Solvent-dependent access to mono- and dinuclear copper(II) assemblies based on a flexible imidazole ligand†

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Seven copper(II) complexes with the less bulky (compared to bis-phenyl-substituted imidazoles used in our previous studies) monodentate 2-phenylimidazole (LH) ligand have been prepared from the general CuII/X/LH (X = NO3, ClO4, BF4, SO4, Cl⁻) reaction system and were structurally characterized by X-ray diffraction. Interestingly, the choice of reaction/crystallisation solvent provides two distinct groups of complexes: methanolic solutions favour mostly the formation of dinuclear products (i.e. [Cu2(OMe)2(NO3)2(LH)4](Σ2MeOH) (1a·2MeOH), [Cu2(O2)2(LH)4](ClO4)2 (2a), [Cu2(OMe)2(LH)4]SiF6 (3), [Cu2(SO4)2(LH)4] (4)), whereas in the presence of acetonitrile, mononuclear cationic complexes were isolated (i.e. [Cu(LH)]NO3 (1b) and [Cu(LH)]4(ClO4)2 (2b)). A notable exception is the mononuclear complex [CuCl2(LH)2] (5) isolated from methanol. The roles of the solvent and inorganic anions on the complex stoichiometry and molecular structure are critically discussed. The complexes’ self-assembly is firmly directed by robust N–H···X (X = O, Cl or F) motifs, leading to varying dimensionalities and packing arrangements depending on the coordinated/counter inorganic ions: 1D tapes (for NO3 in 1b), layers (for ClO4 in 2a and 2b, SiF6 in 3 and Cl⁻ in 5) and 3D networks (for NO3 in 1a and SO4 in 4). Intramolecular π···π interactions enhance the rigidity of certain complexes, and additional weak intermolecular C–H···Y (Y = O, Cl or F), C–H···π and π···π interactions complement the stability of the packing towards 3D assemblies. Lastly, comparisons of the molecular and supramolecular chemistry of the Cu(II)/LH complexes with previously characterized Cu(I) complexes with the bulkier 4,5-diphenylimidazole ligand reveal similarities and differences, which are discussed.

Introduction

Metal–organic coordination complexes nowadays form a topic of intense research in the field of crystal engineering. However, control over the formation and the structural types of the complexes resulting from the self-assembly reactions remains a daunting and challenging task. The outcome often is not only affected by the highly influential forces of metal and ligand coordination preferences, but also by the presence of species such as inorganic ions and solvents of crystallisation. The influence of inorganic ions and crystallisation solvents is usually expected to be more notable in metal complexes with a flexible coordination sphere. Copper(II), for example, has been proven popular in metallosupramolecular chemistry, as it favours a variety of coordination numbers and geometries that can be realized – even controlled to a certain extent – by duly selected ligands and reaction conditions.

Recent reports by our group on a series of complexes employing copper(II) and other 3d metals with the heavily-substituted monodentate ligand 4,5-diphenylimidazole (LH) have plainly demonstrated the dominant role of recurring hydrogen-bond patterns in organizing the individual complexes into supramolecular arrays among a variety of coordination geometries and crystalline environments. However, despite the abundance of aromatic rings, the number of intermolecular π···π stacking interactions observed in these systems is remarkably low, possibly due to steric reasons or/and the weak nature of these interactions. With our previous experience in mind, we sought to use CuII with a similar but

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less bulky—and thus more versatile—ligand, namely 2-phenylimidazole (LH), to investigate the extent to which LH might allow or stimulate a differentiation of the intermolecular interactions in relation with those of 4,5-diphenylimidazole.

Neutral 2-phenylimidazole coordinates to a metal ion via its pyridine-type nitrogen atom. It has a hydrogen-bond donor (the pyrrolic-type nitrogen atom) enabling the formation of supramolecular patterns and is capable of forming two $\pi \cdots \pi$ interactions by means of its aromatic rings. The various ions in the CuX$_2$ salts used (X$^-$ = NO$_3^-$, ClO$_4^-$, BF$_4^-$, SO$_4^{2-}$, Cl$^-$) were chosen for (i) their tendency to coordinate as mono- or bidentate ligands, (ii) their ability to act as counterions, and (iii) their size, shape and charge variation, in order to study their effect on the Cu$^{II}$ coordination geometry and the complex stoichiometry, as well as their spatial role in the motif formation and packing organization. Bromides and thiocyanates were also used as inorganic anions in the CuX$_2$ starting materials, but the obtained products (IR evidence) suffered from poor crystallinity. A total of seven new Cu$^{II}$ complexes of LH are reported herein, prepared and characterized in line with this approach (Scheme 1). One synthetic or crystallization parameter at a time was varied during each set of experiments in order to assess its effect on the product identity. Finally, a comparison of the Cu$^{II}$/LH and Cu$^{II}$/L coordination and supramolecular chemistry is attempted.

Results and discussion

A variety of reactions and crystallization conditions have been methodically studied, aimed at preparing the largest possible number of Cu$^{II}$ complexes of LH. The general synthetic route, together with the individual formulae of the resulting complexes, is illustrated in Scheme 1. All common crystallization solvents were utilised. It turns out that crystalline products were isolated in line with this approach (Scheme 1). One synthetic or crystallization parameter at a time was varied during each set of experiments in order to assess its effect on the product identity. Finally, a comparison of the Cu$^{II}$/LH and Cu$^{II}$/L coordination and supramolecular chemistry is attempted.
intermolecular N–H⋯O(NO$_3$) motifs towards a solid 3D assembly (Fig. 1b). The implementation of the pattern is facilitated by appropriately located MeOH molecules that bridge the complexes via N–H⋯O(MeOH)–H⋯O(NO$_3$) interactions.
Along these interactions, weak C–H⋯O(NO$_3$) and C–H⋯π contacts further interlink the complexes and support the packing (Table S2†). The lack of any intra- or intermolecular aromatic π⋯π contacts in 1a is indicative of their weakness to form at the expense of the dominant N–H⋯O synths.

Replacing MeOH with MeCN as reaction/crystallization solvent in the reaction of Cu(NO$_3$)$_2$ with LH afforded the mononuclear compound 1b, crystallized in Cc. The structure consists of complex [Cu(LH)$_4$]$_2^{2+}$ cations counterbalanced by nitrates (Fig. 2a). The Cu$^{II}$ centre is coordinated by the nitrogen donor atoms of the four ligands in a slightly distorted CuN$_4$ square planar geometry. Analysis of the shape-determining angles using the approach of Yang, Powell and Houser$^{14}$ gives a value of 0.05 for the four-coordinate geometry index $\tau_4$ ($\tau_4$ equals 0 for square planar and 1 for tetrahedral coordination). The ligands of the cation are associated in pairs via two intramolecular π⋯π stacking interactions (Table S3†), resulting in a total of four contacts and providing rigidity to the cation. Despite the differences of complexes 1a and 1b in terms of stoichiometry and coordination geometry, their packing is guided by the same hydrogen-bond pattern. The four N–H groups of each [Cu(LH)$_4$]$_2^{2+}$ cation, lying on the CuN$_4$ plane and pointing outwards in opposite directions, are linked through N–H⋯O(NO$_3$) interactions with the intervening nitrates forming robust tapes (Fig. 2b and c). Weak C–H⋯π(NO$_3$) interactions further link the tapes into layers and ultimately into a 3D network.

Replacement of nitrates by perchlorates in the Cu(ii) salt used for preparing compound 1a in MeOH leads to a similar dinuclear centrosymmetric compound, 2a, except that the perchlorates are not coordinated but are present as counterions. The coordination geometry around the two Cu$^{II}$ centres is best described as distorted square planar ($\tau_4 = 0.17$) and is made up by two nitrogen donor atoms from the ligands and two μ-methoxido oxygen atoms. The Cu⋯Cu distance is 2.994(1) Å. As in 1a, the packing organization of 2a is directed by the same recurrent N–H⋯O interactions. However, its topological arrangement is different (Fig. 3). Each cation is surrounded by a total of six perchlorates; four of them bridge neighbouring complexes via strong N–H⋯O(ClO$_4$) motifs into corrugated layers, whereas the remaining perchlorates connect the layers via weak C–H⋯O(ClO$_4$) contacts. The cis arrangement of the two LH ligands around each Cu$^{II}$ atom, together with the available space around each cation due to the surrounding perchlorates, allows the formation of two intramolecular π⋯π stacking interactions per Cu$^{II}$ moiety. At the same time, the separating action of the perchlorates prevents any reliable intermolecular π⋯π contact from being formed, the shortest one having a centroid-centroid distance of 4.045(1) Å.

The solvent effect observed upon the structures of 1a and 1b is also apparent in the preparation of compounds 2a and 2b; i.e., the latter was isolated by simply replacing MeOH with MeCN (Scheme 1). The asymmetric unit of 2b (space group Aba2) contains half a [Cu(LH)$_4$]$^{2+}$ cation, the other half generated by a $C_2$ axis lying on the CuN$_4$ plane and passing through the metal centre. Complexes 1b and 2b have a similar conformation, the largest deviations occurring in the region of the phenyl rings (Fig. 4a), most likely to comply with packing requirements. Apparently, 2b retains the square planar geometry ($\tau_4 = 0.02$) and the stabilizing intramolecular π⋯π pattern. The four perchlorates around each [Cu(LH)$_4$]$^{2+}$ cation of 2b effectively direct the self-organization into corrugated layers through N–H⋯O(ClO$_4$) motifs (Fig. 4b and c). At a

![Fig. 2](image-url) (a) The [Cu(LH)$_4$]$^{2+}$ cation of compound 1b with the two pairs of intramolecular π⋯π stacking interactions (colored pink and green). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted. (b) Tapes in the crystal structure of 1b formed by the cations and nitrate counterions via strong N–H⋯O motifs. Only species involved in these interactions are shown. (c) Schematic representation of the 1D tapes in 1b.
second level of organisation, a combination of weak C–H⋯O(ClO4−) and C–H⋯π contacts complement the structure towards a 3D network.

Reaction of CuIJBF4)2·6H2O with LH in MeOH yielded compound [Cu2(OMe)2(LH)4]3+ (3), the hexafluorosilicate analogue of [Cu2(OMe)2(NO3)2(LH)4](1a) and [Cu2(OMe)2(LH)4](ClO4)2 (2a), all three isolated using the same solvent. It follows that the atoms coordinated to CuII in complexes 2a and 3 are the same; however, the geometry around Cu1 atom is distorted square planar (τ4 = 0.12), whereas that of Cu2 (τ4 = 0.30) can be best described as a seesaw configuration.14 The Cu⋯Cu distance is 3.034(1) Å. Contrary to 2a, no intramolecular π⋯π stacking is formed. Strong N–H⋯F(SiF62−) interactions dominate the self-assembly of the [Cu2(OMe)2(LH)4]3+ cations of compound 3. Because of the difference in size, charge and number of binding sites between the tetrahedral perchlorate and the octahedral hexafluorosilicate counterions, the cations of 3 are surrounded by four SiF62− ions that connect them into layers (Fig. 5). In turn, adjacent layers are held together in a 3D structure through weak C–H⋯F(SiF62−) contacts and intermolecular π⋯π stacking interactions.

Change of the copper salt to CuSO4·5H2O under the adopted general reaction system in MeOH results in the neutral dinuclear complex [Cu2(SO4)2(LH)4](4) (Fig. 6), in which the CuII centres are bridged by two η1:η1:μ sulfato groups. Given the well-known potentiality of the sulfate ion as a bridging ligand in 3d-metal complexes,15 complex 4 appears to be more thermodynamically stable than the [Cu2(OMe)2(LH)4]SO4 compound (due to MeOH) or the hypothetical mononuclear analogue, i.e. [Cu(LH)]SO4 (4′). Complex 4 is centrosymmetric (P21/c) with a Cu⋯Cu distance of 4.882(1) Å, markedly longer than that of the previous dinuclear complexes. Inspection of the metal geometry in the complex (τ4 = 0.21) clearly suggests a seesaw environment for the coordination of the CuII centres.14 A plethora of intermolecular interactions contribute to the supramolecular...
organization of the complex (Fig. S1†). The anticipated strong N–H⋯OĲSO42− interactions direct the self-assembly and give rise to a 3D network supported by C–H⋯OĲSO42− and C⋯H⋯π contacts, as well as a few aromatic π⋯π stacking interac-
tions (two per complex).

The [CuCl2(LH)2] complex (5) was isolated from the CuII/Cl−/LH reaction mixture using MeOH as solvent, whereas the change to MeCN only resulted in a powdered product whose structure could not be further identified. The complex crystallizes in the Pbc a space group with the CuII atoms situated on the inversion centres of the structure. Thus, i) a square pla-
nar geometry (τ4 = 0.00) is imposed on the CuN2Cl2 group, and ii) the two LH ligands and the two chlorido atoms are ar-
ranged in trans dispositions, thereby preventing the forma-
tion of any intramolecular π⋯π stacking (Fig. 7). The N–H donor groups form the basis of the complexes’ association through strong N–H⋯Cl synthons generating corrugated layers parallel to the ab plane. Infinite inter-
molecular π⋯π stacking interactions within each layer run-
ning along the b axis enhance the internal stability of the layers. The ability of the coordinated chlorides to act as multihydrogen-bonded acceptors enables the formation of weak C–H⋯Cl contacts, interlinking the layers into a 3D architecture.

Based on the structures of most complexes in this study, one can notice the effect of the solvent used in reaction/crys-
tallization experiments upon the isolated compounds. When the non-coordinating MeCN solvent is used, the CuII centres of the resulting mononuclear cationic complexes are coordi-
nated exclusively by the LH ligand. Replacement of MeCN with MeOH as reaction/crystallization solvent in the reactions of CuX2 might introduce a potential competition between MeOH and the inorganic anions for the metal’s coordination sites, leading mostly to dinuclear complexes. This effect is straightforward in complexes 1a·2MeOH, 2a and 3 with the methoxido groups, generated as described above, bridging effec-
tively the two CuII ions. Complex 4 retains a dinuclear character with the sulfate ions bridging the metal centres, whereas the relatively lower bridging affinity of the chlorido

![](image1.png)

**Fig. 5** A part of the crystal structure of 3. (a) The [Cu2(OMe)2(LH)4]2+ cations and the surrounding hexafluorosilicates form layers via strong N–H⋯F motifs. (b) Schematic representation of the layers.

![](image2.png)

**Fig. 6** The centrosymmetric complex [Cu2(SO4)2(LH)4] (4). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted.

![](image3.png)

**Fig. 7** (a) The [CuCl2(LH)2] molecules in 5 are linked via strong N–H⋯Cl synthons generating corrugated layers. (b) Schematic representation of the layers of 5.
ligands is probably responsible for the isolation of the mononuclear complex 5.

The ions used or produced (NO$_3^-$, ClO$_4^-$, SiF$_6^{2-}$, SO$_4^{2-}$ and Cl$^-$) have a significant impact upon both the molecular and supramolecular organization of the structures. As discussed, the ions can be found as coordinated ligands (NO$_3^-$, Cl$^-$, SiF$_6^{2-}$, SO$_4^{2-}$) or as counterions (NO$_3^-$, ClO$_4^-$, SiF$_6^{2-}$) depending not only on their size, shape, charge and ligation ability, but also on the solvent (the case of NO$_3^-$ in 1a·2MeOH and 1b). However, in all cases, the ions contribute decisively to the complexes' self-assembly through persistent N–H···X (X = O, Cl or F) motifs, resulting in structures with varying dimensionalities and packing arrangements. As shown, coordinated ions lead mostly to 3D networks (1a, 4), whereas for the remaining structures, 1D tapes (1b) and 2D layers (2a, 2b, 3, 5) are formed.

All N–H donor groups of the LH ligands in both the mono- and dinuclear complexes are fully engaged in N–H···X synthons, distinctly dominating the molecular association and packing organization. For this purpose, the ligand exhibits a sufficient conformational flexibility to minimize any steric hindrance and facilitates the formation of these hierarchically important synthons [the dihedral angle between the two rings among all ligands ranging from 21.2(3)$^\circ$ to 47.8(2)$^\circ$]. Given the weak and stericly demanding nature of the π···π stacking interactions, it is difficult to rationalise them or extract solid conclusions for the current set of compounds. With the exception of 1a, all structures possess either intra- or intermolecular π···π stacking (Table S3†), but not both types, presumably due to the separating action of the coordinating or intervening counterions. It appears that these subordinate interactions only appear when allowed and certainly not at the expense of the structure-determining synthons.

A comparison of the structural characteristics of 1a·2MeOH, 2a, 5, 1b and 2b with the complexes isolated from the reactions of CuCl$_2$·2H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O and Cu(ClO$_4$)$_2$·6H$_2$O with the bulkier ligand 4,5-diphenylimidazole (L'H) is difficult (mainly due to the different solvents used), but this might be somewhat useful. The formulae of the Cu$^{II}$/L'H complexes are [CuCl$_2$(L'H)$_2$][Me$_2$CO·0.25H$_2$O (6-Me$_2$CO·0.25H$_2$O), [CuCl(L'H)$_2$Cl·0.6H$_2$O (7·0.6H$_2$O), [Cu(L'H)$_2$][ClO$_4$]$_2$·EtOH·CH$_2$Cl$_2$·H$_2$O (8·EtOH·CH$_2$Cl$_2$·H$_2$O) and [Cu(NO$_3$)$_2$(L'H)$_2$]·MeCN (9·MeCN). The ionic compound 7·0.6H$_2$O, prepared in Me$_2$CO and crystallized with n-hexane, and the 1:2 neutral complex 9·MeCN, prepared and crystallized in MeCN, have no counterparts in the Cu$^{II}$/L'H chemistry described in this work. This is rather surprising for the 1b, 9·MeCN pair of nitrate/nitrito complexes, which have been prepared and characterized by exactly the same procedures. This shows that the coordination chemistries of LH and L'H are not identical, although both ligands are monodentate, with the pyridine-type nitrogen being the donor atom. In the presence of NO$_3^-$ ions, which have a moderate coordinating ability, the bulkier L'H ligand forms the 1:2 neutral complex 9·MeCN, thus leading to less steric hindrance in the solid state, while the less bulky LH ligand gives the 1:4 cationic compound. This is not the case with the ClO$_4^-$ ion; its weak coordinating ability has, as a result, the isolation of 1:4 cationic compounds (2b, 8·EtOH·CH$_2$Cl$_2$·H$_2$O) for both ligands. In both 2b and 8·EtOH·CH$_2$Cl$_2$·H$_2$O, the Cu$^{II}$ centre adopts a square planar geometry. The monomeric nature of the two complexes is attributed to the reaction/crystallization solvents (MeCN/Et$_2$O in 2b and CH$_2$Cl$_2$/EtOH/n-pentane in 8·EtOH·CH$_2$Cl$_2$·H$_2$O, EtOH being in a small volume ratio in the latter); thus, the non-isolation of [Cu$_2$(OEt)$_2$(L'H)$_2$][ClO$_4$]$_2$, i.e., an analogue of 2a, seems reasonable. Complexes 5 and 6·Me$_2$CO·0.25H$_2$O have the same 1:2 metal-to-ligand ratio, but a different coordination geometry (trans square planar in 5 and a seesaw one with the two ligands in a syn fashion in 6·Me$_2$CO·0.25H$_2$O), giving further evidence for the differences of the two ligands from the coordination chemistry viewpoint.

At the supramolecular level, in both families of Cu$^{II}$/complexes, the reactions of various copper(II) compounds, and recrystallization (in the case of Cu$^{II}$/L'H complexes) and methanol (in the case of Cu$^{II}$/L'H complexes) contribute actively, when needed, to maximize the number of these motifs. At a second level of organization, additional subordinate C–H···Y (Y = O, Cl) and C–H···π interactions complement the rigidity of the structures for both families. Concerning the intermolecular π···π stacking interactions, there are differences between the corresponding members of the two families, as expected; however, the general rule is that their number is small, indicating their weakness in the two systems and their “reluctance” to form at the expense of stronger interactions. As far as the intramolecular π···π stacking interactions are concerned, a common feature of the [Cu(L'H)$_2$]$_2^{2+}$ (complexes 1b and 2b) and [Cu(L'H)$_2$]$_2^{2+}$ (complex 8·EtOH·CH$_2$Cl$_2$·H$_2$O) cations is the fact that their four ligands are associated in pairs and held tightly via such interactions.

Conclusions

The reactions of various copper(II) sources with 2-phenylimidazole in two selected solvents produced two distinct groups of complexes that exhibit interesting features in their molecular composition and supramolecular association. Methanolic solutions favour mostly the isolation of dinuclear products, whereas mononuclear complexes were isolated in acetonitrile, indicating the crucial role of the solvent upon metal coordination and complex stoichiometry. The ions used or generated (NO$_3^-$, ClO$_4^-$, SiF$_6^{2-}$, SO$_4^{2-}$ and Cl$^-$) in solution, coordinated or as counterions, contribute to the formation of various molecular structures and packing arrangements; however, their distinct function is to direct the self-assembly process via structure-determining N–H···X (X = O, Cl or F) conserved synthons. The flexible 2-phenylimidazole has been proven to be a useful ligand, featuring the necessary adaptability to facilitate the formation of the maximum possible number of intermolecular interactions.
Experimental

All reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. All manipulations were performed under aerobic conditions. Microanalyses (C, H, N) were performed by the University of Patras microanalytical service. FT-IR spectra (4000–400 cm\(^{-1}\)) were recorded using a PerkinElmer PC 16 FT-IR spectrometer with samples prepared as KBr pellets (Fig. S2†).

Preparation of complexes

Safety note: Perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities and treated with great care at all times.

Complex 1a·2MeOH. A solution of LH (0.288 g, 2.00 mmol) and Cu(NO\(_3\))\(_2\)·3H\(_2\)O (0.121 g, 0.50 mmol) in MeOH (25 ml) was stirred for 45 min. The reaction solution was filtered and stored at low temperature (5 °C) to produce blue prismatic crystals of 1a·2MeOH after 4 days; yield ca. 70% [based on Cu(u)].

Complex 1b. A solution of LH (0.288 g, 2.00 mmol) and Cu(NO\(_3\))\(_2\)·3H\(_2\)O (0.121 g, 0.50 mmol) in MeCN (25 ml) was stirred for 45 min. The reaction solution was filtered. Upon slow evaporation of the filtrate, brown prismatic crystals of 1b were obtained after 8 days; yield ca. 70% [based on Cu(u)].

Complex 2a. The preparation of 2a was similar to that of 1a except that CuCl\(_2\)·2H\(_2\)O (0.185 g, 0.50 mmol) was used instead of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. The resultant green solution was layered with Et\(_2\)O (50 ml) to produce bluish prismatic crystals of 2a after 5 days; yield ca. 55% [based on Cu(u)].

Complex 2b. The preparation of 2b was similar to that of 1b except that CuCl\(_2\)·2H\(_2\)O (0.185 g, 0.50 mmol) was used instead of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. The resultant brown solution was layered with Et\(_2\)O (50 ml) to produce brown prismatic crystals of 2b after 3 days; yield ca. 75% [based on Cu(u)].

Complex 3. The preparation of 3 was similar to that of 1a except that Cu(BF\(_4\))\(_2\)·6H\(_2\)O (0.173 g, 0.50 mmol) was used instead of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. The resultant green/blue solution was layered with Et\(_2\)O (50 ml) to produce blue prismatic crystals of 3 after 15 days; yield ca. 25% [based on Cu(u)].

Complex 4. The preparation of 4 was similar to that of 1a except that CuSO\(_4\)·5H\(_2\)O (0.125 g, 0.50 mmol) was used instead of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. Upon slow evaporation of the obtained filtrate, blue prismatic crystals of 4 were obtained after 6 days; yield ca. 55% [based on Cu(u)].

Complex 5. The preparation of 5 was similar to that of 1a except that CuCl\(_2\)·2H\(_2\)O (0.085 g, 0.50 mmol) was used instead of Cu(NO\(_3\))\(_2\)·3H\(_2\)O. The resultant green solution was layered with Et\(_2\)O (50 ml) to produce green prismatic crystals of 5 after 5 days; yield ca. 50% [based on Cu(u)].

Crystallography

Single crystals covered with paratone-N oil were scooped up in cryo-loops at the end of a copper pin. X-ray diffraction data were collected (ω-scans) on a SuperNova A Agilent Technologies diffractometer under a flow of nitrogen gas at 100(2) K using Mo K\(_\alpha\) (\(\lambda = 0.7107 \text{ Å}\)) or Cu K\(_\alpha\) (\(\lambda = 1.5418 \text{ Å}\)) radiation. Data were collected and processed by the CRYSTALS CCD and RED software,16 respectively; the reflection intensities were corrected for absorption by the multiscan method. All structures were solved using direct methods with SIR9217 and SHELXS-9718 and refined by full-matrix least-squares on \(F^2\) with SHELXL-2014/7.19 All non-H atoms were refined anisotropically; carbon-bound H-atoms were included in calculated positions (riding model). All imidazole H-atoms on the pyrrolic type N1 atom, together with the hydroxyl H-atoms of MeOH solvent in compound 1a·2MeOH, were located in difference Fourier maps and refined isotropically, applying soft distance restraints (DFIX).

The structure of 1b was refined as 50:50 twinned by inversion. The disordered
Table 2  Crystal data and structure refinement summary for compounds 1a−2MeOH−5

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<td>94.439(2)</td>
<td>92.226(2)</td>
<td>90.00</td>
<td>99.59(6)</td>
<td>100.83(2)</td>
<td>90.00</td>
</tr>
<tr>
<td>γ°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
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<td>90.00</td>
</tr>
<tr>
<td>Unit cell volume/Å³</td>
<td>2148.68(7)</td>
<td>3448.01(9)</td>
<td>2028.96(9)</td>
<td>3671.0(4)</td>
<td>3913.9(5)</td>
<td>1887.10(7)</td>
<td>1830.37(10)</td>
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<tr>
<td>Temperature/K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td>100(2)</td>
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<tr>
<td>Space group</td>
<td>Cc</td>
<td>P2₁/n</td>
<td>Cc</td>
<td>Aca2</td>
<td>P2₁/n</td>
<td>P2₁/c</td>
<td>Pbca</td>
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<tr>
<td>No. of formula units/unit cell, Z</td>
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<td>4</td>
<td>2</td>
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<tr>
<td>Radiation type</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
<td>CuKα</td>
<td>MoKα</td>
<td>MoKα</td>
</tr>
<tr>
<td>Absorption coefficient, μ/mm⁻¹</td>
<td>1.058</td>
<td>0.697</td>
<td>1.248</td>
<td>0.805</td>
<td>2.282</td>
<td>1.301</td>
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<tr>
<td>No. of reflections measured</td>
<td>23157</td>
<td>16423</td>
<td>9555</td>
<td>13.913</td>
<td>11.985</td>
<td>8551.1</td>
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<td>No. of independent reflections</td>
<td>4661</td>
<td>6685</td>
<td>4200</td>
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<td>4086</td>
<td>1982</td>
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<tr>
<td>R₁ values (I &gt; 2σ(I))</td>
<td>0.0290</td>
<td>0.0358</td>
<td>0.0271</td>
<td>0.0478</td>
<td>0.0282</td>
<td>0.0256</td>
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</tr>
<tr>
<td>Final R₁ values (all data)</td>
<td>0.0258</td>
<td>0.0336</td>
<td>0.0343</td>
<td>0.0317</td>
<td>0.0350</td>
<td>0.0339</td>
<td>0.0256</td>
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<tr>
<td>Final wR² (all data)</td>
<td>0.0696</td>
<td>0.0767</td>
<td>0.0763</td>
<td>0.0762</td>
<td>0.0805</td>
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<td>0.0641</td>
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<tr>
<td>Final R₁ values (all data)</td>
<td>0.0301</td>
<td>0.0383</td>
<td>0.0427</td>
<td>0.0355</td>
<td>0.0501</td>
<td>0.0417</td>
<td>0.0318</td>
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<tr>
<td>Final wR² (all data)</td>
<td>0.0706</td>
<td>0.0794</td>
<td>0.0811</td>
<td>0.0787</td>
<td>0.0877</td>
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<td>Goodness of fit on F²</td>
<td>1.042</td>
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<td>1.059</td>
<td>1.053</td>
<td>1.019</td>
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<td>1454684</td>
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</table>
[SiF$_6$]$^{2-}$ counter ion in 3 has been modelled over two orientations. Geometric/crystallographic calculations were carried out using PLATON,$^{20}$ OLEX2,$^{21}$ X-Seed$^{22}$ and WINGX$^{23}$ packages; molecular/packing graphics were prepared with DIAMOND$^{24}$ and MERCURY.$^{25}$ Experimental details are listed in Table 2.

Acknowledgements

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Notes and references


