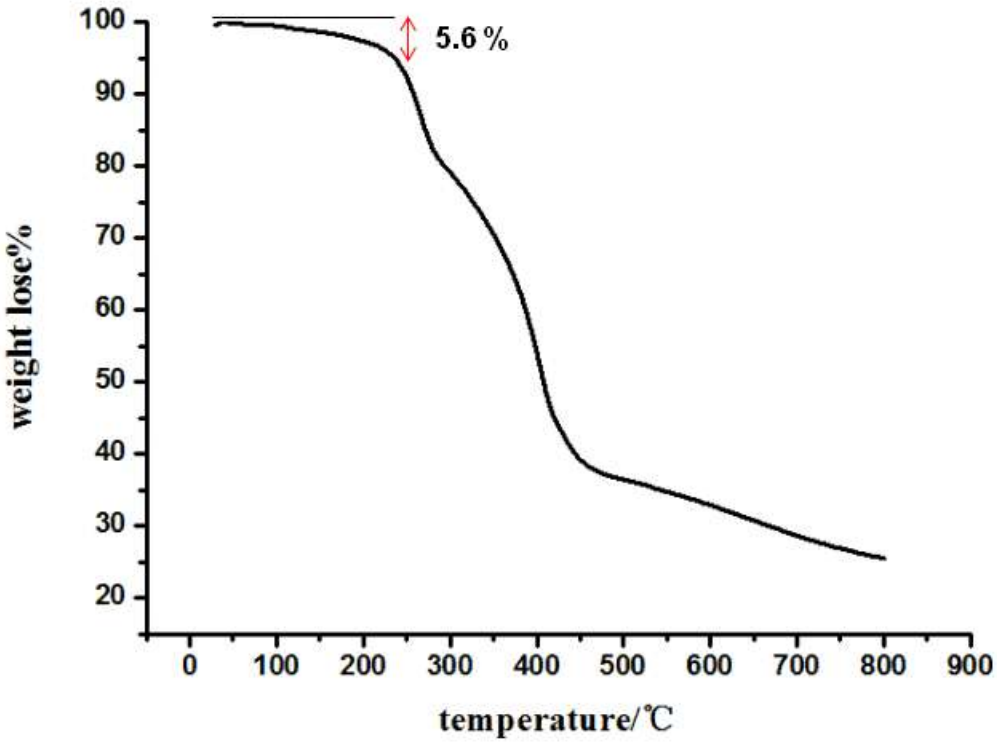



**Figure S5**. TGA plot corresponding to complex **2•2H$_2$O**. The observed weight loss corresponds to 5.6 % of the total weight of the solid.

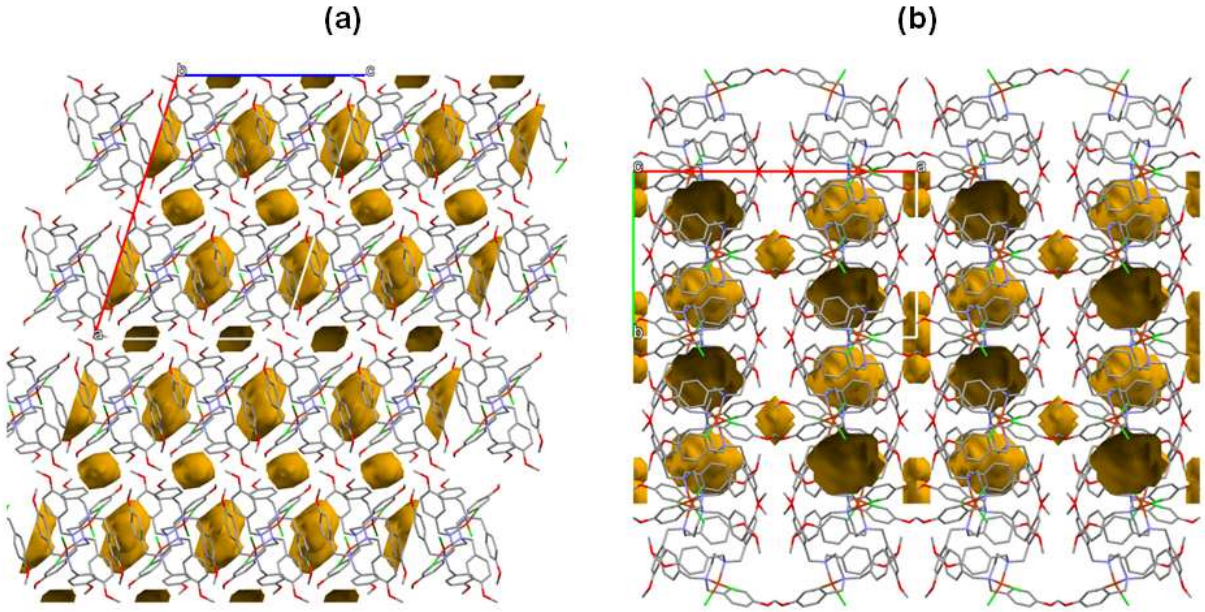



**Figure S6**. View along the *b*- and *c*-axis of the voids generated after manually removing the included water molecules in **2•2H$_2$O.** A 1.2 probe radius was used to determine the contact surface area corresponding to the **6 %** of the unit cell (**419** Å$^3$) area using Mercury 3.1 software.

**Table S1**. Structural data corresponding to **1**[3] and **2•2H$_2$O**.

| **1** | **2•2H$_2$O** |
|---|---|
| $C_{34}$ $H_{42}$ $Cl_4$ $Cu_1$ $N_2$ $O_4$ | $C_{34}$ $H_{33}$ $Cl_2$ $Cu_1$ $N_2$ $O_6$ |
| Mr = 748.04 | Mr = 700.06 |
| Monoclinic *C* 2/*c* | Monoclinic *C* 2/*c* |
| *a* = 25.614(5) | *a* = 26.750(9) |
| *b* = 10.367(2) | *b* = 14.879(4) |
| *c* = 14.328(3) | *c* = 18.279(6) |
| $\alpha$ = 90 | $\alpha$ = 90 |
| $\beta$ = 110.43(3) | $\beta$ = 107.645(5) |
| $\gamma$ = 90 | $\gamma$ = 90 |
| *V* = 3565.1(12) | *V* = 6933(4) |
| *Z* = 4 | *Z* = 8 |
| Mo Kα = 0.71073 | Mo Kα = 0.71073 |
| *T* = 113(3) K | *T* = 113(3) K |
| *D* = 1.394 | *D* = 1.341 |

***Note:** The discrepance in the H atoms in the formula of **2•2H$_2$O** vs**. 1** is due to the fact that one benzene ring and the oxygen of the methoxyl group was refined anisotropically as two closely situated positions with 0.5 occupancies. Therefore, 9 H atoms are missing as the refinement of the disordered ring and methoxyl group was carried out in absence of those H atoms.

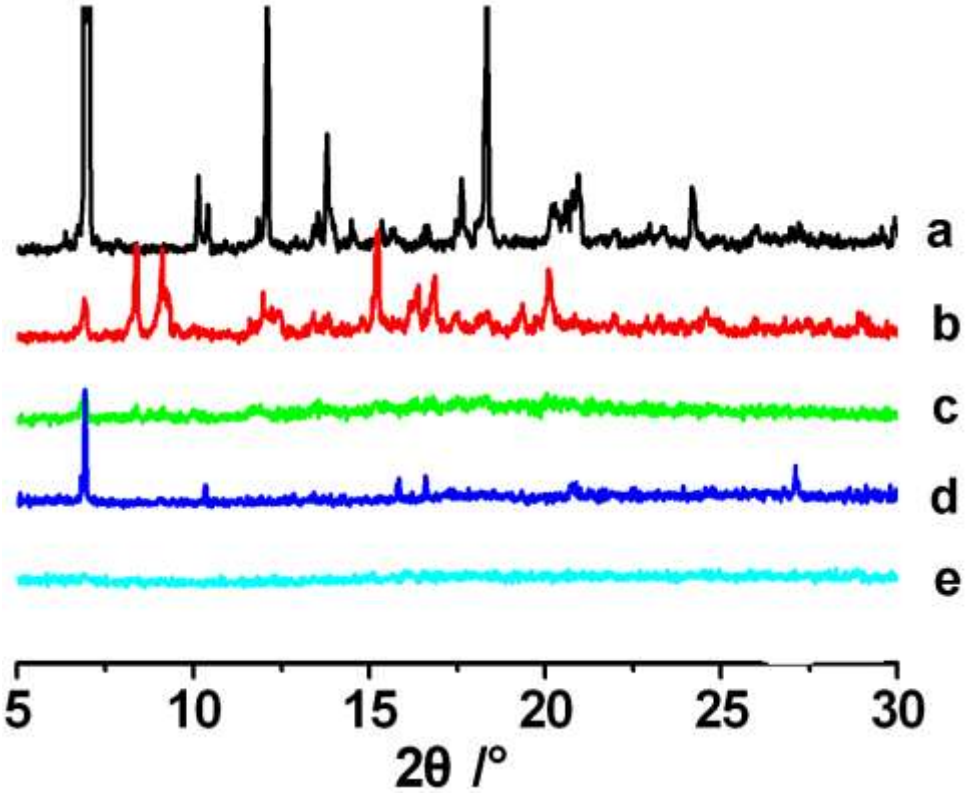



**Figure S7**. Thermal behavior of complex **2•2H$_2$O** (a); heating at 65°C (b) and 90°C(c); placing in a sealed vessel containing concentrated HCl for 2-3 weeks (d and e).

For the solid-state stabilities of **1** and **2•2$H_2O$,** a combination of numerical double-ζ quality basis set (including polarization functions on all atoms, i.e., DNP) and effective core potential was chosen. DNP means double zeta valence basis set (2 functions representing each of the valence orbitals on each atom, (i.e., for carbon we have 2s and 2p orbitals described by 2 functions of type *s* and 2 functions of type *p* with obviously *px py* and *pz* components) plus polarization functions (i.e., expanded functions to better account for intermolecular intereactions or inter-ions intereactions). This specification means that a good dscription of the involved occupied orbitals are used.

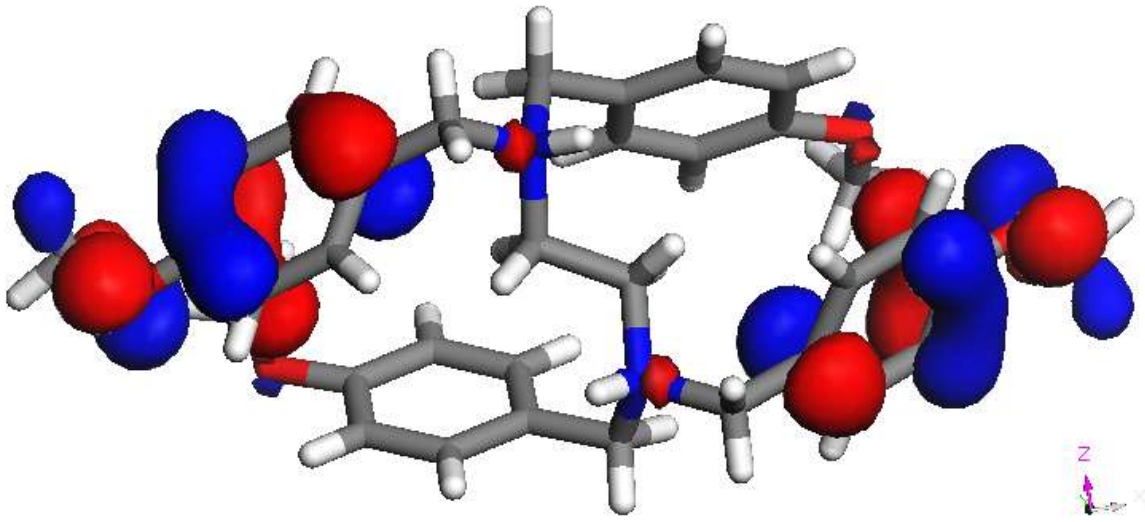



**Figure S8**. Calculated HOMO orbitals in the gas phase of bidentate ligand in **1**.

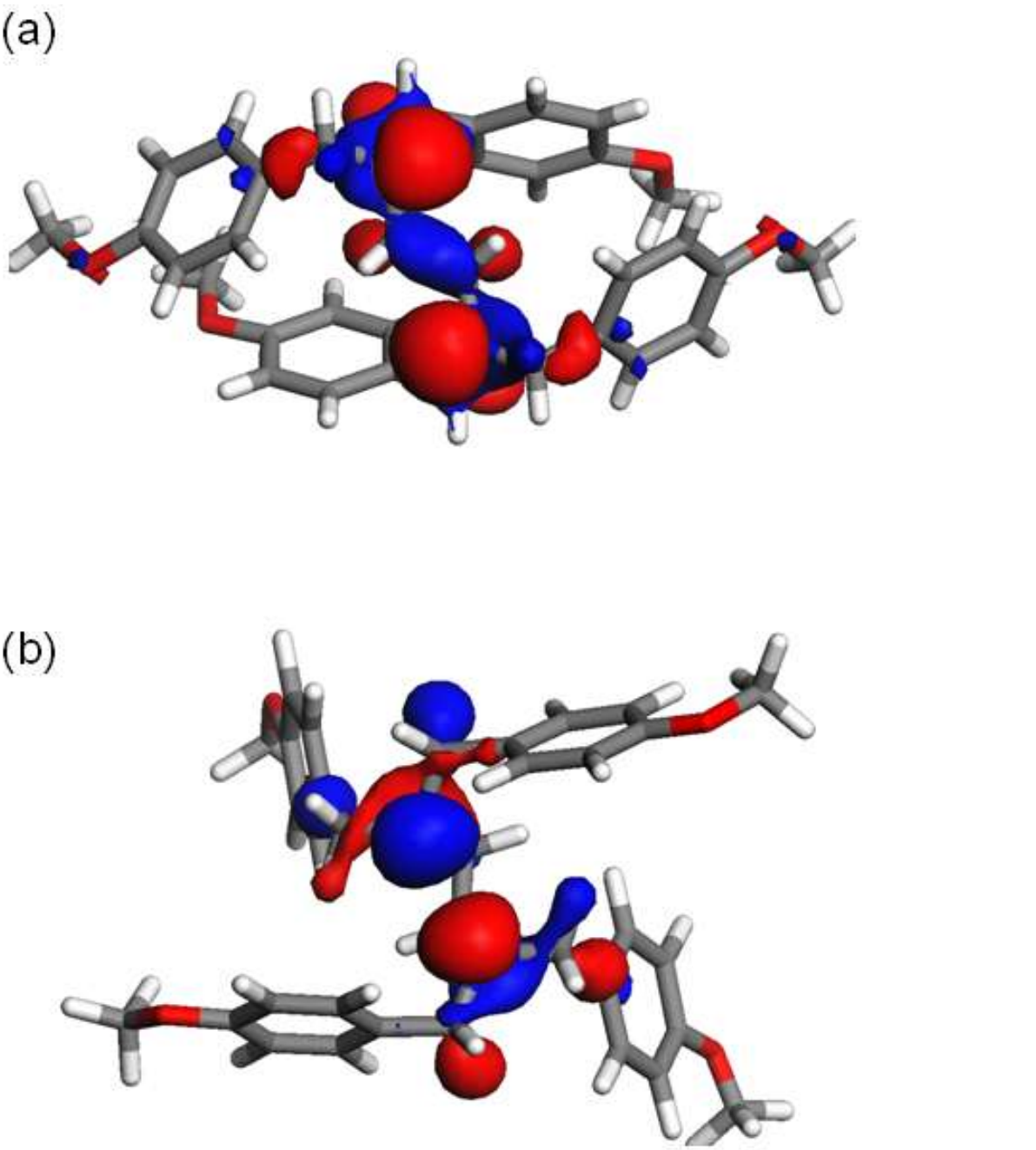



**Figure S9**. (a) Calculated HOMO orbitals in the gas phase of deprotonated bidentate ligand **L**. The absence of the two protons ($H^+$) in **L** shows the frontier orbitals spreading along the chelating -N-C-C-N- backbone. (b) Calculated HOMO orbitals in the gas phase corresponding to the ligand **L** after complexation.

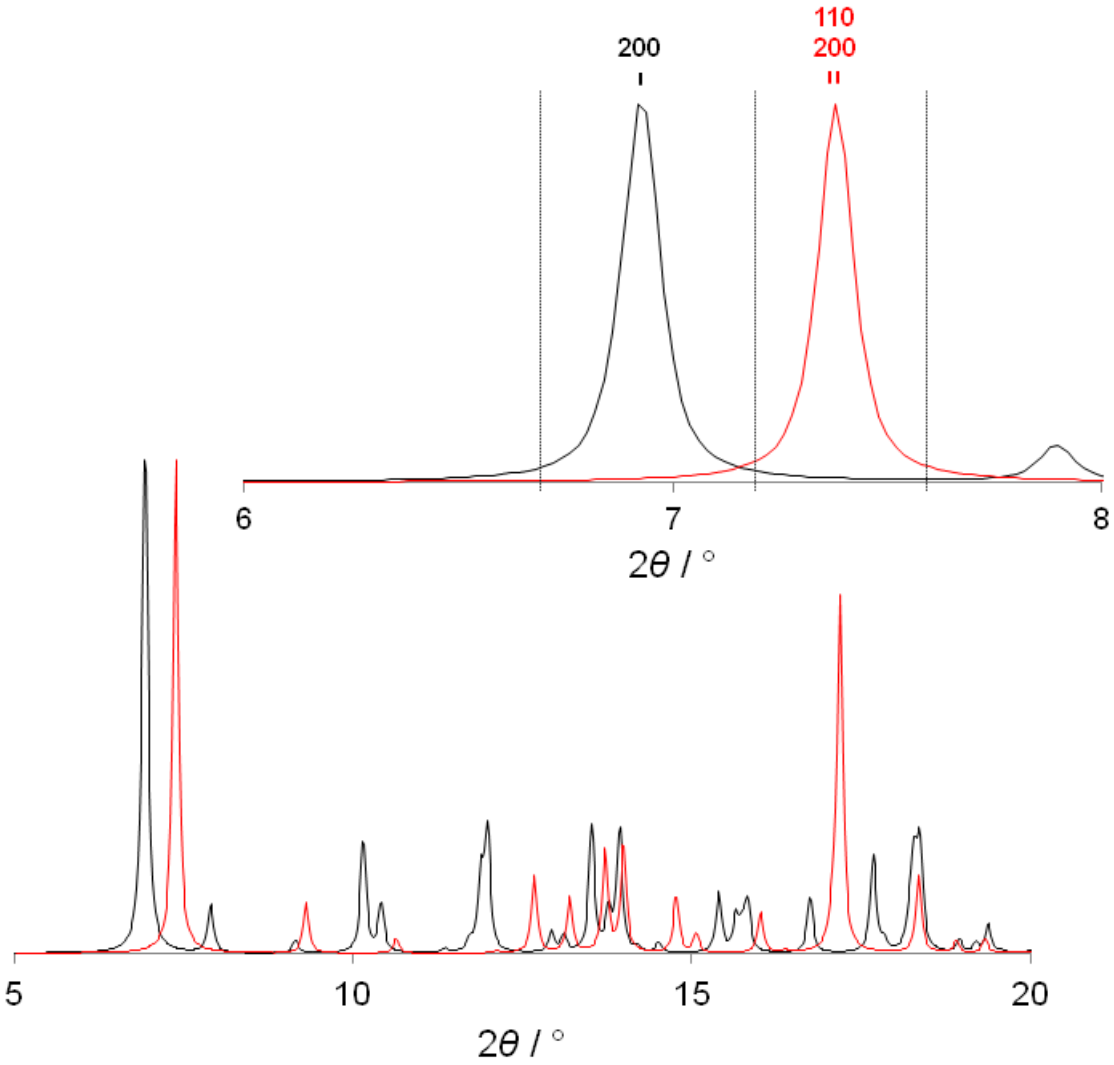



**Figure S10**. The simulated XRPD of **1** and **2•2H$_2$O**. In the inset detailed view of the two reflections suitable to monitor the kinetics of the reaction.

# checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) 1

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

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

# Datablock: 1

Bond precision: C-C = 0.0047 A Wavelength=0.71073

Cell: a=26.750(9) b=14.879(4) c=18.279(6)

alpha=90 beta=107.645(5) gamma=90

Temperature: 113 K

| | Calculated | Reported |
|---|---|---|
| Volume | 6933(4) | 6933(4) |
| Space group | C 2/c | C2/c |
| Hall group | -C 2yc | ? |
| Moiety formula | 8(C34 H33 Cl2 Cu N2 O4), O9, O3 | ? |
| Sum formula | C272 H264 Cl16 Cu8 N16 O44 | C34 H33 Cl2 Cu N2 O6 |
| Mr | 5536.59 | 700.06 |
| Dx,g cm-3 | 1.326 | 1.341 |
| Z | 1 | 8 |
| Mu (mm-1) | 0.827 | 0.829 |
| F000 | 2864.0 | 2896.0 |
| F000' | 2869.98 | |
| h,k,lmax | 35,19,24 | 35,19,24 |
| Nref | 8247 | 8243 |
| Tmin,Tmax | 0.847,0.920 | 0.852,0.922 |

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Tmin'               0.847

Correction method= ?

Data completeness= 1.000        Theta(max)= 27.870

R(reflections)= 0.0634( 7181)      wR2(reflections)= 0.1512( 8243)

S = 1.150              Npar= 498
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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

PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.8 Ratio
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C34

## Alert level C

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 8
From the CIF: _chemical_formula_weight 700.06
TEST: Calculate formula weight from _atom_site_*

| atom | mass | num | sum |
|---|---|---|---|
| C | 12.01 | 34.00 | 408.37 |
| H | 1.01 | 33.00 | 33.26 |
| N | 14.01 | 2.00 | 28.01 |
| O | 16.00 | 5.50 | 87.99 |
| Cl | 35.45 | 2.00 | 70.91 |
| Cu | 63.55 | 1.00 | 63.55 |

Calculated formula weight 692.10

PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ ? Check
PLAT043_ALERT_1_C Check Reported Molecular Weight ..... 700.06
PLAT052_ALERT_1_C Info on Absorption Correction Method Missing ... ? Do !
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... ? Check
PLAT213_ALERT_2_C Atom C20 has ADP max/min Ratio ..... 3.5 prola
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 5.6 Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for O2

## 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:C34 H33 Cl2 Cu1 N2 O6
Atom count from the _atom_site data: C34 H33 Cl2 Cu1 N2 O5.5

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 8
From the CIF: _chemical_formula_sum C34 H33 Cl2 Cu N2 O6
TEST: Compare cell contents of formula and atom_site data

| atom | Z*formula | cif sites | diff |
|---|---|---|---|
| C | 272.00 | 272.00 | 0.00 |
| H | 264.00 | 264.00 | 0.00 |
| Cl | 16.00 | 16.00 | 0.00 |
| Cu | 8.00 | 8.00 | 0.00 |
| N | 16.00 | 16.00 | 0.00 |
| O | 48.00 | 44.00 | 4.00 |

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.13 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 15.36
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 2
PLAT230_ALERT_2_G Hirshfeld Test Diff for O4 -- C34 .. 19.5 su
PLAT230_ALERT_2_G Hirshfeld Test Diff for O4' -- C34 .. 11.0 su
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for O4
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C30
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of O1W
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 16 %
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 %
PLAT431_ALERT_2_G Short Inter HL..A Contact Cl1 .. O5W . 3.09 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 31
C33' -C6 -C28 1.555 1.555 1.555 17.80 Deg.
**And 2 other PLAT779 Alerts**
More ...
PLAT793_ALERT_4_G The Model has Chirality at N2 (Verify) .... S
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

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

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

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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 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.

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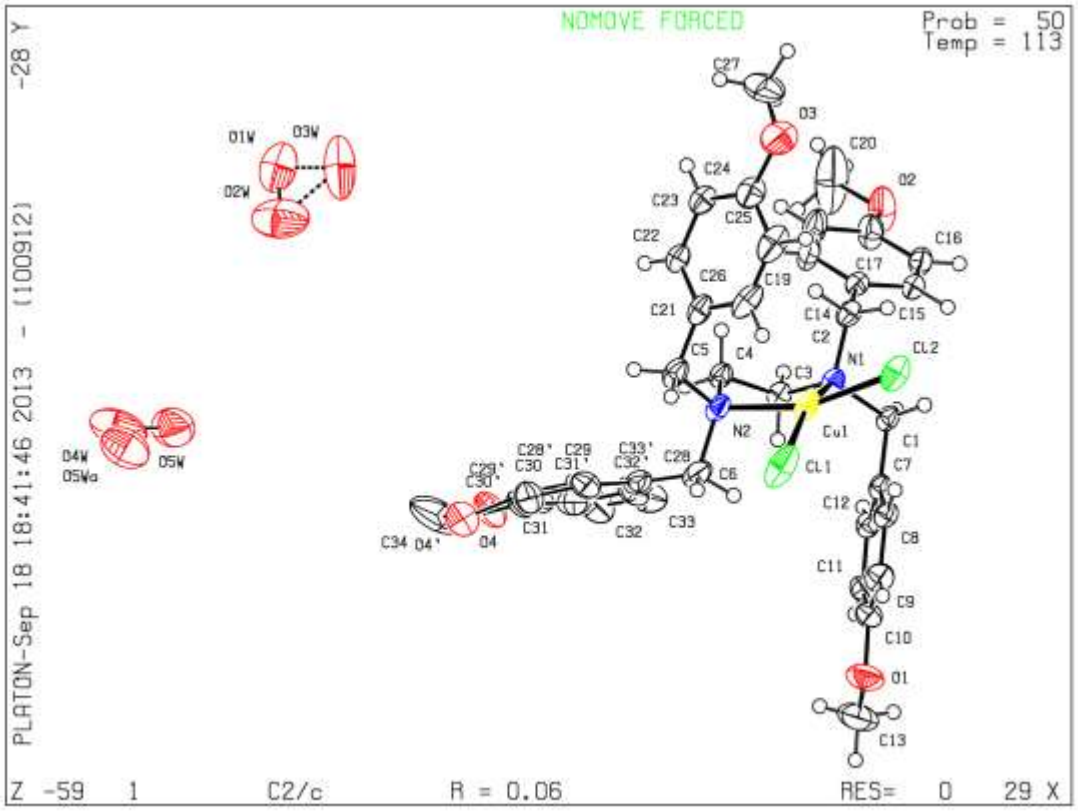
**PLATON version of 01/06/2013; check.def file version of 24/05/2013**

# **Datablock 1** - ellipsoid plot




## References

1 CrystalClear Software: Crystal Clear Version 1.3, Rigaku/Molecular Structure Corp, The Woolands, TX, 2001.

2 G. M. Sheldrick, SHELXTL Reference Manual, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA 1996. G. M. Sheldrick, *Acta Cryst*., 2008. **A64**, 112.

3 F. Guo, M. Q. Zhang, N. Lu, J. Tong, H. Y Guan, B. X Wang, *CrystEngComm*, 2011, **13**, 6753.