Synthesis of unsymmetrical 1,8-naphthyridine-based ligands for the assembly of tri-and tetra-nuclear copper(II) complexes

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Felix Bacher,[a] James A. Isaac,[a] Christian Philouze,[a] David Flot,[b] Aurore Thibon-Pourret,*[a] and Catherine Belle*[a]

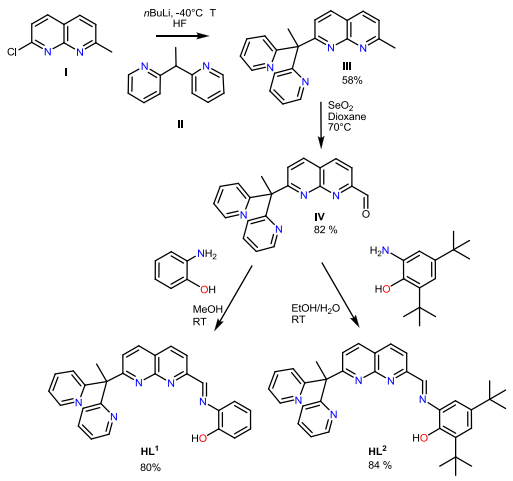
Abstract: A synthetic route for unsymmetrical 1,8-naphthyridine spacer based ligands is presented. Reaction of a 7-ethyldipyridyl-1,8-naphthyridine-2-carboxaldehyde intermediate with 2-aminophenol or 4,6-di-tert-butyl 2-aminophenol led to the ligands **HL^1** and **HL^2** respectively. Both combined two distinct binding sites: a dipyridyl and an iminophenol site linked through a 1,8-naphthyridine spacer. Treatement of **HL^1** with copper(II) triflate in presence of triethylamine/H_2O in acetonitrile afforded a tetranuclear complex (**1^{tox}**·2CH_3CN). X-ray analysis revealed that the structure is constituted by association of two identical dinuclear units in which the imine is oxidized to an amide group during the complexation. The coordination capabilities from the corresponding free amide ligands **H_2L^{1ox}** and **H_2L^{2ox}**, prepared by an independent route, were explored using copper(II) triflate in presence of triethylamine/H_2O. From amide ligand **H_2L^{1ox}**, X-ray diffraction studies evidenced the similar formation of a tetranuclear copper complex (**1^{tox}**·2DMF) compared to the one isolated after complexation with the imine ligand **HL^1**. In contrast, **H_2L^{2ox}**, where the amido phenol arm diplays two additional tert-butyl groups, has allowed the formation of a trinuclear copper complex (**2^{triox}**·H_2O).

Introduction

Among the nitrogenous heterocyclics, 1,8-naphthyridine based compounds display various biological activities relevant to therapeutic areas[1] or to scaffolds with applications for recognition and/or sensing DNA as supramolecular noncovalently bond assemblies.[2,3] As part of these efforts during the last years, the significance of 2,7-disubstituted 1,8-naphthyridine based ligands displays a growing importance in the field of organometallic/coordination chemistry. The 1,8-naphthyridine core is able to stabilize two metal ions in close proximity such as nickel(II),[4,5] cobalt,[6] ruthenium,[7,8,9] or copper(I)[10,11,12] and (II)[4,13]. The corresponding intramolecular electronic interactions between the metal centers are strongly influenced by the short metal-metal distances, impacting the corresponding redox, magnetic, spectroscopic and reactivity properties. In previous works from our laboratory, using the symmetrical dipyridylethane naphthyridine ligand, we prepared a mixed valence $Cu^{II}Cu^{III}$ intermediate[14] and demonstrated the ability of such species in C–H activation.[15] In an extension of ours works, we targeted unsymmetrical naphthyridine-based ligands as employment of such entities are still very limited.[16] Unsymmetrical ligands are highly desirable to provide distinctive environments for metal ions or to access well-defined heterobimetallic complexes. Improvements in the field have an intense interest because they may be relevant for the development of complexes for cooperative reactivity studies with applications to catalytic systems.

Results and discussion

The synthesis of unsymmetrical ligands **HL^1** and **HL^2** are completed from 2-chloro-7-methyl-1,8-naphthyridine (**I**)[17,18] (Scheme 1). First, the introduction of the dipyridyl arm is achieved by lithiation (n-BuLi, 1.1 eq) at -40°C followed by addition of **II** (2,2'-dipyridylethyl) using a procedure adapted from Tilley.[10] Subsequently, oxidation of the methyl group to the aldehyde is completed using 1.4 eq of selenium dioxide in dioxane at 70°C, followed by condensation with 2-aminophenol or 4,6-di-tert-butyl 2-aminophenol leading to **HL^1** and **HL^2** respectively. Next, **HL^1** and **HL^2** in acetonitrile solution were treated independently with $Cu(OTf)_2$, where OTf^- = $CF_3SO_3^-$, in the presence of triethylamine (5 eq) and H_2O (10 eq). From **HL^1** as the ligand, red crystals suitable for X-Ray analysis were obtained after slow diffusion of diethylether into an acetonitrile solution.



Scheme 1. Synthetic route for imine ligands **HL^1** and **HL^2**

All the crystal-structure parameters are given in the experimental section (Table 1). The crystal structure of the complex **1^{tox}**·2CH_3CN ([Cu_4(**L^{1ox}**)$_2$(μ-OH)$_2$](CF_3SO_3)$_2$)·2CH_3CN shows two symmetry-related dinuclear units linked to form the tetranuclear entity with two associated acetonitrile molecules (Fig. 1). The molecular entity is folded around the crystallographic two-fold axis occurring through the center of the parallelogram defined by the Cu2 O3 Cu2' and O3' atoms. The Cu1…Cu2 and the Cu1…Cu1' distances (2.943 and 3.137 Å respectively) are shorter compared to the Cu1…Cu2' distance

of 3.437 Å and to the longer Cu2…Cu2' distances (4.108 Å). Considering these distances, the Cu_4O_4 core reveals a distorted double open cubic arrangement.[19,20] In each dinuclear unit, the two copper atoms Cu1 and Cu2 are connected by one hydroxido and one phenoxido bridges. The two-ligand compartments provide dissimilar coordination environments and thereby induce different coordination geometries for each copper. Cu1 is found in a distorted octahedral geometry with axial positions occupied by the phenoxido oxygen O1' from the other dinuclear unit at 2.589 Å and the oxygen atom O6A from a triflate at 2.668 Å in a weak interaction. The copper at the dipyridyl site (Cu2) is in a square pyramid whose apical position is occupied by the naphthyridine nitrogen N2 atom at 2.227(3) Å (τ parameter equal to 0.067).[21] Additional prominent parameter of this resolved structure is the oxidation of the imine bond in the ligand to the corresponding deprotonated amide ligand $\mathbf{L^{1ox}}$ (Scheme 2). The C21-O2 bond length is 1.244(4) Å, consistent with a double bond character for the carbonyl group as reported for amide groups.[22,23] Presence of the C=O from an amide is also confirmed by IR with the presence of the two ν_{CO} stretching vibration bands located at 1622 and 1600 cm^{-1} (Fig. S1).[23] The C21-N3 bond length of 1.326(1) displays a single bond character comparable to those found in coordinated deprotonated amide in copper(II) complexes.[23] Similar reaction in argon atmosphere and in dry conditions led to a black oil whose characterization failed in our hands.

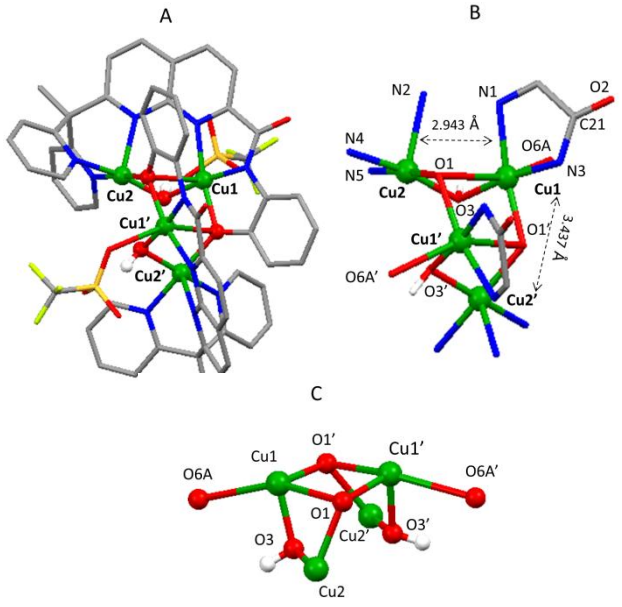
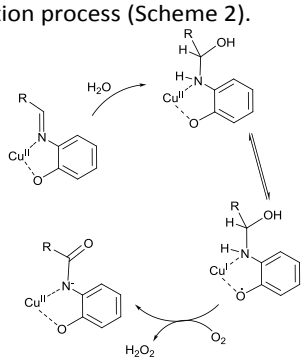


Fig. 1. A: Molecular structure of $[Cu_4(\mathbf{L^{1ox}})_2(\mu\text{-}OH)_2](CF_3SO_3)_2{\cdot}2CH_3CN$ ($\mathbf{1^{tox}}$ ·$2CH_3CN$), hydrogen atoms (except for hydroxido bridges) were removed for clarity; **B**: Isolated view of the tetranuclear core with partial atom numbering; **C:** Other view and simplified representation of the coordination environment of the four metal center in $\mathbf{1^{tox}}$. Selected bond lengths (Å) and angles (°): Cu1…Cu2 2.943, Cu1 …u2' 3.437, Cu1…Cu1' 3.137, Cu2…Cu2' 4.108, Cu1 O1' 2.587(2), Cu1 O1 1.983(2), Cu1 O3 1.877(2), Cu1 N1 2.062(3), Cu1 N3 1.885(3), Cu2 O1 2.040(2), Cu2 O3 1.915(2), Cu2 N2 2.227(3), Cu2 N4 1.963(3), Cu2 N5 2.012(3); Cu1 O1 Cu2' 117.36(10), O1 Cu1 N1 165.63(10), O3 Cu1 O1 90.05(9), O3 Cu1 N1 103.52(10), O3 Cu1 N3 172.62(11), N3 Cu1 O1 84.09(11), N3 Cu1 N1 82.73(11), Cu1 O3 Cu2 101.77(9), O1 Cu2 N2 98.51(9), O3 Cu2 O1 91.56(9), O3 Cu2 N2 96.67(9), O3 Cu2 N4 170.99(11), O3 Cu2 N5 90.70(10), N4 Cu2 O1 91.18(11), N4 Cu2 N2 91.40(11), N4 Cu2 N5 85.92(12), N5 Cu2 O1 174.98(10), N5 Cu2 N2 85.67(11). Symmetry operation: ' = 1-x, +y, 3/2-z.

Few examples of such imine function oxidation upon coordination by a copper(II) ion in presence of O_2/H_2O are described in literature.[22,24,25,26] They suggest involvement of a radical formation from the non-innocent iminopyridine moiety during the oxidation process (Scheme 2).



Scheme 2. Proposed mechanism for imine to amide transformation according reference 22.

The ESI mass spectrum of $\mathbf{1^{tox}}{\cdot}2CH_3CN$ in acetonitrile (Fig. S2-S3) displays a peak centered at *m/z* = 1326.9 assigned to $[2M\text{-}CF_3SO_3]^+$ where M = $[Cu_2(\mathbf{L^{1ox}})(\mu\text{-}OH)](CF_3SO_3)$, consistent with the presence of the tetranuclear species in acetonitrile solution. Indeed a peak at *m/z* = 589 assigned to the mono-charged fragment $[M\text{-}CF_3SO_3]^+$ is observed. The latter may originate also from fragmentation under the ESI-MS conditions, this likely suggests that the tetranuclear and the corresponding dinuclear species are both present in acetonitrile solution.

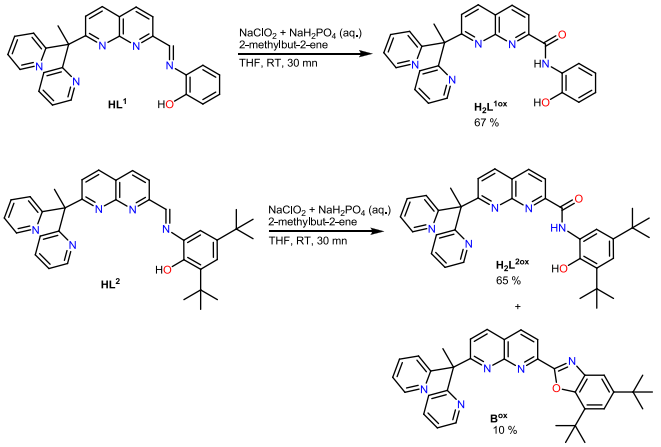
Treatment of imine $\mathbf{HL^2}$ with $Cu(OTf)_2$ in acetonitrile solution and in the presence of triethylamine/H_2O led to a green oil but so far we have not been able to isolate any complexes with intact or modified ligand. Nevertheless, the observed ligand transformations from $\mathbf{HL^1}$ prompted us to access the amide functionality by a copper free mode. Interestingly amides can be accessed from the corresponding imines by Pinnick oxidation, which is standardly used to prepare acids from aldehydes, using sodium chlorite under buffered conditions as reported by Tomioka[27] (Scheme 3). Corresponding ligands $\mathbf{H_2L^{1ox}}$ and $\mathbf{H_2L^{2ox}}$ possessing an amide function are obtained in 30 min at room temperature in good yield.

The oxidation reaction can also be conducted directly from aldehyde **IV** by two successive steps without isolation of the intermediate imine as described in the experimental procedure (*method B*) of the synthesis of $\mathbf{H_2L^{1ox}}$, leading to an improved yield of 82%. During the purification of $\mathbf{H_2L^{2ox}}$, 10% of a benzoxazole ($\mathbf{B^{ox}}$) compound was recovered resulting of an unwanted ring formation (Scheme 3).

Ligand $\mathbf{H_2L^{1ox}}$ in acetonitrile solution was treated with $Cu(OTf)_2$ in the presence of triethylamine/H_2O giving a dark-red precipitate after addition of THF. Black crystals suitable for X-Ray analysis were obtained after slow diffusion of di-

isopropyl ether into a DMF solution of the complex. The X-ray structure of the complex displays a tetranuclear entity **1**^{tox}·2DMF ([Cu_4(**L**^{1ox})$_2$(μ-OH)$_2$](CF_3SO_3)$_2$)·2DMF analogous to the tetranuclear complex **1**^{tox}·2CH_3CN provided after reaction with a copper(II) triflate and **HL**^{1} ligand (see above). Bond distances and angles are displayed in the ESI (Table S1).

The ligand **H$_2$L**^{2ox}, corresponding to **H$_2$L**^{1ox} but with additional tert-Butyl groups in ortho and para positions of the phenol group, was obtained by oxidation of **HL**^{2} using a classical synthetic route (Scheme 3).



Scheme 3. Imine/amide ligands used in this work

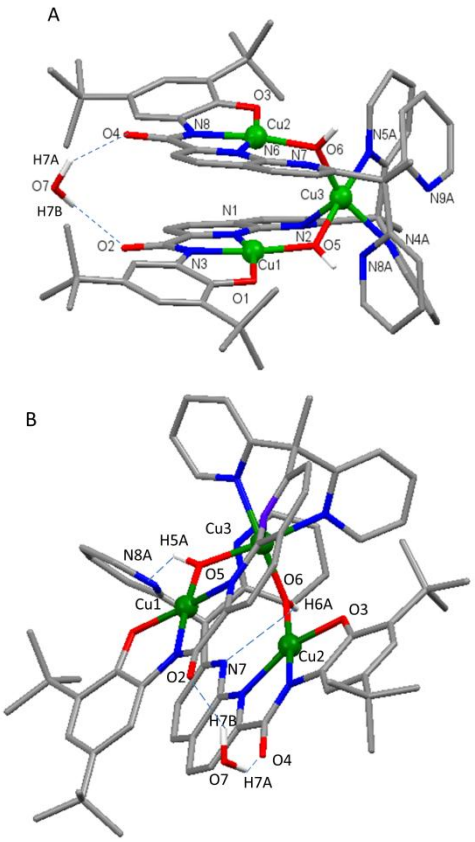


Fig. 2. A: Molecular structure of form **a** of [Cu_3(**L**^{2ox})$_2$(μ-OH)$_2$]·H_2O (**2**^{triox}·H_2O). Hydrogen atoms (except for the hydroxido bridges and H_2O solvent molecule) were removed for clarity. Selected bond lengths (Å) and angles (°): Cu1…Cu2 3.278, Cu1…Cu3A 3.303, Cu2…Cu3A 3.236, Cu1-O1 1.929(6), Cu1-O5 1.877(6), Cu1-N1 2.129(7), Cu1-N3 1.904(7), Cu2-O3 1.923(6), Cu2-O6 1.875(7), Cu2-N6 2.094(7), Cu2-N8 1.905(8), Cu3-O5 1.938(6), Cu3-O6 1.877(5) , Cu3-N2 2.318(7), Cu3-N4A 2.041(8), Cu3-N5A 2.013(12); O1 Cu1 N1 161.5(3), O5 Cu1 O1 94.2(3), O5 Cu1 N1 100.9(3), O5 Cu1 N3 172.7(3), N3 Cu1 O1 84.5(3), N3 Cu1 N1 81.7(3), O6 Cu2 N6 100.4(3), O6 Cu2 O3 94.6(3), O6 Cu2 N8 171.8(3), O3 Cu2 N6 161.9(2), N8 Cu2 N6 82.0(3), N8 Cu2 O3 84.5(3), Cu2 O6 Cu3A 119.2(4), Cu1 O5 Cu3A 119.9(3), O6 Cu3A O5 93.7(2), O6 Cu3A N2 119.4(3), O6 Cu3A N4A 155.3(4), O6 Cu3A N5A 91.1(3), O5 Cu3A N2 91.1(3), O5 Cu3A N4A 90.0(3), O5 Cu3A N5A 174.9(4), N4A Cu3A N2 84.9(4), N5A Cu3A N2 85.2(5), N5A Cu3A N4A 86.3(4); **B**: Other view with plot of H-bonding interactions represented in blue dashed lines.

The reaction with the copper salt ($Cu(OTf)_2$) in an acetonitrile solution of **H$_2$L**^{2ox} in the presence of water (10 eq.) and after treatment with triethylamine conduced to the complex which was precipitated with THF.

Dark blue needles suitable for X-ray analysis were obtained after di-isopropylether diffusion into a DMF solution. A neutral complex [Cu_3(**L**^{2ox})$_2$(μ-OH)$_2$]·H_2O (**2**^{triox}·H_2O) is isolated. This new complex contains three copper cations, each of which is bound to two ligands forming a "saddle-shaped" arrangement (Fig. 2). The unit appears as a mixture of two forms **a** and **b** with **a/b** ratio of 65/35. The form **a** (Fig. 2) displays two of the three copper cations (Cu1 and Cu2) in a slightly distorted square-planar geometry when the third copper atom (Cu3) occupying a distorted square-pyramidal geometry (τ parameter equal to 0.3).[21] For Cu1 and Cu2, the coordination sphere around each Cu atom is comprised of two O-atoms: one from the phenoxido and one of a bridging hydroxido (connected with the Cu3A atom) and two N-atoms: one from the naphthyridine ligand and one from the deprotonated amide group. In the axial position the Cu3A is bound to one naphthyridine nitrogen N2 atom at a distance of 2.318(7) Å and the equatorial positions are occupied by nitrogen atoms N4A and N5A from one pyridine arm (at 2.041(8) and 2.013(12) Å respectively) while the pyridines linked to the other naphthyridine moiety are non-coordinated. Interestingly, in form **b**, a coordination switch is observed around Cu3A as the equatorial positions are occupied by N8B and N9B (non-coordinated nitrogen on **a**) while N4B and N5B become non-coordinated. Between the two forms a shift of 2.0 Å is noticed for Cu3. A view showing the combination of

forms **a** and **b** is depicted in the ESI (Fig. S4 with bond distances and angles around Cu3A in **b**). For both forms, two oxygen atoms (O5 and O6) from the hydroxido bridges complete the coordination sphere.

In form **a,** Cu3-O5 and Cu3-O6 distances are of 1.938(6) and 1.877(5) Å respectively. The Cu3-O5-Cu1 and Cu3-O6-Cu2 angles (119.9(3) and 119.2(4)°) are rather similar with a Cu3…Cu1 distance of 3.303 Å and a shorter Cu3…Cu2 distance of 3.236 Å while the Cu1…Cu2 distances is of 3.278 Å.

In addition, the presence of a non-coordinated water molecule in a twofold interaction with amide oxygen O2 and O4 by hydrogen bonding (O2…H7BO7 and O4….H7AO7 with *d*(O2…O7) = 2.795(12) Å and *d*(O4…O7) = 2.830(13) Å) is observed. Furthermore the bridging hydroxido group O5H5A is in quite common H-bonding interaction[28] with the nitrogen N8A of a pyridyl arm (O5H5A…N8A) with *d*(O5…N8A) = 2.943(14) whereas the hydroxido group O6H6A is in H-bonding interaction with nitrogen N7 from a naphthyridine moiety (O6H6A…N7) with *d*(O6…N7) = 2.887(9) Å.. In solution, the ESI mass spectrum of $\mathbf{2^{triox}}\cdot H_2O$ in acetonitrile displays no peaks associated to a trinuclear entity. Only a peak at 718.2 assigned to the mono-charged $[Cu_2(\mathbf{L^{2ox}})(OH)_2] + H^+$ dimer (see Fig. S5 with experimental and theoretical isotopic patterns) was identified. This suggests that all these non-covalent and weak interactions participate to the stabilization of the overall structure in solid state.

Conclusions

The presented work displays the development of a useful synthetic route for unsymmetrical 1,8-naphthyridine based ligands bearing two different complexing arms in the 2,7 position. The described precursors can be utilized to synthesize a diversity of unsymmetrical ligands. Two examples of ligands (**HL^1** and **HL^2**) bearing a dipyridyl arm and different substituted iminophenol arms are described herein as well as their coordination behavior with copper(II) triflate. The corresponding complexes clearly show a distinct reactivity on the iminophenol moiety. **HL^1** appears to be a non-innocent ligand as during the copper complexation, the facile oxidation of the imine group led to a carboxamide arm affording the tetranuclear copper complex $[Cu_4(\mathbf{L^{1ox}})_2(\mu\text{-}OH)_2](CF_3SO_3)_2\cdot 2CH_3CN$ ($\mathbf{1^{tox}}\cdot 2CH_3CN$). This behavior is not observed from **HL^2** ligand bearing in ortho and para positions of the phenol group, a tert-butyl set. For comparison purposes we have prepared by chemical oxidations on **HL^1** and **HL^2** the corresponding free ligands **H_2L^{1ox}** and **H_2L^{2ox}** possessing an amide function. After reaction with a copper(II) salt, the structure of the complex obtained from **H_2L^{1ox}** displays a tetranuclear entity similar to the one obtained from **HL^1**, while with **H_2L^{2ox}** a trinuclear complex is isolated. Thus, unsymmetrical ligands described herein have been proven to be good scaffolds for the preparation of tri- and tetra-nuclear copper complexes reflecting their versatility. Aspects concerning the formation of additional heterobimetallic compounds, will subsequently be explored.

Experimental section

General. All reagents were purchased from commercial sources and used as received. Solvents were distilled by standard methods before use. ESI mass spectra were recorded on an Esquire 300 plus Bruker Daltonis or ZQ 2000, MK II Z-spray from Waters fitted with a syringe pump. NMR spectra were recorded on a Bruker AM 300, a Bruker Avance or a unity Plus 500 MHz Varian spectrometer with the deuterated solvent as a lock. Ligands **HL^1**, **HL^2**, **H_2L^{1ox}** and **H_2L^{2ox}** were fully characterized by ^{1}H and ^{13}C spectroscopy (Figures S6-S13). The spectra were in agreement with the proposed formulae and all signals could be assigned using two dimensional NMR techniques (COSY, HSQC and HMBC). For atom numbering scheme see ESI, Scheme S1. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer (equipped with ATR accessory) as neat solids.

Synthetic procedures.

Synthesis of compound III. A solution of 1,1-di-(2-pyridyl)ethane (**II**)[29] (1.1 g, 6.0 mmol, 1.1 eq) in dry THF (75 mL) was placed under argon and cooled to -40°C. A 2.5 M solution of n-BuLi (2.4 mL, 6.0 mmol, 1.1 eq) was added slowly and the resulting red solution stirred for 20 min before adding slowly 1.0 g of **I** (5.6 mmol, 1.0 eq) synthesized using a published literature procedure.[17] The solution was left to stir over night and the temperature allowed to rise to room temperature. The red solution was then evaporated to 30 mL, cooled over ice and 70 mL H_2O was added slowly. The solution was extracted with DCM (3 x 100 mL), the organic phase dried over $MgSO_4$, filtered, evaporated and purified by column chromatography (aluminium oxide, neutral, with a gradient of pentane/ethyl acetate) to yield **III** as an orange solid (1.3g, 4.1 mmol, 72 %). ^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 8.51 (2H, d, J = 4.9 Hz, H^{14}), 8.26 (1H, d, J = 8.2 Hz, H^6), 8.22 (1H, d, J = 8.5 Hz, H^4), 7.72 (2H, td, J = 1.6 Hz, J = 7.7 Hz, H^{16})), 7.48 (1H, d, J = 8.3 Hz, H^7), 7.28 (1H, d, J = 8.4, H^3), 7.25 (2H, m, H^{15}), 7.18 (2H, d, J = 8.0 Hz, H^{17}), 2.67 (3H, s, H^{19}), 2.30 (3H, s, H^{18}). ^{13}C-NMR (100 MHz, DMSO-*d*6), δ (ppm): 169.23 (Cq, C^{10}), 165.65 (Cq, C^{12}), 162.43 (Cq, C^8), 154.69 (Cq, C^2), 148.87 (CH, C^{14}), 137.42 (CH, C^6), 136.79 (CH, C^{16}), 136.59 (CH, C^4), 123.75 (CH, C^{17}), 123.14 (CH, C^7), 122.73 (CH, C^3), 122.02 (CH, C^{15}), 119.22 (Cq, C^5), 61.19 (Cq, C^{11}), 27.63 (CH, C^{19}), 25.39 (CH_3, C^{18}). Anal Calcd for $C_{21}H_{18}N_4\cdot 0.5EtOAc$: C, 74.47; H, 5.99; N, 15.12. Found: C, 74.37; H, 5.68; N, 15.33. ESI-MS, *m/z* = 465 $(M+K)^+$, 349 $(M+Na)^+$, 327 $(M+H)^+$.

Synthesis of IV. Dioxane (40 mL) was added to a mixture of **III** (0.4 g, 1.2 mmol, 1 eq) and SeO_2 (0.25g, 2.3 mmol., 1.9 eq), heated to 70°C and stirred overnight. The purple precipitate was filtered and the filtrate was evaporated. Water (60 mL) was added, then the pH was increased to 7 using $NaHCO_3$ and the resulting mixture was extracted with DCM (4 x 75 mL). The organic phase was dried over $MgSO_4$, filtered, evaporated and dried under vacuum to give **IV** as a beige solid (0.35 g, 1.0 mmol, 82%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 10.35 (1H, s, H^{19}), 8.55 (2H, d, J = 4.8 Hz, H^{14}), 8.30 (1H, d, J = 8.2 Hz, H^3), 8.09 (1H, d, J = 8.3, H^4), 8.06 (1H, d, J = 8.4 Hz, H^6), 7.70 (1H, d, J = 8.6 Hz, H^7), 7.64 (2H, td, J = 1.9 Hz, J = 7.9 Hz, H^{16}), 7.28 (2H, d, J = 7.9 Hz, H^{17}), 7.14 (2H, dd, J = 4.8 Hz, J = 7.3 Hz, H^{15}), 2.52 (3H, s, H^{18}). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 193.83 (CH,

C^{19}), 171.19 (Cq, C^{10}), 165.34 (Cq, C^{12}), 154.84 (Cq, C^{2}), 154.24 (Cq, C^{8}), 148.88 (CH, C^{14}), 138.31 (CH, C^{4}), 136.42 (CH, C^{16}), 135.11 (CH, C^{6}), 127.19 (CH, C^{7}), 123.98 (Cq, C^{5}), 123.06 (CH, C^{17}), 121.54 (CH, C^{15}), 117.91 (CH, C^{3}), 61.09 (Cq, C^{11}), 27.29 (CH_3, C^{18}). Anal Calcd for $C_{21}H_{16}N_4O$·0.125EtOAc: C, 73.40; H, 4.90; N, 15.87. Found: C, 73.21; H, 4.89; N, 16.13. ESI-MS, *m/z* = 341 $(M+H)^+$.

Synthesis of imine HL^1. The aldehyde **IV** (200 mg, 0.59 mmol) and 2-aminophenol (64 mg, 0.59 mmol) were mixed with methanol (10 mL). The reaction was stirred at room temperature overnight. The yellow precipitate was filtered off, washed with a small amount of methanol and dried in vacuo to give **HL^1** as a yellow powder (206 mg, 81%). ^{1}H ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.39 (s, 1H, O*H*), 8.95 (s, 1H, H^{19}), 8.67 – 8.59 (m, 1H, H^{3}), 8.57 – 8.46 (m, 3H, H^{14}, H^{4}), 8.35 (d, *J* = 8.6 Hz, 1H, H^{6}), 7.76 (td, *J* = 7.8, 1.8 Hz, 2H, H^{16}), 7.47 – 7.37 (m, 2H, H^{7}, H^{26}), 7.32 – 7.21 (m, 4H, H^{17}, H^{15}), 7.22 – 7.14 (m, 1H, H^{24}), 6.97 (dd, *J* = 8.1, 1.2 Hz, 1H, H^{23}), 6.94 – 6.85 (m, 1H, H^{25}), 2.34 (s, 3H, H^{18}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.26 (Cq, C^{8}), 165.49 (Cq, C^{12}), 159.39 (CH, C^{19}), 157.75 (Cq, C^{2}), 154.77 (Cq, C^{10}), 152.45 (Cq, C^{22}), 148.95 (CH, C^{14}), 138.19 (CH, C^{4}), 136.94 (CH, C^{16}), 136.71 (Cq, C^{21}), 136.62 (CH, C^{6}), 129.48 (CH, C^{24}), 125.06 (CH, C^{7}), 123.74 (CH, C^{17}), 122.24 (Cq, C^{5}), 122.14 (CH, C^{15}), 120.22 (CH, C^{26}), 120.15 (CH, C^{25}), 119.89 (CH, C^{3}), 117.02 (CH, C^{23}), 61.29 (Cq, C^{11}), 27.60 (CH_3, C^{18}). Anal Calcd for $C_{27}H_{21}N_5O$·1.2H_2O: C, 71.57; H, 5.21; N, 15.46. Found: C, 71.48; H, 5.37; N, 15.60. ESI-MS (MeOH), *m/z* = 432 $([M + H]^+)$.

Synthesis of imine HL^2. A mixture of aldehyde **IV** (200 mg, 0.59 mmol) and 2-amino-4,6-di-tert-butylphenol[30] (130 mg, 0.59 mmol) in 14mL of EtOH : H_2O (1 : 0.55) was stirred at room temperature overnight. The yellow precipitate was filtered off, washed with EtOH : H_2O, 1 : 0.55 and dried under vacuum to give **HL^2** as yellow powder (271 mg, 84%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.04 (s, 1H, H^{19}), 8.89 – 8.77 (m, 2H, H^{3}, H^{22}), 8.55 – 8.48 (m, 3H, H^{4}, H^{14}), 8.33 (d, *J* = 8.6 Hz, 1H, H^{6}), 7.74 (dd, *J* = 10.9, 4.7 Hz, 2H, H^{16}), 7.48 – 7.42 (m, 2H, H^{7}, H^{26}), 7.31 – 7.22 (m, 5H, H^{17}, H^{15}, H^{24}), 2.33 (s, 3H, H^{18}), 1.43 (s, 9H, H^{28}), 1.30 (s, 9H, H^{30}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.19 (Cq, C^{8}), 165.49 (Cq, C^{12}), 157.76 (Cq, C^{2}), 157.56 (CH, C^{19}), 154.76 (Cq, C^{10}), 149.70 (Cq, C^{22}), 148.92 (CH, C^{14}), 141.28 (Cq, C^{25}), 138.04 (CH, C^{4}), 136.90 (CH, C^{16}), 136.59 (CH, C^{6}), 135.70 (Cq, C^{23}), 134.97 (Cq, C^{21}), 124.92 (CH, C^{7}), 124.08 (Cq, C^{5}), 123.75 (CH, C^{17}), 122.21 (CH, C^{24}), 122.11 (CH, C^{15}), 120.38 (CH, C^{3}), 112.07 (CH, C^{26}), 61.28 (Cq, C^{11}), 35.14 (Cq, C^{27}), 34.72 (Cq, C^{29}), 31.84 (CH_3, C^{30}), 29.83 (CH_3, C^{28}), 27.56 (CH_3, C^{18}). Anal Calcd for $C_{35}H_{37}N_5O$·2EtOH: C, 73.67; H, 7.77; N, 11.01. Found: C, 73.44; H, 8.02; N, 11.33. ESI-MS (DCM), *m/z* = 544 $([M + H]^+)$.

Synthesis of amide H_2L^{1ox}. *Method A*. $NaClO_2$ (266 mg, 5 eq), THF (5 mL), 2-methylbut-2-ene (623 µL, 10 eq) and aq. NaH_2PO_4 (3.3 M, 891 µL, 5 eq) were united in a flask. The imine **HL^1** was dissolved in THF (5 mL) and added dropwise. An intense red color appeared. 20 min after complete addition the reaction was diluted with EtOAc (30 mL) and washed with water, 10% $Na_2S_2O_3$ and brine (10 mL each). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The raw product was purified on a silica gel column via gradient elution, starting with EtOAc : Pentane 1 : 1 and ending with 100% EtOAc giving **H_2L^{1ox}** after evaporation as a yellow solid (220 mg, 67%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 1H, H^{20}), 10.39 (s, 1H, H^{22}), 8.69 (d, *J* = 8.3 Hz, 1H, H^{4}), 8.55 – 8.49 (m, 2H, H^{14}), 8.45 – 8.35 (m, 3H, H^{6}, H^{3}, H^{26}), 7.77 (td, *J* = 7.8, 1.9 Hz, 2H, H^{16}), 7.50 (d, *J* = 8.6 Hz, 1H, H^{7}), 7.32 – 7.25 (m, 4H, H^{15}, H^{17}), 7.04 – 6.95 (m, 2H, H^{23}, H^{24}), 6.92 – 6.86 (m, 1H, H^{25}), 2.37 (s, 3H, H^{18}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.25 (Cq, C^{8}), 165.37 (Cq, C^{12}), 161.65 (Cq, C^{19}), 153.17 (Cq, C^{10}), 152.29 (Cq, C^{2}), 149.04 (CH, C^{14}), 147.23 (Cq, C^{22}), 140.26 (CH, C^{4}), 137.09 (CH, C^{16}), 136.51 (CH, C^{6}), 126.49 (Cq, C^{21}), 126.23 (CH, C^{7}), 124.88 (CH, C^{24}), 123.66 (CH, C^{17}), 123.16 (Cq, C^{5}), 122.24 (CH, C^{15}), 119.93 (CH, C^{26}), 119.79 (CH, C^{25}), 119.68 (CH, C^{3}), 115.33 (CH, C^{23}), 61.42 (Cq, C^{11}), 27.62 (CH_3, C^{18}). Anal Calcd for $C_{27}H_{21}N_5O_2$·H_2O: C, 69.66; H, 4.98; N, 15.04. Found: C, 69.72; H, 4.83; N, 15.09. ESI-MS (CH_3CN), *m/z* = 448 $([M + H]^+)$.

Method B. The aldehyde **IV** (200 mg, 0.59 mmol) and 2-aminophenol (64 mg, 0.59 mmol) were mixed with methanol (10 mL) in a 25 mL round bottom flask. The reaction was stirred at room temperature overnight. The next day the solvent was removed under reduced pressure, the crude product was directly used for the next step. $NaClO_2$ (266 mg, 5 eq), THF (5 mL), 2-methylbut-2-ene (623 µL, 10 eq) and aq. NaH_2PO_4 (3.3 M) (891 µL, 5 eq) were united and the crude product from the previous step dissolved in THF (5 mL) was added dropwise. 20 min after complete addition the reaction was diluted with EtOAc (30 mL) and washed with water, 10% $Na_2S_2O_3$ and brine (10 mL each). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The raw product was purified as described above. Yield: 220 mg, 83%.

Synthesis of amide H_2L^{2ox}. The aldehyde **IV** (200 mg, 0.59 mmol) and 2-amino-4,6-di-*tert*-butylphenol (130 mg, 0.59 mmol) were mixed with 14 mL of EtOH : H_2O (1 : 0.5) (14 mL). The reaction was stirred at room temperature overnight. The next day the solvent was removed under reduced pressure, the crude product was directly used for the next step. $NaClO_2$ (266 mg, 5 eq), THF (5 mL), 2-methylbut-2-ene (623 µL, 10 eq) and aq. NaH_2PO_4 (3.3 M) (891 µL, 5 eq) were united and the crude product from the previous step dissolved in THF (10 mL) was added dropwise. 20 min after complete addition the reaction was diluted with EtOAc (50 mL) and washed with water, 10% $Na_2S_2O_3$ and brine (10 mL each). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The raw product was purified on a silica gel column via gradient elution, starting with EtOAc : Pentane (1 : 1) and ending with 100% EtOAc. Yield: 214 mg, 65%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.65 (s, 1H, H^{20}), 8.69 (d, *J* = 8.3 Hz, 1H, H^{4}), 8.59 (s, 1H, H^{22}), 8.55 – 8.52 (m, 2H, H^{14}), 8.41 (d, *J* = 8.7 Hz, 1H, H^{6}), 8.36 (d, *J* = 8.3 Hz, 1H, H^{3}), 7.93 (d, *J* = 2.3 Hz, 1H, H^{26}), 7.77 (td, *J* = 7.8, 1.9 Hz, 2H, H^{16}), 7.47 (d, *J* = 8.6 Hz, 1H, H^{7}), 7.32 – 7.22 (m, 4H, H^{17}, H^{15}), 7.11 (d, *J* = 2.3 Hz, 1H, H^{24}), 2.38 (s, 3H, H^{18}), 1.41 (s, 9H, H^{28}), 1.29 (s, 9H, H^{30}). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.28 (Cq, C^{8}), 165.40 (Cq, C^{12}), 162.93 (Cq, C^{19}), 153.41 (Cq, C^{10}), 152.71 (Cq, C^{2}), 149.08 (CH, C^{14}), 144.83 (Cq, C^{22}), 142.48 (Cq, C^{25}), 140.02 (CH, C^{4}), 139.09 (Cq, C^{23}), 137.12 (CH, C^{16}), 136.61 (CH, C^{6}), 128.59 (Cq, C^{21}), 126.05 (CH, C^{7}), 123.62 (CH, C^{17}), 123.04 (Cq, C^{5}), 122.25 (CH, C^{15}), 120.02 (CH, C^{3}), 120.00 (CH, C^{24}), 118.18 (CH, C^{26}), 61.46

(Cq, C^{11}), 35.31 (Cq, C^{27}), 34.63 (Cq, C^{29}), 31.88 (CH_3, C^{30}), 30.37 (CH_3, C^{28}), 27.73 (CH_3, C^{18}). Anal Calcd for $C_{35}H_{37}N_5O_2{\cdot}0.9H_2O$: C, 72.99; H, 6.79; N, 12.16. Found: C, 73.22; H, 7.06; N, 11.90. ESI-MS (CH_3CN), *m/z* = 560 ($[M + H]^+$).

Synthesis of tetranuclear complexes $1^{tox}{\cdot}2CH_3CN$ and $1^{tox}{\cdot}2DMF$ $1^{tox}{\cdot}2CH_3CN$. A solution of copper triflate (84 mg, 0.22 mmol, 2 eq) in acetonitrile (5 mL) was added to a solution of **HL^1** (50 mg, 0.116 mmol, 1eq) in acetonitrile (25 mL). Triethylamine (50 µL, 5 eq) were added, giving a dark red solution. The reaction was stirred at room temperature for 12 h. The mixture was concentrated under vacuum, at ca. 10 mL and left to recrystallize by slow diffusion of diethylether to give the complex $1^{tox}{\cdot}2CH_3CN$ as dark-red crystals of $C_{56}H_{40}Cu_4F_6N_{10}O_{12}S_2{\cdot}2CH_3CN$. ESI-MS ($CH_3CN$), *m/z*, *z* = 1, 1327 ($[2M\text{-}OTf]^+$); 590 ($[M\text{-}OTf]^+$) with M = $C_{27}H_{20}N_5O_3Cu_2{\cdot}CF_3SO_3$.

$1^{tox}{\cdot}2DMF$. A solution of copper triflate (81 mg, 0.22 mmol, 2 eq) in acetonitrile (5 mL) was added to a solution of **H_2L^{1ox}** (50 mg, 0.11 mmol, 1eq) in acetonitrile (5 mL). Water (20 µL, 10 eq) and triethylamine (61 µL, 4 eq) were added, giving a dark red-brown solution. The reaction was stirred at room temperature for 3 h. Then THF (100 mL) was added. A dark red-brown precipitate was filtered off, washed with THF and dried in vacuo. The raw product (52 mg) was recrystallized from DMF solution by slow diffusion of di-isopropyl ether. The recrystallized product was filtered off after 12 days, washed with di-isopropyl ether: DMF (5 : 1) then with di-isopropylether and dried under vacuum. Yield: 47 mg, 73%. Anal Calcd for $C_{56}H_{40}Cu_4F_6N_{10}O_{12}S_2{\cdot}2DMF$: C, 45.87; H, 3.35; N, 10.35. Found: C, 45.93; H, 3.32; N, 10.11. ESI-MS (CH_3CN), *m/z, z = 1,* 1327 ($[2M\text{-}OTf]^+$); 590 ($[M\text{-}OTf]^+$) with M = $C_{27}H_{20}N_5O_3Cu_2{\cdot}CF_3SO_3$.

Synthesis of trinuclear complex $[Cu_3(L^{2ox})_2(OH)_2]$ ($2^{triox}{\cdot}H_2O$): A solution of copper triflate (104 mg, 0.29 mmol, 2 eq) in acetonitrile (8 mL) was added to a solution of **H_2L^{2ox}** (50 mg, 0.14 mmol, 1eq) in acetonitrile (5 mL). Water (26 µL, 10 eq) and triethylamine (90 µL, 4.5 eq) were added, giving a dark blue solution. The reaction was stirred at room temperature for 3 h. After, the reaction was stored at 4°C for 1 h. A blue precipitate was filtered off, washed with acetonitrile and dried in vacuo. The raw product (30 mg) was recrystallized from DMF solution by slow diffusion of di-isopropyl ether. The recrystallized product (dark-blue needles of $2^{triox}{\cdot}H_2O$) was filtered off after several days, washed with di-isopropyl ether and dried in vacuo giving 26 mg of blue powder (22%). Anal Calcd for $C_{70}H_{72}Cu_3N_{10}O_6{\cdot}1.1H_2O{\cdot}0.45Cu(CF_3SO_3)_2$: C, 54.90; H, 4.82; N, 9.03. Found: C, 54.62; H, 4.59; N, 9.32.

Crystal Structure Determination and Refinement: Measurements for $1^{tox}{\cdot}2CH_3CN$ and $1^{tox}{\cdot}2DMF$ were made on a Bruker-Nonius Kappa diffractometer with an APEXII detector and a multilayer mirror monochromatized Mo(Kα) radiation (λ = 0.71073 Å) from an Incoatec microsource at 200 K. The data were collected with phi and omega scans. Data were integrated and corrected for Lorentz and polarization factors with Eval 14, then corrected for absorption with Sadabs and merged with Xprep. Crystallographic structures were solved using charge flipping methods implemented by Superflip. C, N, O, S, Cl, and Cu atoms were refined anisotropically by the full matrix least-squares method using ShelxL-2013[31] run under Olex2.[32] H atoms were calculated on idealized positions and constrained on their bearing atoms.

Measurements for $2^{triox}{\cdot}H_2O$ were undertaken on a thin needle (0.168 x 0.014 x 0.014 mm) at the ESRF ID23_1 beamline on a 2 circles Maatel mini-diffractometer (MD2M) with a DECTRIS Pilatus_6M_F detector and a Silicon 111 monochromatized radiation (λ = 0.729 Å) at 100 K. The data were collected with mxCuBE in phi scan mode and integrated and corrected for Lorentz and polarization factors with XDS, then corrected for absorption with Sadabs and finally merged with Xprep. The crystallographic structure was solved and refined as above. The refinement was uneasy since the crystal is a twin and displays large voids were the solvent cannot be ordered. Moreover as described above $2^{triox}{\cdot}H_2O$ displays a statistical disorder by itself. All these elements combined together led to a rather low resolution despite the use of a synchrotron source.

The crystal data of $1^{tox}{\cdot}2CH_3CN$, $1^{tox}{\cdot}2DMF$ and $2^{triox}{\cdot}H_2O$ details of the data collections are given in Table 1.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge The French research agency for support (ANR-13-BSO7-0018) and ICMG FR 2607 (PCN-ICMG). This work has been partially supported by Labex ARCANE (ANR-11-LABX-0003-01) and CBH-EUR-GS (ANR-17-EURE-0003).

Table 1. Experimental details for the X-ray crystal structures of $\mathbf{1}^{\mathbf{tox}}\cdot 2CH_3CN$, $\mathbf{1}^{\mathbf{tox}}\cdot 2DMF$ and $\mathbf{2}^{\mathbf{triox}}\cdot H_2O$

Compound	$\mathbf{1}^{\mathbf{tox}}\cdot 2CH_3CN$	$\mathbf{1}^{\mathbf{tox}}\cdot 2DMF$	$\mathbf{2}^{\mathbf{triox}}\cdot H_2O$
Chemical Formula	$[Cu_4(C_{54}H_{40}N_{10}O_6)\cdot 2(CF_3SO_3)]\cdot 2(C_2H_3N)$	$[Cu_4(C_{54}H_{40}N_{10}O_6)\cdot 2(CF_3SO_3)]\cdot 2(C_3H_7NO)$	$[Cu_3(C_{70}H_{72}N_{10}O_6S)]\cdot H_2O$
Formula mass	1559.37	1623.45	1358.01
Morphology	plate	plate	needle
Color	Red-dark	black	Blue-dark
Crystal size (mm)	0.47 × 0.30 × 0.20	0.26 × 0.22 × 0.22	0.168 × 0.014 × 0.014
Crystal system	monoclinic	monoclinic	triclinic
Space group	C 1 2/c 1	C 1 2/c 1	*P*-1
a [Å]	22.949(5)	22.475(5)	14.798(3))
b [Å]	11.893(2)	12.394(3)	15.401(3)
c [Å]	22.443(5)	22.723(5)	16.328(3)
α [°]	90.00	90.00	107.44(3)
β [°]	91.65(3)	91.06(3)	116.00(3)
γ [°]	90.00	90.00	91.19(3)
Unit-cell volume [$Å^3$]	6125(2)	6329(2)	3140.0(14)
D_x ($g\cdot cm^{-3}$)	1.691	1.704	1.436
T [K]	200	200	100
Z	4	4	2
μ [mm^{-1}]	1.531	1.487	1.138
Total reflections	54508	27897	35660
Unique reflections	7031	6189	16002
Obsd. reflections	5882 ($F > 2\sigma$)	4960 ($F > 2\sigma$)	8810($F > 2\sigma$)
Rint.	0.0614	0.0793	0.0655
R^a	0.0422	0.0560	0.1296
$R(w)^a$	0.1083	0.1249	0.3859
Goodness of fit *S*	1.111	1.087	1.375
$\Delta\rho_{min}/\Delta\rho_{max}$ ($e\cdot Å^{-3}$)	-0.700/0.507	-0.794/0.119	-1.181/1.806

[a] Refinement based on F where $w = 1/[\sigma^2(Fo)^2 + (0.0466p)^2 + 22.6631p]$ with $p = (Fo^2 + 2Fc^2)/3$ for $\mathbf{1}^{\mathbf{tox}}\cdot 2CH_3CN$; $w = 1/[\sigma^2(Fo)^2 + (0.0550p)^2 + 44.5733p]$ with $p = (Fo^2 + 2Fc^2)/3$ for $\mathbf{1}^{\mathbf{tox}}\cdot 2DMF$; $w = 1/[\sigma^2(Fo)^2 + (0.2000p)^2]$ with $p = (Fo^2 + 2Fc^2)/3$ for $\mathbf{2}^{\mathbf{triox}}\cdot H_2O$.

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