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Solvatomorphism with polar protic/aprotic and non-polar solvents in a series of complexes derived from the 5-phenylimidazole/ tetrafluoroborate/copper(II) reaction system†

Maria-Ioanna Delegkou, Panagiotou, Nikos Panagiotou, b Constantina Papatriantafyllopoulou, ^{Dbc} Anastasios Tasiopoulos, ^{Db}

In a search to explore the structural landscape of possible copper(III) complexes with the 4-phenylimidazole/ tetrafluoroborate combination, considerable solvatomorphism has emerged. The utilization of a wide variety of crystallization solvents (polar protic, polar and non-polar aprotic) resulted in a series of seventeen crystalline solvatomorphs with the general formulae $[Cu(BF_4)_2(HL)_4] \cdot x(solvent)$ [HL = 5-phenylimidazole, x(solvent) = 2(acetone)-2(water) (1), 2(methanol) (2), 2(ethanol) (3), 2(1-propanol) (4), 1.4(2-propanol) (5), 2(1-butanol) (6), 2(iso-butanol) (7), 1.33(tert-butanol) (8), 2(1-pentanol) (9), 2(dimethylformamide) (10), 1.2(acetone) (11), 2(tetrahydrofurane) (12), 1.85(1,4-dioxane) (13), 0.86(ethyl acetate) (14), 1(diethyl ether) (15), 0.7(diisopropyl ether) (16), 1(n-hexane) (17)]. A reaction using the CH₂Cl₂/ MeCN solvent system produced crystals of the [Cu(HL)₄(MeCN)(H₂O)_{0.4}](BF₄)₂ complex (18). Crystallization with nitromethane yielded [Cu{SiF₂O(OMe)}₂(HL)₄]-0.8MeNO₂ (19·0.8MeNO₂), due to the in situ reaction of fluoride ions from BF₄⁻ ions with the glass surface of the vial used to grow crystals. The structures have been solved by single-crystal X-ray diffraction and the complexes were characterized by thermal analysis and infrared spectroscopy. The crystallization solvents are located in channels, with the exception of 1.33(tert-butanol) (8) and 1.2(acetone) (11) residing in lattice pockets. An analysis to understand the role of the solvents in the molecular self-assembly process is described. Depending on the hydrogen-bond functionalities of each solvent, three distinct cases emerge i) the solvents link neighboring [Cu(BF₄)₂(HL)₄] molecules via N-H···O_{solvent}-H···F intermolecular associations (polar protic solvents, compounds 1-9), ii) they are terminally connected to $[Cu(BF_4)_2(HL)_4]$ molecules (polar aprotic solvents, compounds 10-13) and iii) they simply reside in channels without any involvement in supramolecular motifs (non-polar solvents, compounds 14-17). The final crystal packings result from the concerted action of robust N-H···F synthons and the above described interactions involving the solvent molecules.

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Introduction

Two important crystallization parameters are the solvent used and the environmental conditions during storage of the reaction solution (e.g. temperature, relative humidity).1 Different solvents interact differently with a specific solute, affecting greatly the crystallization process.² The presence of guest lattice solvent molecules within the crystal can affect the molecular conformation of the host molecule in the structure, as well as the type and strength of intermolecular interactions that characterize the crystal lattice, resulting in different physicochemical properties, such as thermodynamic stability, density, solubility, dissolution rate.

Solvatomorphism, also named pseudopolymorphism, refers to the ability of a compound to yield crystal structures with unit cells that differ in their elemental composition through the inclusion of various amounts or types of solvent molecules,³ or shortly, the term solvatomorphism is used for designating solvate diversity of a particular host compound.⁴ There has been a long discussion and interesting arguments among experts in the field on the use of the terms solvatomorph and pseudopolymorph (or supramolecular

^a Department of Chemistry, University of Patras, 26504 Patras, Greece. E-mail: nastopoulos@upatras.gr

^b Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

^c National University of Ireland Galway, H91 TK 33 Galway, Ireland

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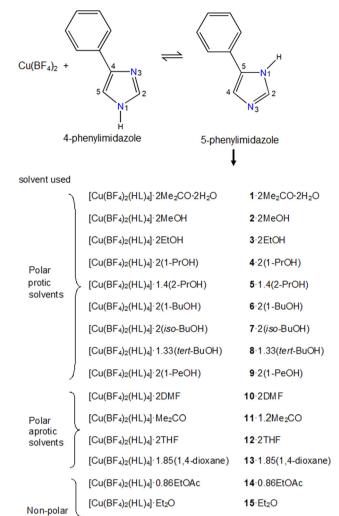
solvents

CH₂Cl₂/MeCN

MeNO₂

isomer, co-crystal, solvate, or even false polymorph or quasipolymorph) that could describe, as clear and concise as possible, the above category of crystalline structures.⁵⁻¹³ Reaching consensus on this issue is important for scientific communication, and possibly also for intellectual property purposes.¹⁴ In the current study we opted for the term solvatomorphism, to point out that the crystalline structures $[Cu(BF_4)_2(HL)_4] \cdot x(solvent)$ presented here, where HL is 5-phenylimidazole, differ in the type of solvent incorporated during crystallization of the molecule. Polymorphism (the phenomenon wherein the same substance exhibits different crystal packing arrangements¹⁵) and solvatomorphism have been interesting topics in crystal structure engineering in relation to the implications on the crystal packing (structural patterns, pre-desired topologies) and, ultimately, to the potential impact on the properties of crystalline solids (crystal property engineering). 16-18 With respect solvatomorphism in particular, the effect of the solvent on the organization of the supramolecular systems (based on solute-solvent specific interactions) is well-known and of great interest, both for academic studies and practical applications. 19-21 For example, this has implications in pharmaceutical compounds (affecting their bioavailability, stability, purification process, among other factors, and hence the performance of the drug), in biological systems (where denaturation of proteins, by altering the protein solvent environment, results in significant changes in their biological activities), in the material sciences (e.g. in the selfassembly of MOFs, 22,23 in organic and inorganic functional nanomaterials, 24,25) to cite a few areas. It is noted that for some important compounds, such as active pharmaceutical ingredients (APIs), solvatomorphs are the only kind of crystalline forms available for use in single-crystal X-ray diffraction studies.

Over the last years we have prepared and studied a series of 3d metal complexes with substituted imidazole ligands to identify the trends and patterns upon which their molecular and supramolecular assembly is organized, particularly with respect to intermolecular hydrogen-bond motifs and other weak interactions.26-31 With respect to this, we directed the present study to the use of the relatively small and flexible 4-phenylimidazole ligand (HL, Scheme 1) in combination with the tetrafluoroborate salt of copper(II). Copper(II) is an interesting and popular metal ion in coordination chemistry and has been named 'chameleon'32 as it favours a variety of coordination numbers and geometries33 that can be realized by properly selecting the ligands and the reaction conditions. The 3d⁹ configuration makes copper(II) subject to Jahn-Teller distortion and this plays a predominant role in its stereochemistry. Thus, square planar or distorted tetrahedral (4-coordinate), square pyramidal or trigonal bipyramidal (5-coordinate), as well as distorted octahedral (6-coordinate) geometries dominate the coordination chemistry of copper(II). Imidazole and its derivatives34,35 are, among others, particularly interesting ligands in bioinorganic36,37 metallosupramolecular chemistry, employed,



Scheme 1 The general synthetic route and the crystallographically determined formulae of the Cu(II) complexes with 5-phenylimidazole (HL) as ligand. The initially used 4-phenylimidazole ligand is present in all complexes as its 5-phenylimidazole tautomeric form.

 $[Cu{SiF_2O(OMe)}_2(HL)_4]\cdot 0.8MeNO_2$ 19·0.8MeNO₂

16:0.7DIPE

17 · (n-hexane)

[Cu(BF₄)₂(HL)₄]·0.7DIPE

[Cu(BF₄)₂(HL)₄]·(n-hexane)

 $[Cu(HL)_4(MeCN)(H_2O)_{0.4}](BF_4)_2$

example, in the synthesis of clusters, coordination polymers and MOFs. 38,39 4-phenylimidazole can coordinate to a metal ion via its pyridine-type N3-atom towards mononuclear species. At the supramolecular level, the ligand has a hydrogen-bond donor (the pyrrolic-type N1-atom) enabling the formation of strong motifs $^{38,40-43}$ and is also capable of forming $\pi\cdots\pi$ stackings $^{44-46}$ through its 5- and 6-membered aromatic rings.

The tetrafluoroborate ion usually acts as a counter-ion in coordination compounds. Due to its small size, non-nucleophilicity, resistance to coordination and stability, the BF_4^- ion finds extensive uses as the anion in ionic liquids, as a substitute for ClO_4^- ion that forms explosive salts, as a spectator for chelates of catalytic transition metals (*e.g.* Au,

Pd, Pt) and as a counter-ion to highly reactive cations, such nitrosonium, nitronium, pyrylium, aryldiazonium, triethoxonium (in Meerwein's salt) and iodonium (in Barluenga's reagent).⁴⁷ During the last 40 years or so, there have been reports showing that the BF4 on is not always stable, and that reaction with the ligand or the metal ion in coordination complexes may occur, often resulting in Fcontaining compounds. 48,49 Another interesting aspect of the chemistry of BF4 is that sometimes it can coordinate to metal ions in a terminal (monodentate) or bridging manner, but seldom coordination is strong.⁵⁰⁻⁵² We have, therefore, chosen as a source of copper(II) the Cu(BF₄)₂·6H₂O salt in order to study the tetrafluoroborate coordination ability and provide the copper(II) ion with the conditions to realize the optimal coordination geometry from the 5-phenylimidazole/ tetrafluoroborate ligand system available.

Following this approach, we have prepared and characterized a total of nineteen new Cu(ii) complexes (Scheme 1). Notable solvatomorphism was observed among them and, utilizing a variety of crystallization solvents, seventeen of these compounds (1–17) were found to be solvatomorphs with the general formula $[Cu(BF_4)_2(HL)_4]\cdot x$ (solvent). Alongside, compounds $[Cu(HL)_4(MeCN)(H_2O)_{0.4}](BF_4)_2$ (18) and $[Cu\{SiF_2O(OMe)\}_2(HL)_4]\cdot 0.8MeNO_2$ (19-0.8MeNO₂) were also isolated and characterized (see below). All structures (molecular and supramolecular) have been studied and compared to explore the role of the solvent molecules (in terms of hydrogen-bonding capacity, size, shape) in the solvatomorph self-assembly process in the solid state.

Experimental

Materials and instruments

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. IR spectra (4000–400 cm⁻¹) were recorded on a Perkin-Elmer PC 16 FT-IR spectrometer with the samples prepared as KBr pellets. Thermal decomposition measurements for selected complexes were performed using a Shimadzu TGA 50 analyzer under air; the rate of the temperature increase was 10 °C min⁻¹.

Preparation of complexes

Synthesis of $[Cu(BF_4)_2(HL)_4]$ - $2Me_2CO$ - $2H_2O$ (1- $2Me_2CO$ - $2H_2O$). Solid $Cu(BF_4)_2$ - $6H_2O$ (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in Me_2CO (25 mL). The resultant green solution was stirred for 30 min, then filtered and the mauve filtrate was layered with n-hexane (5 mL/5 mL). Pale purple crystals of $1\cdot 2Me_2CO\cdot 2H_2O$ were obtained after eight days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 65% (based on HL). Anal. calcd for $1\cdot 2H_2O$ (found values in parentheses): Coultiesize Coultiesiz

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -2MeOH (2·2MeOH). Solid $Cu(BF_4)_2$ ·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in MeOH (25 mL). The resultant blue solution was stirred for 30 min, then filtered and the violet filtrate was layered with Et_2O/n -hexane (5 mL/5 mL). Violet crystals of 2·2MeOH were obtained after three days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 80% (based on the metal). Anal. calcd for 2 (found values in parentheses): C 53.13 (53.48), H 3.96 (3.82), N 13.77 (13.99)%. IR bands (KBr, cm⁻¹): 3342mb, 3148m, 2980w, 2923w, 1616w, 1590w, 1488m, 1452w, 1424w, 1276w, 1168m, 1126s, 1072s, 1038s, 932m, 828m, 760s, 692m, 646m, 512m, 375w.

Synthesis of [Cu(BF₄)₂(HL)₄]·2EtOH (3·2EtOH). Solid $Cu(BF_4)_2 \cdot 6H_2O$ (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in EtOH (25 mL). The resultant green solution was stirred for 30 min, then filtered and stored in a closed vial at room temperature. Light violet crystals of 3·2EtOH were obtained after six days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 65% (based on HL). Anal. calcd for 3 (found values in parentheses): C 53.13 (53.41), H 3.96 (3.86), N 13.77 (13.94)%. Selected IR bands (KBr, cm⁻¹): 3346mb, 3148m, 1614w, 1592w, 1490m, 1454m, 1276w, 1168m, 1130s, 1074s, 1040s, 932m, 760s, 692m, 646m, 520m.

Synthesis of [Cu(BF₄)₂(HL)₄]·2(1-PrOH) [4·2(1-PrOH)]. Solid Cu(BF₄)₂·6H₂O (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in 1-PrOH (25 mL). The resultant blue-green solution was stirred for 30 min, then filtered and stored in a closed vial at room temperature. Light violet crystals of 4·2(1-PrOH) were obtained after three days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 65% (based on HL). Anal. calcd for 4·2(1-PrOH) (found values in parentheses): C 54.01 (53.81), H 5.18 (5.08), N 12.00 (12.31)%. Selected IR bands (KBr, cm⁻¹): 3342mb, 3148 m, 1616w, 1590w, 1488 m, 1452 m, 1276w, 1168 m, 1126s, 1072s, 1040s, 932 m, 760 s, 692 m, 646 m, 512w.

Synthesis of $[Cu(BF_4)_2(HL)_4]\cdot 1.4(2\text{-PrOH})$ [5·1.4(2-PrOH)]. Solid $Cu(BF_4)_2\cdot 6H_2O$ (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in 2-PrOH (25 mL). The resultant blue solution was stirred for 30 min, then filtered and the violet filtrate was layered with n-hexane (5 mL/5 mL). Violet crystals of 5·1.4(2-PrOH) were obtained after six days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 45% (based on HL). Anal. calcd for 5 (found values in parentheses): C 53.13 (52.86), H 3.96 (3.84), N 13.77 (14.07)%. Selected IR bands (KBr, cm⁻¹): 3440mb, 3146mb, 1486m, 1450m, 1173m, 1125s, 1069s, 1038s, 930m, 761s, 684m, 642m, 515m.

Synthesis of $[Cu(BF_4)_2(HL)_4]\cdot 2(1-BuOH)$ [6·2(1-BuOH)]. Solid $Cu(BF_4)_2\cdot 6H_2O$ (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in 1-BuOH (25 mL). The resultant violet slurry was stirred for 30 min, then filtered and the clear blue filtrate was layered with n-hexane (5 mL/5 mL). Light violet crystals of 6·2(1-BuOH)

were obtained after three days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 45% (based on the metal). Anal. calcd for $6\cdot 2(1-BuOH)$ (found values in parentheses): C 54.93 (54.61), H 3.96 (3.81), N 11.65 (11.97)%. Selected IR bands (KBr, cm⁻¹): 3425mb, 3140mb, 1490 m, 1448m, 1169m, 1128s, 1071s, 1041s, 927m, 759s, 680m, 645m, 517m.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -2(iso-BuOH) [7-2(iso-BuOH)]. Solid $Cu(BF_4)_2 \cdot 6H_2O$ (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in iso-BuOH (25 mL). The resultant mauve slurry was stirred for 30 min, then filtered and the clear pale blue filtrate was layered with n-hexane (5 mL/5 mL). Pale purple crystals of 7-2(iso-BuOH) were obtained after three days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 50% (based on the metal). Anal. calcd for 7-2(iso-BuOH) (found values in parentheses): C 54.93 (54.61), H 5.45 (5.62), R 11.65 (11.97)%. Selected R bands (RBr, R cm⁻¹): 3338mb, 3126m, 1492m, 1456m, 1178m, 1126s, 1070s, 1041s, 932m, 772s, 698m, 646m, 518w.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ ·1.33(tert-BuOH) [8·1.33(tert-BuOH)]. Solid $Cu(BF_4)_2$ ·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in tert-BuOH (25 mL). The resultant dark violet solution was stirred for 30 min, then filtered and stored in a closed vial at room temperature. Violet crystals of 8·1.33(tert-BuOH) were obtained after three days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried $in\ vacuo$. Yield ca. 35% (based on the metal). Anal. calcd for 8 (found values in parentheses): C 53.13 (53.49), H 3.96 (3.75), N 13.77 (13.43)%. Selected IR bands (KBr, cm⁻¹): 3430sb, 3138mb, 1488m, 1446m, 1173m, 1131s, 1074s, 1045s, 931m, 757m, 684m, 644m, 520w.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -2(1-PeOH) [9·2(1-PeOH)]. Solid $Cu(BF_4)_2$ ·6H₂O (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in 1-PeOH (25 mL). The resultant lilac slurry was stirred for 30 min, then filtered and the pale green filtrate was layered with $Et_2O(5 \text{ mL/5 mL})$. Mauve crystals of 9·2(1-PeOH) were obtained after five months, they were collected by filtration, washed with $Et_2O(2 \times 5 \text{ mL})$ and dried *in vacuo*. Yield *ca.* 40% (based on the ligand). Anal. calcd for 9·2(1-PeOH) (found values in parentheses): C 55.80 (55.44), H 5.70 (5.60), N 11.32 (11.61)%. Selected IR bands (KBr, cm⁻¹): 3418sb, 3127mb, 1492m, 1444m, 1170m, 1134s, 1079s, 1043s, 928m, 762s, 682m, 641m, 516w.

Synthesis of [Cu(BF₄)₂(HL)₄]·2DMF (10·2DMF). Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in CH₂Cl₂/DMF (25 mL/3 mL). The mixture was stirred for 40 min, the resultant blue solution was filtered and the violet filtrate was layered with Et₂O/n-hexane (5 mL/5 mL). Violet crystals of 10·2DMF were obtained after three days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 70% (based on the metal). Anal. calcd for 10·2DMF (found values in parentheses): C 52.55 (52.31), H 4.83 (4.70),

N 14.59 (14.89)%. Selected IR bands (KBr, cm⁻¹): 3148m, 1650s, 1614m, 1590m, 1492m, 1454m, 1388m, 1170 m, 1130s, 1072s, 1038s, 964m, 762s, 692m, 648 m, 520w.

Synthesis of $[Cu(BF_4)_2(HL)_4]\cdot 1.2Me_2CO$ (11·1.2Me₂CO). Solid $Cu(BF_4)_2\cdot 6H_2O$ (0.138 g, 0.40 mmol) was added under stirring to a solution of HL (0.144 g, 1.0 mmol) in Me₂CO (25 mL). The resultant green solution was stirred for 30 min, then filtered and the violet filtrate was layered with n-hexane (5 mL/5 mL). Light violet crystals of 11·1.2Me₂CO were obtained after eight days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried *in vacuo*. Yield *ca*. 60% (based on HL). Anal. calcd for 11 (found values in parentheses): C 53.13 (52.82), H 3.96 (3.80), N 13.77 (14.09)%. Selected IR bands (KBr, cm⁻¹): 3130mb, 1674s, 1491m, 1440m, 1168m, 1137s, 1074s, 1041s, 932m, 761s, 679m, 642m, 518m.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -2THF (12-2THF). Solid $Cu(BF_4)_2$ -6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in THF (25 mL). The resultant dark violet solution was stirred for 30 min and a violet slurry appeared, which was then filtered and the clear violet filtrate was layered with Et_2O (5 mL/5 mL). Violet crystals of 12-2THF were obtained after five days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 65% (based on the metal). Anal. calcd for 12 (found values in parentheses): C 53.13 (53.46), H 3.96 (3.87), N 13.77 (12.81)%. Selected IR bands (KBr, cm⁻¹): 3122mb, 1489m, 1441m, 1169m, 1141s, 1078s, 1044s, 930m, 759s, 680m, 640m, 512w.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -1.85(1,4-dioxane) [13·1.85(1,4-dioxane)]. Solid $Cu(BF_4)_2$ · $6H_2O$ (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in 1,4-dioxane (25 mL). The resultant violet solution was stirred for 30 min and a violet slurry appeared, which was then filtered and the clear light violet filtrate was layered with Et_2O (5 mL/5 mL). Violet/pink crystals of 13·1.85(1,4-dioxane) were obtained after four days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 60% (based on the metal). Anal. calcd for 13·1.85(1,4-dioxane) (found values in parentheses): C 53.35 (52.97), H 4.84 (5.02), N 11.47 (11.19)%. Selected IR bands (KBr, cm⁻¹): 3134mb, 1484m, 1450m, 1167m, 1129s, 1071s, 1043s, 927m, 756m, 678m, 642m, 523m.

Synthesis of $[Cu(BF_4)_2(HL)_4]$ -0.86EtOAc (14-0.86EtOAc). Solid $Cu(BF_4)_2$ -6 H_2O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in ethyl acetate (25 mL). The resultant mauve slurry was stirred for 30 min and a violet solid appeared which was then filtered; the pale violet filtrate was stored at low temperature (5 °C). Violet crystals of 14-0.86EtOAc were obtained after five days, they were collected by filtration, washed with Et_2O (2 × 5 mL) and dried *in vacuo*. Yield *ca.* 45% (based on the metal). Anal. calcd for 14 (found values in parentheses): C 53.13 (52.79), H 3.96 (3.82), N 13.77 (14.09)%. Selected IR bands (KBr, cm⁻¹): 3128mb, 1701m, 1482m, 1449m, 1171m, 1126s, 1073s, 1045s, 931m, 755m, 679m, 648m, 514w.

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of $[Cu(BF_4)_2(HL)_4] \cdot Et_2O$ $(15 \cdot \text{Et}_2\text{O}).$ Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in iso-pentanol (25 mL). The resultant blue/green solution was stirred for 30 min, then filtered and the violet filtrate was layered with Et₂O (5 mL/5 mL). Violet crystals of 15·Et₂O were obtained after five days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried in vacuo. Yield ca. 70% (based on the metal). Anal. calcd for 15 (found values in parentheses): C 53.13 (53.39), H 3.96 (3.80), N 13.77 (14.12)%. Selected IR bands (KBr, cm⁻¹): 3135mb, 1479m, 1450m, 1169m, 1130s, 1071s, 1042s, 930m, 757s, 676m, 644m, 515w.

Synthesis of $[Cu(BF_4)_2(HL)_4] \cdot 0.7DIPE$ (16·0.7DIPE). Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in nitromethane (25 mL). The resultant pale blue solution was stirred for 75 min and a dark blue/green slurry appeared which was then filtered; the clear dark blue/green filtrate was layered with diisopropyl ether (DIPE) (5 mL/5 mL). Violet crystals of 16.0.7DIPE were obtained after seven days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried in vacuo. Yield ca. 40% (based on the metal). Anal. calcd for 16 (found values in parentheses): C 53.13 (53.43), H 3.96 (3.81), N 13.77 (14.10)%. Selected IR bands (KBr, cm⁻¹): 3152mb, 1482m, 1451m, 1171m, 1128s, 1069s, 1046s, 928m, 756s, 674m, 645m, 515w.

Synthesis of $[Cu(BF_4)_2(HL)_4] \cdot (n-hexane) [17 \cdot (n-hexane)]$. Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in tert-BuOH (25 mL). The resultant dark blue solution was stirred for 30 min, then filtered and the violet filtrate was layered with n-hexane (5 mL/5 mL). Violet crystals of 17·(n-hexane) were obtained after five days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried in vacuo. Yield ca. 40% (based on the metal). Anal. calcd for 17 (found values in parentheses): C 53.13 (53.50), H 3.96 (3.79), N 13.77 (13.50)%. Selected IR bands (KBr, cm⁻¹): 3149mb, 2940m, 1480m, 1449m, 1169m, 1127s, 1074s, 1044s, 930m, 757s, 672m, 643m, 516w.

Synthesis of $[Cu(HL)_4(MeCN)(H_2O)_{0.4}](BF_4)_2$ (18). Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in CH₂Cl₂/MeCN (20 mL/5 mL). The resultant dark mauve slurry was stirred for 30 min, then filtered and the clear mauve filtrate was layered with Et₂O/n-hexane (5 mL/5 mL). Violet crystals of 18 were obtained after four days, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried in vacuo. Yield ca. 60% (based on the metal). Anal. calcd for 18 (found values in parentheses): C 52.89 (52.61), H 4.19 (3.99), N 14.62 (14.96)%. Selected IR bands (KBr, cm⁻¹): 3435wb, 3150wb, 2170w, 1479m, 1451m, 1167m, 1130s, 1076s, 1042s, 928m, 759s, 670m, 647m, 518w.

Synthesis of [Cu{SiF₂O(OMe)₂(HL)₄]·0.8MeNO₂ (19·0.8MeNO₂). Solid Cu(BF₄)₂·6H₂O (0.086 g, 0.25 mmol) was added under stirring to a solution of HL (0.144 g, 1.00 mmol) in MeNO₂ (25 mL). The resultant dark blue/green slurry was stirred for 75 min, then filtered and the clear blue/green filtrate was stored at low

temperature (5 °C). Violet crystals of 19·0.8MeNO2 were obtained after a week, they were collected by filtration, washed with Et₂O (2 × 5 mL) and dried in vacuo. Yield ca. 60% (based on the metal). Anal. calcd for 19.0.8MeNO₂ (found values in parentheses): C 50.87 (51.22), H 4.41 (4.19), N 13.46 (13.11)%. Selected IR bands (KBr, cm⁻¹): 3150mb, 1561m, 1479m, 1482m, 1440m, 1376m, 1168m, 1128s, 1072s, 1043m, 1026m, 931m, 758m, 669m, 648m, 517w.

X-ray crystallography

Suitable single-crystals of the compounds, covered with paratone-N oil, were mounted in cryo-loops at the end of a copper pin. Diffraction data were collected (ω-scans technique) on a SuperNova Rigaku diffractometer under a flow of nitrogen gas at 100(2) K using Mo K α radiation (λ = 0.7107 Å), with the exception of compounds 5.1.4(2-PrOH) and 9.2(1-PeOH), for which Cu K α radiation ($\lambda = 1.5418 \text{ Å}$) was used. Crystallographic data are listed in Table 1. Data were collected and processed by the CRYSALIS CCD and RED software,⁵³ respectively; the reflection intensities were corrected for absorption by the multiscan method. The structures were solved using direct methods (SIR92 (ref. 54) SHELXT⁵⁵) or the charge flipping algorithm (Superflip^{56,57}) and the models were refined by full-matrix least-squares on F^2 with SHELXL-2019/3. All non-H atoms were refined anisotropically; carbon-bound H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms (riding model). The structure of 16 was refined as a non-merohedral twin with a 32:68 components ratio. All imidazole H-atoms on the pyrrolic-type N1 atom of the ligands, together with the hydroxyl H-atoms of the protic solvents in compounds 2-9 and the water H-atoms in compounds 1 and 18 were located in difference Fourier maps, and refined isotropically applying soft distance restraints (DFIX). Considerable disorder has been observed in most of the crystal structures. A two-part disorder model was applied to the BF₄ ions in complexes 1, 2, 3, 7, 10, 11 and 13, while the highly disordered BF₄ ion in complex 5 is best modelled over three sites (three-component model). Similar treatment has been applied for the analogous disordered ${SiF_2O(OMe)}^-$ ion in compound 19. The HL ligands are also affected by positional disorder: this includes the phenyl ring in molecules 5 (triply disordered), 7, 13 and 15 (two sites) and the entire HL ligand in complex 11. Partial occupancies have been assigned after detailed refinement for the solvent molecules in compounds 5.1.4(2-PrOH), 11.1.2Me₂CO, 13.1.85(1,4-dioxane), 14.0.86EtOAc, **16**·0.7DIPE and 19.0.8MeNO₂. The solvents in 3.2EtOH, 7.2(iso-BuOH), 9.2(1-PeOH), 12·2THF, 14·0.86EtOAc, 15·Et₂O, 16·0.7DIPE and the coordinated MeCN in complex 18 have also been modelled over two sites; of these, the EtOAc, Et₂O and DIPE solvents (in complexes 14, 15 and 16, respectively) are orientationally disordered about an inversion centre and the coordinated MeCN (in complex 18) about a two-fold axis.

Geometric/crystallographic calculations were carried out using PLATON,⁵⁹ OLEX2 (ref. 60) and WINGX⁶¹ packages;

Compound reference	$1.2 \mathrm{Me_2CO}.2 \mathrm{H_2O}$	$2.2 \mathrm{MeOH}$	3.2EtOH	4·2(1-PrOH)	5·1.4(2-PrOH)
Chemical formula Formula mass/g mol ⁻¹ Crystal system Space group a/λ b/λ c/λ a/δ	C ₃₆ H ₃₂ B ₂ CuF ₈ N ₈ ·2(C ₃ H ₆ O)·2(H ₂ O) 966.04 Monoclinic P ₂₁ /c 8.8391(5) 26.4003(12) 9.9765(5) 90 106.136(5)	,	, , , , , , , , , , , , , , , , , , , ,	C ₃₆ H ₃₂ B ₂ CuF ₈ N ₈ ·2(C ₃ H ₈ O) 934.04 Triclinic P ₁ 9.1101(3) 9.9335(4) 13.3316(6) 104.812(4) 94.552(3)	C ₃₆ H ₃₂ B ₂ CuF ₈ N ₈ ·1.4(C ₃ H ₈ O) 897.99 Triclinic PI 9.0160(8) 9.6842(7) 13.7262(8) 69.875(6) 80.108(7)
y/o Unit cell volume/ \mathring{A}^3 Z, Z Temperature/ K Radiation type, μ/mm^{-1} No. of reflections measured No. of independent reflections R_{int} Final R_1 values $(I > 2\sigma(I))$ Final R_1 values $(I > 2\sigma(I))$ Final R_1 values (all data) Final R_1 values (all data) R_1 R_2 R_3 R_4 R_4 R_5 R_4 R_5 R_4 R_5 R_4 R_5 R_4 R_5 $R_$	900 2236.3(2) 2, 0.5 100(2) MoKα, 0.573 4369 0.073 0.0442 0.0839 0.0715 0.0925 1.025 0.369, -0.500 2342307	107.642(5) 1033.13(12) 1, 0.5 100(2) MoKa, 0.609 7482 4053 0.027 0.0442 0.0983 0.0509 0.1036 1.056 0.446, -0.518 2342308	106.907(9) 1044.43(18) 1, 0.5 100(2) MoKca, 0.605 7679 3665 0.038 0.0667 0.1458 0.0867 0.1456 1.055 0.812, -0.724 2.342.309	104.842(4) 1113.81(8) 1, 0.5 100(2) MoKCa, 0.569 9553 4810 0.036 0.0431 0.0970 0.0577 0.1051 1.072 0.577, -0.504 2.342.310	72.626(7) 1070.77(15) 1, 0.5 100(2) CuKα, 1.400 6493 3806 0.046 0.0845 0.2183 0.0962 0.2317 1.026 0.781, -0.646 2.342.311
Compound reference	6·2(1-BuOH)	7·2(iso-BuOH)	8·1.33(tert-BuOH)	9·2(1-PeOH)	10·2DMF
Chemical formula Formula mass/g mol ⁻¹ Crystal system Space group a/k b/k a/k Unit cell volume/ a/k a/k Temperature/K Radiation type, μ/\min^{-1} No. of reflections measured No. of independent reflections R into R radius $(I > 2a/I)$ Final R_1 values $(I > 2a/I)$ Final R_1 values ($I > 2a/I)$ Final R_1 values (all data) Final R_1 values (all data) Goodness of it on F^2	$C_{36}H_{32}B_2CuF_8N_8\cdot 2(C_4H_{10}O)$ 962.09 Triclinic $P\bar{I}$ 9.2340(6) 9.9950(8) 105.451(6) 94.995(5) 1132.28(15) 1, 0.5 1100(2) MoK α , 0.562 8034 3926 0.070 0.070 0.0634 0.1504 0.1503 1.182	$C_{36}H_{32}B_2CuF_8N_8 \cdot 2(C_4H_{10}O)$ 962.09 Triclinic P_1 9.2904(12) 9.9448(16) 14.0725(19) 110.200(13) 94.866(11) 1105.768(12) 1151.1(3) 1, 0.5 100(2) MoK α , 0.553 8798 4261 0.0061 0.0061 0.0061 0.00565 0.1292 0.0796	$C_{36}H_{32}B_2CuF_8N_8\cdot 1.33(C_4H_{10}O)$ 912.68 Triclinic Pi 15.0482(5) 15.3209(5) 16.1054(7) 100.57(3) 32.34.0(2) 3, 1.5 1100(2) MoK α , 0.585 29.587 12.042 0.057 0.057 0.057 0.1353 0.1358	C ₃₆ H ₃₂ B ₂ CuF ₈ N ₈ ·2(C ₅ H ₁₂ O) 990.14 Triclinic P ₁ 9.3029(7) 9.439(8) 14.3527(11) 73.234(7) 73.433(7) 73.433(7) 1187.02(17) 1, 0.5 100(2) CuKa, 1.323 7751 4456 0.022 0.0347 0.0872 0.0401 0.0922 1.634	$C_{36}H_{32}B_2CuF_8N_8 \cdot 2(C_3H_7NO)$ 960.05 Triclinic $P\bar{1}$ 9.0724(7) 9.8173(7) 14.3397(9) 75.963(6) 71.693(6) 71.693(6) 71.238(7) 1133.80(15) 1, 0.5 100(2) MoK α , 0.563 9021 4665 0.028 0.0401 0.0911 0.0941

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Compound reference	6 ·2(1-BuOH)	7.2(iso-BuOH)	8 ·1.33(<i>tert</i> -BuOH)	9·2(1-PeOH)	10	10.2DMF
$\Delta ho_{ m max}, \Delta ho_{ m min}/e \ { m \AA}^{-3}$ CCDC number	0.491, -0.543 2342312	0.394, -1.008 2342313	1.081, -0.614 2342314	0.341, -0.373 2342315		0.482, -0.447 2342316
Compound reference	$11.1.2 \mathrm{Me_2CO}$	12.2THF	13·1.85(1,4-dioxane)	14·0.86EtOAc		$15.\mathrm{Et_2O}$
Chemical formula Formula mass/g mol ^{–1}	$C_{36}H_{32}B_{2}CuF_{8}N_{8}\cdot 1.2(C_{3}H_{6}O)$ 883.55	$C_{36}H_{32}B_2CuF_8N_8 \cdot 2(C_4H_8O)$ 958.06	$C_{36}H_{32}B_{2}CuF_{8}N_{8}\cdot 1.85(C_{4}H_{8}O_{2})$ 976.85		$C_{36}H_{32}B_2CuF_8N_8\cdot0.86(C_4H_8O_2)$ 889.62	$C_{36}H_{32}B_{2}CuF_{8}N_{8}\cdot C_{4}H_{10}O$ 887.97
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic		Triclinic
Space group	$Par{ ext{I}}$	$Par{ ext{I}}$	$Par{1}$	$Par{1}$		$Par{ ext{I}}$
$a/{ m \AA}$	8.950(3)	9.4113(9)	9.2398(7)	8.6393(5)		8.5831(9)
b/A	9.655(3)	10.2218(12)	9.9904(9)	9.7696(6)		9.7612(11)
c/A	13.284(4)	12.8120(12)	12.6976(12)	12.8911(8)		12.8928(11)
α/ο	73.31(3)	87.054(9)	78.043(8)	99.164(5)		98.221(8)
B/C	8/./5(2)	/5.1/9(9)	85.634(/)	93.555(5)		93.854(8)
y/c	/2.5/(3) 1047 E(E)	/0./05(10) 1132-9(3)	/3.908(/)	100.361(6)		107.301(10)
OILL CEIL VOLUILE/A	1047.0(3)	1123.8(2)	1101.33(1/)	1024.08(11)		1013.80(19)
L, L Temperature/V	1, 0.3	1, 0.3	1, 0.3	$\frac{1,0.5}{100(2)}$		1, 0.3
Padiation time "/mm ⁻¹	$MoK_{CC} = 0.600$	Moka 0 566	100(Z) Moka 0 582	100(2) MoKa 0.615		100(z) Moka 0 620
No. of reflections measured	7907	9610	8689	6976		7573
No. of independent reflections	3654	4635	3848	3594		4186
Rint	0.075	0.046	0.052	0.028		0.038
Final R, values $(I > 2\sigma(I))$	0.0891	0.0565	0.0898	0.0555		0.0466
Final w $R(F^2)$ values $(I > 2\sigma(I))$	0.2167	0.1380	0.2293	0.1438		0.0922
Final R, values (all data)	0.1478	0.0761	0.1355	0.0619		0.0703
Final w $R(F^2)$ values (all data)	0.2647	0.1537	0.2690	0.1500		0.1025
Goodness of fit on \vec{F}^2	1.043	1.061	1.020	1.045		1.033
$\Delta ho_{ m max}$, $\Delta ho_{ m min}/{ m e}~{ m \mathring{A}}^{-3}$	0.773, -0.742	0.538, -0.541	0.895, -0.703	1.144, -1.149	•	0.524, -0.426
CCDC number	2342317	2342318	2342319	2342320		2342321
Compound reference	16·0.7DIPE	17·(<i>n</i> -hexane)	18		19 ·0.8MeNO ₂	
Chemical formula	$C_{36}H_{3}$,B,CuF ₈ N ₈ ·0.70(C ₆ H ₁₄ O)	$C_{36}H_{14}O)$ $C_{36}H_{3}$,B,CuF ₈ N ₈ ·C ₆ H ₁₄		$C_{38}H_{358}OCuN_9O_{040}(BF_4)$	$C_{38}H_{38}CuF_4N_8O_4Si_2.0.8(CH_3NO_2)$	Si ₂ ·0.8(CH ₃ NO ₂)
Formula mass/g mol ⁻¹	885.37				915.32	
Crystal system	Triclinic	Triclinic	Orthorhombic	ombic	Monoclinic	
Space group	$Par{ m I}$	$Par{1}$	Pnn2		P2/n	
$a/ {A}$	8.7016(6)	8.7411(10)	11.1724(4)	(4)	17.5681(7)	
$b/ ilde{ ilde{A}}$	9.8158(8)	9.7698(14)	12.3470(6)	(9)	9.8878(3)	
$c/ ilde{ ext{A}}$	12.9608(14)	12.811(2)	13.8235(6)	(9)	24.2057(9)	
α/\circ	96.464(8)	97.513(13)	06		06	
9/0	96.268(8)	93.679(12)	06		96.253(3)	
2//0	106.150(7)	107.576(12)	06		90	
Unit cell volume/A	1045.07(16)	1027.8(3)	1906.89(14)	14)	4179.8(3)	
Z, Z	1, 0.5	1, 0.5	2, 0.5		$^{4, 1}$	
Temperature/K	100(2)	100(2)	100(2)	999	100(2) MoV: 0.554	
No of reflections measured	3674	7520	10 Δ13 10 Δ13	0500	MUNA, 0.654	
No. of independent reflections	3674	4022	4140		37 126	
Rint		0.032	0.042		0.054	
Final R_1 values $(I > 2\sigma(I))$	0.0855	0.0508	0.0453		0.0610	
Final w $R(F^2)$ values $(I>2\sigma(I))$	0.2155	0.1155	0.1162		0.1546	

Table 1 (continued)

Compound reference	16.0.7DIPE	$17 \cdot (n\text{-hexane})$	18	$19.0.8 \rm MeNO_2$
Final R_1 values (all data)	0.1009	0.0640	0.0543	0.0778
Final $wR(F^2)$ values (all data)	0.2269	0.1261	0.1259	0.1676
Goodness of fit on F^2	1.101	1.060	1.021	1.061
$\Delta ho_{ m max}, \Delta ho_{ m min}/{ m e \ \AA}^{-3}$	1.339, -1.089	1.473, -0.997	0.636, -0.410	1.057, -0.693
ՄՈՍՄ niimber	0340200	0240202	0240204	72/7275

molecular/packing graphics were prepared with MERCURY. 62 Photos of the crystals are shown in Fig. S1. \dagger

Results and discussion

Synthetic comments

A variety of reactions were initially studied with the aim of preparing the largest possible number of complexes exploring the Cu(II)/HL/tetrafluoroborate system. Our trials included differing reactant ratios and concentrations, solvents, crystallization conditions and temperatures. It soon turned out that the reaction system yielded solvatomorphic compounds of the general formula $[Cu(BF_4)_2(HL)_4] \cdot x$ (solvent). Utilizing a variety of crystallization solvents (polar protic, polar aprotic and nonpolar) a series of seventeen crystalline solvatomorphs have been isolated. The general synthetic route with the individual formulae of the resulting complexes are illustrated in Scheme 1. A schematic illustration of the molecular structure of the solvatomorphs is shown in Scheme 2. Cu(II) is air stable and the synthetic work was thus conducted under aerobic conditions in the normal laboratory atmosphere. Attempts with iso-pentanol (15), MeNO₂ (16) and tert-BuOH (17) as main reaction solvents did not produce exactly the anticipated solvatomorphs with respect to the included solvents; instead, the solvents used in the layering technique for crystal growth were found within the crystals, resulting in the 15·Et₂O, 16·0.7DIPE and 17·(n-hexane) solvatomorphs, respectively. In the synthesis of compound 18, using CH₂Cl₂/MeCN as reaction solvents, the two tetrafluoroborato ligands in the anticipated [Cu(BF₄)₂(HL)₄] molecule have been replaced by a MeCN and a partially occupied water molecule (40%), producing crystals of the cationic [Cu(HL)₄(MeCN)(H₂O)_{0.4}](BF₄)₂ complex (Fig. S2a†). The compounds were obtained by reactions with a metal-to-ligand ratio of 1:2.5 or 1:4 and have an octahedral geometry at the metal centre; their colour is violet or mauve.

As in all reactions, $Cu(BF_4)_2 \cdot 6H_2O$ was used as the metal source in the synthesis of $19 \cdot 0.8 MeNO_2$; however, the final crystalline product was identified as $[Cu\{SiF_2O(OMe)\}_2(HL)_4] \cdot 0.8 MeNO_2$ (Schemes 3 and 4, Fig. S3a†). The coordinated $\{SiF_2O(OMe)\}^-$ ions, which appear for the first time in coordination chemistry, were

Scheme 2 Schematic representation of the general molecular structure of 1–17 which have the same coordination entity.

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Scheme 3 The overall reaction of $Cu(BF_4)_2$ with 4-phenylimidazole in a glass vessel using nitromethane as solvent. The difluorosilicate dianion is released into the solution upon attack of the glass surface by the 'naked' tetrafluoroborate anion. The final product contains the tautomer 5-phenylimidazole as ligand.

actually generated in situ by the reaction of fluoride anions from BF₄ with the glass surface of the vial used to grow crystals of the complex. The proposed mechanism (Scheme 5) involves the following steps:

- i) Initial formation of the complex I in which two molecules of nitromethane act as bidentate ligands and two molecules of 5-phenylimidazole as monodentate ligands. The complexation of nitromethane serves to facilitate the subsequent attack of its methyl group by the difluorosilicate anion.
- ii) The difluorosilicate dianion (II), released from the glass surface upon attack of silicon atoms on the surface by tetrafluoroborate anions (Scheme 4), then partially displaces the nitromethane from the metal cation leading to the new complex III. The driving force for the liberation of the difluorosilicate dianion from the glass surface is the formation of the very strong Si-F bonds.⁴⁷
- iii) Facile intramolecular S_N2 reaction of the complexed difluorosilicate anion on the neighbouring methyl group then leads to methylation of the difluorosilicate dianion with simultaneous formation of nitrite anion (complex IV). The latter is then displaced by a third molecule of 5-phenylimidazole to provide the new complex V.
- iv) Steps 2 and 3 are then repeated with a second difluorosilicate dianion to give the final complex through the intermediate complexes VI and VII.

Four final remarks concerning our above mentioned mechanistic ideas are worthy of note at this point: (a) Further replacement in II by fluorides is not probable, because silicon bears a large number of electrons (totally 24!) around it, while

Scheme 4 Simplified mechanism for the liberation of silicate dianions to the nitromethane solution upon attack of tetrafluoroborate anions on the glass surface. The silicate dianions are further attacked by tetrafluoroborate anions to give finally the difluorosilicate dianion II.

O is with +I (and +M) effects. Therefore, silicon cannot be attacked by other nucleophiles; moreover, O2- is an extremely bad leaving group, much worse than the already very bad HO leaving group. (b) Recent theoretical studies⁶³ have shown the possibility of gradual replacement of OH groups by F atoms in silicon dioxide until the formation of SiF4; in the theoretical study, however, the etchant was HF molecule, while in our experimental work the attacking species is F (from BF₄). The glassware used in our laboratory is borosilicate glass. This has a more complicated structure compared to that of the simple silica glass used in the calculations, because it contains B atoms in the lattice and intermediate Na+ ions, but again the dominant species is SiO2. (c) It is well known in organic chemistry that the nitro group can play diverse roles that make several transformations;64 and (d) Reactions in which fluoride species attack to glassware to form silicon-fluoride compounds have been described in the literature.⁴⁸

All attempts to employ chlorinated compounds (CH₂Cl₂, CHCl₃) as crystallization solvents failed to give crystalline materials. Also attempts to prepare solvatomorphs [Cu(HL)₄(BF₄)₂] using DMSO as the reaction solvent were in vain, probably due to the excellent donor capacity of this solvent which is readily coordinated to copper(II) hampering complexation with HL and BF₄.

Scheme 5 Proposed mechanism for the formation of the final complex from the reaction of copper(III) tetrafluoroborate with 4-phenylimidazole (HL) in a glass vessel using nitromethane as solvent. We assume that the ligand HL is in its tautomeric 5-phenylimidazole form from the start of the reaction.

All crystalline products were characterized by IR spectroscopy, microanalyses, single-crystal X-ray diffraction and TGA experiments (for selected compounds). Various trials to obtain crystals of the solvent-free forms, including triethyl orthoformate as a drying agent and several solvent mixtures, were in vain.

Final complex (19)

Description of the structures

To facilitate discussion and molecular comparison, the same numbering scheme has been assigned (where applicable) to the HL ligand atoms and the coordinated tetrafluoroborate ions for all compounds presented herein (Fig. 1). Paper CrystEngComm

Fig. 1 View of the structure of solvatomorph $1\cdot2\text{Me}_2\text{CO}\cdot2\text{H}_2\text{O}$. Displacement ellipsoids are drawn at the 50% probability level. Atoms generated by symmetry through the inversion centre located on the copper ion are not labelled. Only the major-occupancy disorder components of the BF₄ $^-$ ions are shown.

The X-ray structure determination of all compounds (1–19) revealed that the initially used 4-phenylimidazole ligand (HL) is present as its 5-phenylimidazole tautomeric form. This rearrangement, termed as annular tautomerism of 4(5)-phenylimidazole,^{65–67} is a result of the amphoteric character of the imidazole and involves the exchange of a proton from the pyrrole-type atom N1 to the pyridine-type atom N3. Tautomerism is accompanied by a significant change in ligand conformation and it is thus likely that the 5-phenyl form of the HL ligand is the most favourable one in terms of the formation of these complexes.

Compounds 1-17 crystallize in the $P\bar{1}$ space group, with the exception of 1.2Me₂CO·2H₂O crystallizing in P2₁/c (Table 1). The asymmetric unit of these compounds, except for 8.1.33(tert-BuOH), contains half a [Cu(BF₄)₂(HL)₄] host molecule (Z' = 1/2), with the copper(II) atom situated on an inversion centre. In 8:1.33(tert-BuOH) there are one and a half host molecules in the asymmetric unit (Z' = 3/4), in which one of the two symmetry-independent copper(II) atoms is in a general position (Cu1) and the second one (Cu2) on an inversion centre. As previously mentioned, the isolated crystalline product 18, [Cu(HL)₄(MeCN)(H₂O)_{0.4}](BF₄)₂, using CH₂Cl₂/MeCN as solvents, is not the expected solvatomorph; however it has been included in the study for comparison purposes. It has molecular symmetry, with a C_2 axis passing through the N_{MeCN} -Cu- O_{H_2O} direction of the complex (Z' = 1/2) and crystallizes in the Pnn2 space group (Fig. S2a†). The replacement of the BF₄ ligands with {SiF₂O(OMe)} coordinated ions in the solvatomorph 19.0.8MeNO₂ has an impact on its molecular and crystal symmetry (Fig. S3†): the complex lacks molecular symmetry and crystallizes in the P2/ n space group. The coordination geometry in all complexes (1-19) is distorted octahedral: this involves the pyridine-type nitrogen atom from the four ligands in the equatorial positions; in the axial positions there are two fluorine atoms from the terminal BF_4^- ions (1-17), or one $O_{H,O}$ and one N_{MeCN} atom (18), or two O atoms from the monodentate ${SiF_2O(OMe)}^-$ ions (19). The $Cu^{II} - F_{BF_4}$ bonds in 1-17 are weak (2.44-2.55 Å) and the metal centre is in an axially elongated octahedral environment (4 + 2); this is a consequence of the Jahn-Teller effect, typical for 3d9 systems. BF₄ was traditionally considered as a typical example of a 'noncoordinating ion' 40 years ago or so. However, with the advent of single-crystal X-ray crystallography, it became evident that this anion can also be coordinated. To account for the coordination of this complex anion (and other anions such as $CF_3SO_3^-$, ClO_4^- , AlX_4^- , MF_6^- with X = Cl, Br, I; M = P, As, Sb, etc.), the term 'weakly coordinating anion' (WCA) was coined.⁵¹ This expression allows for weak coordination, but also includes the potential of such complexes to serve as precursors of the 'noncoordinated' cation, for example, in catalytic processes. Thus, in complexes 1-17, the BF4 ion can be best described as WCA.

The bond lengths and angles observed for the current complexes are similar (e.g. the Cu^{II} – N_{HL} bond lengths range from 1.99 to 2.02 Å). To compare the conformation of the $[Cu(BF_4)_2(HL)_4]$ molecules in compounds 1–17, the relative orientation of the imidazole rings within each complex, as well as the orientation of the phenyl ring relative to the imidazole ring for each HL ligand are reported in Table 2. It appears that the conformation of the complexes is similar, with variations that presumably help to minimize steric hindrance, facilitate the effective formation of intermolecular synthons, and accommodate the included solvents.

Table 2 The dihedral angles (°) between the least-squares calculated planes through the atoms of the imidazole and phenyl rings of the $[Cu(BF_a)_2(HL)_a]$ molecules for solvatomorphs **1–17**^{α}

Compound	ImA/ImB	ImA/PhRA	ImB/PhRB
1	66.1(1)	8.0(1)	26.4(1)
2	81.0(1)	12.0(2)	23.4(1)
3	80.6(2)	13.9(2)	27.8(2)
4	88.3(1)	16.7(1)	14.3(1)
5	79.5(2)	4.1(3)	$4.4(3)/41.0(3)/34.3(3)^b$
6	88.2(2)	18.5(2)	18.4(3)
7	82.1(1)	16.4(2)	$7.9(2)/26.7(2)^{b}$
8 ^c	86.5(1)	7.9(1)	21.7(3)
9	82.4(1)	6.8(1)	15.1(1)
10	73.8(1)	2.6(2)	22.4(1)
11^d	81.3(5)/79.9(5)	11.6(4)	29.5(7)/20.1(7)
12	83.4(1)	13.4(2)	25.6(2)
13	84.4(3)	4.3(3)	$21.5(8)/48.9(8)^{b}$
14	80.2(2)	17.0(2)	31.5(2)
15	79.7(1)	17.4(1)	$23.4(3)/44.2(3)^b$
16	83.0(3)	29.8(4)	15.7(3)
17	84.1(1)	28.3(1)	17.7(1)

^a ImA: imidazole ring N1A-C2A-N3A-C4A-C5A; ImB: imidazole ring N1B-C2B-N3B-C4B-C5B; PhRA: phenyl ring C6A-C7A-C8A-C9A-C10A-C11A; PhRB: C6B-C7B-C8B-C9B-C10B-C11B. ^b Values for all orientations of the disordered phenyl ring PhRB. ^c For comparison with the HL ligands of the other structures, only the centrosymmetric [Cu(BF₄)₂(HL)₄] molecule of 8·1.33(tert-BuOH) is reported. ^d Values for the two orientations B and C of the disordered ligand B.

Considering the similarities in the unit-cell dimensions, the same space group $(P\bar{1})$ and Z' (= 1/2) and the similar internal arrangement in the related crystal lattices [in this instance, the conformation of the $Cu(BF_4)_2(HL)_4$ host molecules], compounds 1–17 (with the exception of 1 and 8) could be described as isostructural solvatomorphs. However, the different hydrogen-bonding capabilities of the solvent molecules lead to variations in the networks of intermolecular interactions formed (see below).

The geometrical parameters of the strong H-bonding motifs for all compounds are given in Table 3. The supramolecular structures of the compounds are sorted and studied into three groups based on the type of solvent they contain (polar protic, polar aprotic and non-polar) and the resulting hydrogen-bonding patterns (synthons).

The supramolecular patterns of a molecule in its crystalline environment are visualized by the 3D molecular Hirshfeld surface, defined by the molecule *and* the proximity of its nearest neighbours, and therefore encode information about all its intermolecular interactions. To addition, the accompanying 2D fingerprint plots provide information for the relative contribution of the various types of interactions on the Hirshfeld surfaces. Hirshfeld surfaces and associated fingerprints for three representative structures with different solvent type, 6·2(1-BuOH) with polar protic solvent, 10·2DMF with polar aprotic solvent and 17·(*n*-hexane) with non-polar solvent, along with detailed description, are given in Fig. S4.†

i) Polar protic solvents: compounds 1-9. The solvents included in these compounds are H₂O+Me₂CO (1), MeOH (2), EtOH (3), 1-PrOH (4), 2-PrOH (5), 1-BuOH (6), iso-BuOH (7), tert-BuOH (8) and 1-PeOH (9) and (except Me2CO) have an effective donor-acceptor capability. The mixture of water and acetone is considered as a polar protic solvent, because of the presence of the former. The [Cu(BF₄)₂(HL)₄] molecules also feature classical hydrogen-bond donors (the imidazole N-H group) and acceptors (the tetrafluoroborate fluorine atoms). Therefore, these groups are expected to be involved in solute-solvent hydrogen-bonding packing patterns in the solid state. Analysis of the crystal structures of the isostructural compounds 2-7 and 9 shows that they all have the same packing organization. The molecules are assembled in 1D tapes by intermolecular N1A-H1A···F2 patterns along the b axis and by N1B-H1B···O_{solvent}-H···F3 patterns along the a axis (Fig. 2). These cross-linked tapes along a and bform rigid 2D layers parallel to the ab plane of the unit cell, with the solvents and two of the four ligands of the complexes protruding on either side of the layers. In the latter motif along a, the alcohol solvents act as both donors and acceptors bridging neighboring molecules and, apparently, as spacers, allowing the HL ligands to acquire the proper conformation to form these motifs. For example, for compound 2.2MeOH, the distance N1A···F2A is 2.683(4) Å, and the distance N1B···F3A is 4.378(4) Å. As shown in Table 1, the increasing molecular size of the included alcohols is accompanied by a gradual increase of the unit cell parameters and the corresponding volumes. However, this

Table 3 Geometry (Å, °) of the strong hydrogen-bonding motifs in compounds 1-19 a

D-H···A	D-H	H···A	D···A	<(DHA)
1·2Me ₂ CO·2H ₂ O				
N1A-H1A···F2A ⁱ	0.88(2)	1.93(2)	2.796(10)	166(2)
N1B-H1B···O1¹	0.86(2)	1.92(2)	2.777(3)	173(3)
O1-H1···F3A ⁱⁱ	0.81(2)	2.03(2)	2.832(5)	168(3)
O1–H2···O2 ⁱⁱⁱ	0.84(2)	1.94(2)	2.776(3)	174(3)
2·2MeOH				
N1A-H1A···F2A ^{iv}	0.85(2)	1.91(2)	2.683(4)	152(3)
N1B-H1B···O1	0.85(2)	1.95(2)	2.804(3)	177(3)
O1-H1···F3A ^{vi}	0.85(2)	1.90(3)	2.705(9)	158(4)
3·2EtOH	0.00(0)	1 02(2)	0.700(6)	151(5)
N1A-H1A···F2A ^{iv}	0.86(2)	1.93(3)	2.722(6)	151(5)
N1B-H1B···O1 O1-H1···F3A ^{vii}	0.86(2) $0.86(2)$	1.96(3) 1.90(1)	2.798(6) 2.671(8)	165(6) $148(4)$
4·2(1-PrOH)	0.80(2)	1.90(1)	2.071(8)	140(4)
N1A-H1A···F2 ^{iv}	0.85(2)	1.91(2)	2.749(2)	168(3)
N1B-H1B···O1 ^v	0.86(2)	1.96(2)	2.812(2)	173(3)
O1-H1···F3 ^{vi}	0.83(3)	1.95(3)	2.775(2)	173(3)
5·1.4(2-PrOH)	0.03(3)	1.55(5)	2.773(2)	173(3)
N1A-H1A···F2A ^{viii}	0.85(5)	2.03(6)	2.757(11)	143(6)
N1B-H1B···O1 ^{vii}	0.86(4)	1.86(5)	2.721(11)	176(9)
O1-H1···F3A	0.82(5)	1.79(5)	2.586(12)	163(5)
6·2(1-BuOH)	0.02(0)	1 5(0)	2.000(12)	100(0)
N1A-H1A···F2 ^{ix}	0.85(2)	1.93(3)	2.754(5)	161(5)
N1B-H1B···O1 ^{vii}	0.86(2)	1.93(2)	2.773(5)	168(5)
O1-H1···F3	0.84(2)	1.97(3)	2.767(5)	159(6)
7·2(iso-BuOH)	-(-)	-101 (0)	(0)	(-)
N1A-H1A···F2A ^{iv}	0.84(2)	1.97(2)	2.812(7)	176(3)
N1B-H1B···OA1 ^{vii}	0.83(2)	2.10(2)	2.925(10)	172(4)
OA1-HA1···F3A	0.84(2)	1.99(4)	2.790(9)	160(9)
8·1.33(tert-BuOH)	()			()
N1A-H1A···F10 ^x	0.85(2)	2.05(2)	2.805(3)	148(3)
N1B-H1B···F2 ^{xi}	0.85(2)	2.00(2)	2.820(3)	163(3)
N1C-H1C···O1 ^{xii}	0.83(2)	1.97(2)	2.778(4)	163(4)
N1D-H1D···O2	0.86(2)	1.96(2)	2.811(4)	168(3)
N1E-H1E···F6	0.85(2)	1.91(2)	2.741(3)	164(3)
N1F-H1F···F3 ^{xiii}	0.85(2)	2.04(2)	2.857(3)	161(3)
O1-H1···F11 ^{xiv}	0.84(2)	2.01(2)	2.841(3)	170(4)
O2-H2···F7 ^{ix}	0.84(2)	2.08(3)	2.844(3)	150(4)
9·2(1-PeOH)				
N1A-H1A···F2 ^{viii}	0.85(2)	2.01(2)	2.818(2)	159(2)
N1B-H1B···O1 ^{vii}	0.85(2)	1.92(2)	2.755(2)	164(2)
O1-H1…F3	0.80(2)	2.01(2)	2.806(2)	171(3)
10·2DMF				
N1A-H1A···F2A ^{xi}	0.84(2)	1.95(2)	2.786(7)	169(3)
N1B-H1B···O1 ^{x11}	0.84(2)	1.96(2)	2.776(3)	164(2)
11·1.2Me ₂ CO	0.0=(-)	0.0=(-)	2.622(=)	4.0(=)
N1A-H1A···F2A ^{xv}	0.85(2)	2.07(5)	2.832(7)	149(7)
N1B-H1B···O1	0.86(2)	2.03(1)	2.839(2)	157(6)
N1C-H1C···F3B ^{vii}	0.86(2)	2.00(4)	2.855(2)	172(2)
12.2THF	0.05(0)	0.40(0)	2.0(5(2)	174(2)
N1A-H1A···F2 ^{xii} N1B-H1B···OA ^{xvi}	0.85(2)	2.12(2)	2.965(3)	171(3)
	0.85(2)	1.95(2)	2.778(7)	164(4)
13 ·1.85(1,4-dioxane) N1A–H1A···F2A ^{iv}	0.05(0)	2 02(4)	2 922(1)	156(7)
N1A-H1A···F2A N1B-H1B···O1	0.85(2)	2.02(4)	2.823(1)	156(7)
14·0.86EtOAc	0.85(2)	2.06(4)	2.840(1)	153(8)
N1A-H1A···F2 ^{ix}	0.84(2)	1.97(2)	2.768(4)	157(4)
N1B-H1B···F3 ^{vii}			1 1	` '
15·Et ₂ O	0.84(2)	2.14(3)	2.869(4)	146(4)
N1A-H1A···F2 ^{xi}	0.84(2)	1.96(2)	2.754(3)	157(3)
N1B-H1B···F3 ^{vii}	0.84(2) $0.85(2)$	2.13(2)	2.866(3)	144(2)
16·0.7DIPE	0.03(2)	4.13(4)	2.000(3)	144(4)
N1A-H1A···F2 ^{xii}	0.86(2)	2.06(4)	2.862(7)	155(7)
N1B-H1B···F3 ^{viii}	0.86(2)	2.00(4) $2.00(4)$	2.782(6)	150(7)
17·(<i>n</i> -hexane)	0.00(2)	2.00(4)	2.702(0)	130(7)
N1A-H1A···F2 ^{xvii}	0.85(2)	2.11(2)	2.876(3)	149(3)
11111 11111 112	0.03(2)	2.11(2)	2.070(3)	149(3)

Table 3 (continued)

D-H···A	D-H	$H\cdots A$	D···A	<(DHA)
N1B-H1B···F3 ^{xviii}	0.84(2)	1.98(2)	2.770(3)	155(3)
18				
N1A-H1A···F1 ^{xix}	0.87(3)	1.99(3)	2.825(6)	161(6)
N1B-H1B···F2 ^{xx}	0.86(3)	1.96(3)	2.792(5)	161(5)
O1-H1…F3	0.85(2)	1.57(2)	2.414(9)	179(9)
19.0.8MeNO ₂				
N1A-H1A····F4 ^{xxi}	0.86(2)	1.94(3)	2.719(5)	150(4)
N1B-H1B···F2 ^{xxii}	0.86(2)	1.87(2)	2.686(5)	158(4)
N1C-H1C···F3A ^{iv}	0.86(2)	1.98(2)	2.828(5)	168(4)
N1D-H1D···F1	0.86(2)	1.98(2)	2.828(4)	169(4)

trend is not evident in compounds 4·2(1-PrOH) and 5·1.4(2-PrOH), probably due to the different shapes of the two isomer solvents or the partial occupancy of 2-PrOH in the crystal lattice.

The molecular self-assembly in the hydrated compound $1\cdot 2 \text{Me}_2\text{CO}\cdot 2 \text{H}_2\text{O}$ (Fig. 1) is directed by the same type of hydrogen-bonding patterns as in compounds 2–7 and 9, forming 2D layers parallel to the ac plane of the unit cell (Table 3). In addition, the second H-atom of the water molecule, which is not involved in this pattern, forms a strong $O_w\text{-H}\cdots O_{\text{acetone}}$ interaction with a lattice acetone solvent molecule. It appears that the above presented $P\bar{1}$ crystal lattice of the isostructural compounds 2–7 and 9 can no longer accommodate the additional acetone molecule,

and eventually $1.2 \text{Me}_2 \text{CO} \cdot 2 \text{H}_2 \text{O}$ crystallizes in the $P2_1/c$ space group.

Compound 8·1.33(tert-BuOH), in $P\bar{1}$ with 1.5 [Cu(BF₄)₂(HL)₄] molecules in the asymmetric unit, seems more complicated. Nevertheless, the molecules are similarly linked via N-H···F and N-H···O_{tert-BuOH}-H···F patterns forming rigid 2D layers parallel to the (10 $\bar{1}$) plane of the unit cell with the solvents and two of the four ligands of each complex lying on either side of the layers.

In all **1–9** structures, all hydrogen-bond donor and acceptor groups of the molecules and solvents are fully engaged in hydrogen-bonding motifs (see Table 3). When not hindered by steric effects or the prevailing stronger patterns, some weak $\pi\cdots\pi$ interactions between the aromatic rings of the ligands in the layers and between adjacent layers, along with a few non-classic C-H···F/O and C-H··· π interactions, are also observed and help to stabilize the structures (Fig. S4†).

ii) Polar aprotic solvents: compounds 10-13. The solvents included in these compounds are DMF (10), Me₂CO (11), THF (12), and 1,4-dioxane (13), featuring only hydrogen-bond acceptors. The [Cu(BF₄)₂(HL)₄] molecules in all compounds are assembled in 1D tapes by intermolecular N1A-H1A···F2 patterns along the b axis (or along a in 12.2THF), a pattern also encountered in compounds 1-9 (see Fig. 3 for the structure of 12·2THF). Their solvents are also hydrogenbonded to the second donor group of the complexes forming N1B-H1B···O_{solvent} interactions (Fig. S4†). The structures are further extended according to the particular features of each structure and solvent. In solvatomorphs 10 and 12, the 1D tapes are connected in 2D layers [parallel to the (222) plane in 10 and the ab plane in 12] via weak $\pi \cdots \pi$ contacts and their 3D structures are completed through weak C-H \cdots π and C-H···F interactions. In solvatomorph 11 (Fig. S5†), the positional disorder of a HL ligand (orientations B and C) and the partial occupancy of the acetone solvent allow this ligand

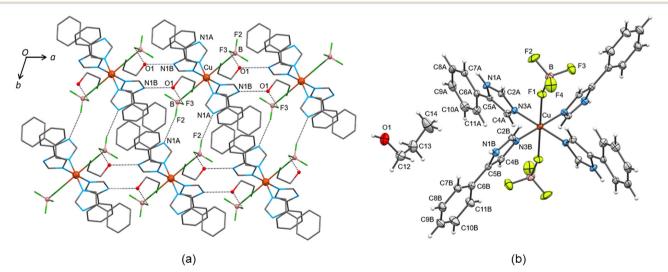


Fig. 2 The structure of solvatomorph $4\cdot2(1-\text{PrOH})$. (a) View of a 2D layer parallel to the *ab* plane organized by N1B–H1B···O1_(1-PrOH)–H···F3 motifs along the *a* axis and N1A–H1A···F2 motifs along the *b* axis. (b) The molecular structure of $4\cdot2(1-\text{PrOH})$. Displacement ellipsoids are drawn at the 50% probability level. Atoms generated by symmetry through the inversion centre located on the copper(II) ion are not labelled.

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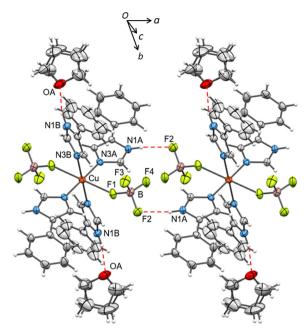


Fig. 3 View of a 1D tape in the crystal packing of 12-2THF formed by intermolecular N1A-H1A···F2 patterns along the a axis (shown in red dashed lines). Both orientations of the disordered THF solvent molecules are shown. Displacement ellipsoids are drawn at the 50% probability level. Only selected atoms have been labelled.

to participate, in addition to the described N1B-H1B···O1_{acetone} interaction, in a second one (N1C-H1C···F3B) forming 1D tapes along the a axis. Weak $\pi \cdots \pi$, C-H $\cdots \pi$ and C-H···F interactions contribute in stabilizing its 3D structure (Fig. S5†). The asymmetric unit in compound 13, contains two halves of centrosymmetric 1,4-dioxane solvent molecules The first solvent bridges, through (Fig. 4). centrosymmetrically-related oxygen atoms O1 and O1*, two neighboring [Cu(BF₄)₂(HL)₄] molecules in the [101] direction: N1B-H1B···O1-//-O1*···H1B-N1B. This interaction together with N1A-H1A···F2A along the b axis form a compact 2D structure parallel with the (101) plane. Some $\pi \cdots \pi$ interactions and other weak contacts between these layers organize the 3D assembly of the structure. The second 1,4-dioxane molecule (O2) is not involved in any major bonding pattern, except for two weak C-H···O interactions with the first dioxane molecule on either side.

iii) Non-polar solvents: compounds 14-17. The solvents included in these compounds are EtOAc (14), Et₂O (15), DIPE (16), and n-hexane (17). The solvatomorph 14 with ethyl acetate has been included in this category; ethyl acetate is commonly referred to as a non-polar to weak polar aprotic solvent. Analysis of the crystal structures of these compounds shows that they all have the same packing organization. Due to the inability of the included solvents to participate in strong hydrogen-bonding patterns with the HL ligands (as in all previous structures), the [Cu(BF₄)₂(HL)₄] molecules are oriented to form directly hydrogen-bonding motifs with each other. As shown in Table 3 and Fig. 5, intermolecular N1A-H1A···F2 and N1B-H1B···F3 interactions link the molecules

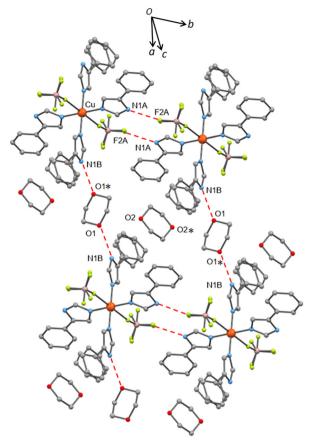


Fig. 4 View of a 2D layer of solvatomorph 13:1.85(1,4-dioxane). The layer is organized by strong synthons shown in red dashed lines. Both orientations of the disordered phenyl rings of a HL ligand and the BF4 ions are shown. Only selected atoms have been labelled.

into tapes along the a and b axes forming 2D layers parallel with the ab plane, whereas the solvents and two of the four phenyl rings of the ligands are located on either side of the layers. A few weak $\pi \cdots \pi$ and C-H $\cdots \pi$ contacts are also observed within the layers of the structures. Weak $\pi \cdots \pi$ or/ and C-H \cdots π contacts between the aromatic rings of adjacent layers contribute to the structure extension and stabilization in 3D. A visualization of the intermolecular interactions in compound 17·(n-hexane) is shown in Fig. S4.† Practically, the solvents only form few and very weak interactions, without any structural implications, with the rest of the structures, i.e. C-H···O (14) and C-H···F (14, 15 and 17). The solvent atoms in these compounds have rather elongated thermal ellipsoids; this is probably due to the lack of significant interactions with the rest of their structure.

Compounds 18 and 19·0.8MeNO₂. Although the structure of $[Cu(HL)_4(MeCN)(H_2O)_{0.4}](BF_4)_2$ (18) (Fig. S2a†) differs from the solvatomorphs 1-17, the presence of the same hydrogenbond donor and acceptor groups results in the formation of the same supramolecular synthons (N-H···F and Owater-H···F, Table 3). Each BF_4 counterion links three surrounding [Cu(HL)₄(MeCN)(H₂O)_{0.4}] molecules leading to the assembly of a robust 3D structure in the *Pnn*2 space group (Fig. S2b†).

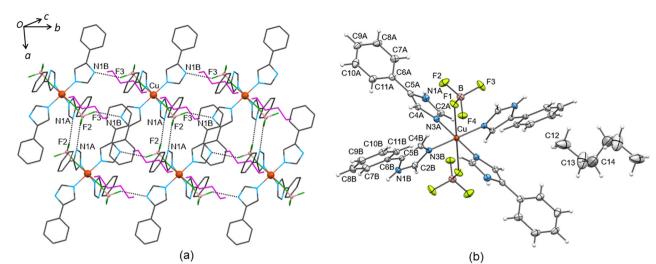


Fig. 5 The structure of solvatomorph $17 \cdot (n-\text{hexane})$. (a) View of a 2D layer parallel to the *ab* plane organized by N1A–H1A···F2 motifs along the *a* axis and N1B–H1B···F3 motifs along the *b* axis. The *n*-hexane solvents are drawn in magenta colour. (b) The molecular structure of $17 \cdot (n-\text{hexane})$. Displacement ellipsoids are drawn at the 50% probability level. Atoms generated by symmetry through the inversion centre located on the copper(ii) ion are not labelled.

Some $\pi\cdots\pi$ contacts complement the intermolecular organization. Similarly, the N–H···F synthons are also the driving force in the molecular self-assembly of compound $[Cu\{SiF_2O(OMe)\}_2(HL)_4]\cdot 0.8MeNO_2$ (19·0.8MeNO₂), Fig. S3b.† The packing resembles that of compounds 14–17 and the structure crystallizes in the P2/n space group. The molecules are linked by N–H···F interactions forming 2D layers parallel with the ab plane, with the nitromethane solvents and two of the four phenyl rings of the ligands located on either side of the layers. Some weak C–H····O and C–H····F contacts between the nitromethane solvents and ligands of neighboring layers are also observed.

Location and role of the solvents in the crystal structures. Examination of the crystal structures of the 17 solvatomorphs shows that the solvents are located in channels (in most cases) or lattice pockets⁷³ (Fig. 6). The void space, calculated by PLATON as $V_{\text{void}}/V_{\text{cell}}$ (%) after the removal of the solvent molecules, ranges from 16.0% to 30.1% (Table 4); similar values are obtained using the VOIDS option in Mercury software. Compounds 18 and 19.0.8MeNO2 are also included for comparison. The difference observed in compounds 4.2(1-PrOH) and 5·1.4(2-PrOH), 25.0% and 20.9%, respectively, could possibly be related to the difference in solvent shape; however, the phenyl ring close to the 2-PrOH solvent is triply disordered and only the major-occupancy conformer of this ring was retained in the calculations. As reported, the structure of 8·1.33(tert-BuOH) is different (Z = 3) from the other isomers 6.2(1-BuOH) and 7.2(iso-BuOH) and the tert-BuOH solvents are pairwise encapsulated in lattice pockets (Fig. S6†). The structure of 13·1.85(1,4-dioxane) contains two half 1,4-dioxane molecules in the asymmetric unit lying on inversion centres and arranged alternately in channels along the b axis (Fig. 7). All four non-polar solvents in compounds 14-17 (EtOAc, Et₂O, DIPE and n-hexane, respectively) are located on inversion centres. Thus, the ratio of the $[Cu(BF_4)_2(HL)_4]$ host molecule to the included solvent is reduced to 1:1, contrary to 1:2 (or 1:1.33 in 8) observed in the preceding structures. The 1:2 ratios are dictated by the need to fully exploit all strong hydrogen-bond donor and acceptor groups, whereas in compounds 14–17 this is not necessary because the solvents are not engaged in any strong hydrogen-bonding pattern. In addition, the placement of the solvents on inversion centres helps to reduce the relative volume (%) they occupy within the unit cell and to accommodate them efficiently, considering they are large and elongated in shape. There is no solvent included in the crystal structure of 18 but only BF_4^- counterions located in lattice pockets (Fig. S7†); likewise, the nitromethane solvent in 19·0.8MeNO₂ is also located in lattice pockets.

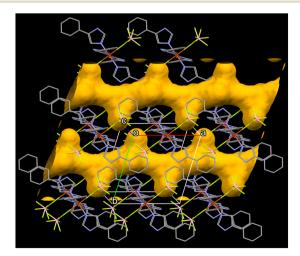


Fig. 6 View of the 3D structure of solvatomorph 2·2MeOH showing the channels (in yellow) along the *a* axis that contain the MeOH solvent molecules. The hydrogen atoms have been omitted. The channels were drawn using MERCURY.

Table 4 Void space and location of solvents in the compounds of this study

Compound ^a	$V_{ m void}/V_{ m cell}$ (%)	$SG^b(Z)^c$	Void space of solvents or counterions (for 18)
1·2Me ₂ CO·2H ₂ O	25.4	P2 ₁ /c (2)	Channels along <i>c</i>
2·2MeOH	17.5	$P\bar{1}$ (1)	Channels along a
3·2EtOH	17.6	$P\bar{1}$ (1)	Channels along a
4·2(1-PrOH)	25.0	$P\bar{1}$ (1)	Channels along a
$5.1.4(2-PrOH)^d$	20.9	$P\bar{1}$ (1)	Channels along [110]
6·2(1-BuOH)	26.2	$P\bar{1}(1)$	Channels along a
7·2(iso-BuOH) ^d	25.3	$P\bar{1}$ (1)	Channels along a
8·1.33(tert-BuOH)	19.6	$P\bar{1}$ (3)	Lattice pockets
9·2(1-PeOH)	30.1	$P\bar{1}(1)$	Channels along a
10 ·2DMF	26.9	$P\bar{1}(1)$	Channels along a
$11 \cdot 1.2 \text{Me}_2 \text{CO}^d$	16.3	$P\bar{1}$ (1)	Lattice pockets
12·2THF	24.9	$P\bar{1}(1)$	Channels along a
13·1.85(1,4-dioxane)	20.8	$P\bar{1}(1)$	Channels along b
14·0.86EtOAc	19.1	$P\bar{1}$ (1)	Channels along a
15·Et ₂ O	16.0	$P\bar{1}$ (1)	Channels along a
16·0.7DIPE	21.6	$P\bar{1}(1)$	Channels along a
17 ·(<i>n</i> -hexane)	20.2	$P\bar{1}(1)$	Channels along a
18	10.9	Pnn2(2)	Lattice pockets (BF ₄ ⁻)
19 ·0.8MeNO ₂	9.5	P2/n (4)	Lattice pockets

^a 1 to 17: [Cu(BF₄)₂(HL)₄]. ^b SG: space group. ^c Z: number of molecules in the unit cell. ^d Only the major-occupancy conformer of a disordered phenyl ring close to the solvent is used in the calculations.

IR study and TGA data in brief

The selected IR wavenumbers for the complexes cited in the Experimental Section refer to crushed, freshly isolated crystals; for this reason, the spectra exhibit bands of the lattice solvents. The presence of H-bonded H₂O or alcohol lattice molecules in 1-9 is proven by the appearance of a medium-to-strong intensity band at ~3400 cm⁻¹ assigned to the v(OH) mode; the broadness of the band is indicative of the participation of the -OH groups in H-bonds. This band is absent, as expected, from the spectra of 10-19, with the exception of 18; the spectrum of the latter shows a weak broad band assigned to v(OH) of the coordinated H2O

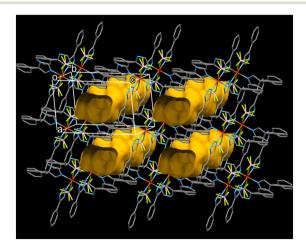


Fig. 7 View of the 3D structure of solvatomorph 13:1.85(1,4-dioxane) showing the channels (in yellow) along the b axis that contain the 1,4-dioxane solvent molecules. The hydrogen atoms have been omitted. The channels were drawn using MERCURY.

molecule.⁷⁴ The bands at ~1675 (1, 11), 1650 (10) and 1701 cm⁻¹ (14) can be safely assigned to the characteristic v(C=0)mode of the carbonyl (1, 11), amide (10) and ester (14) functionalities that are present in the lattice solvents of the complexes. The v(C = N) mode of the coordinated MeCN is hardly seen in the spectrum of 18, while the mediumintensity bands at 1561 and 1376 cm⁻¹ in the spectrum of 19 are attributed to the $v_{as}(NO_2)$ and $v_s(NO_2)$, respectively, vibrations of the lattice MeNO2.75 A common weak to medium, broad feature in the spectra of all the complexes is due to the v(NH) mode of the 5-phenylimidazole ligands, the broadness again indicating the participation of the N-H group in H bonds.

The band at 1026 cm⁻¹ in the spectrum of **19** is assigned⁷⁴ to the v(Si-F) mode of the tetrahedral $SiF_2O(OMe)^-$ ligand. The presence of tetrafluoroborato ligands (1-17) and BF₄ counterions (18) is manifested by the appearance of the characteristic v(BF) and $\delta(FBF)$ bands. The four normal modes of vibration of the 'free', i.e. uncoordinated (T_d) BF₄ ion are the $v_1(A_1)$ [$v_s(BF)$], $v_2(E)$ [$\delta_d(FBF)$], $v_3(F_2)$ [$v_d(BF)$] and $v_4(F_2)$ [$\delta_d(FBF)$] ones;⁷⁴ only v_3 and v_4 are IR-active. Monodentate coordination of the BF₄ group (as in 1-17) lowers the symmetry from T_d to C_{3v} , splitting each of the triply degenerate modes, v_3 and v_4 , into two components (F_2 \rightarrow A₁ + E). The previously IR-inactive modes, ν_1 and ν_2 , are activated in this process, i.e. monodentate coordination.^{74–76} Common bands due to the BF₄ ligands in 1-17 appear at \sim 1070, \sim 1040, \sim 760 and 515 cm⁻¹, the first and the third ones probably overlapping with HL vibrations since they also appear in the spectrum of free 4-phenylimidazole. We tentatively assign the three high-wavenumber bands to the A_1 + E components of v_3 and to the activated v_1 mode (exact assignments would be risky), and the band at ~ 515 cm⁻¹

arising from the splitting of ν_3 and/or from the activated ν_2 mode. All these spectral characteristics reveal a lower symmetry of the BF₄ ion due to monodentate coordination. However, none of compounds 1–17 exhibits all six vibrations corresponding to the $C_{3\nu}$ symmetry. This is probably due to the masking of the additional expected bands by ligand's vibrations; however, this feature has also been explained six vibrations; however, this feature has also been explained to our surprise, the four BF₄ bands appear also in the spectrum of la although this complex contains purely ionic $(T_{\rm d})$ tetrafluoroborate counterions. This might be due to the involvement of the anions in H bonds, which makes BF₄ to spectroscopically behave as 'pseudocoordinated'.

Thermogravimetric (TG) data are available for complexes 2-5, 7, 10, 12, 15 and 17 (Fig. S8†). The samples were in the form of crushed (powdered) crystals and thus they were not completely dried, but contained various amounts of lattice solvents. For this reason, an in-depth discussion is not possible. The samples lose the lattice solvents at low temperatures, mainly dependent on their boiling point. Thus, the removal of MeOH in 2.2MeOH is complete at ~70 °C, whereas that of DMF in 10.2DMF is complete at ~190 °C. The observed experimental trend might be a coincidence since it is known that boiling point is a bulk property while this is not the case for single crystals that include lattice solvents. Thermally stable intermediates are clearly visible at temperatures above those of the complete loss of lattice solvents, corresponding to the unsolvated compounds. The main decomposition of the complexes occurs at ~300 °C and is rather similar for most samples. For 3.2EtOH, 10.2DMF, 12-2THF and 15-Et₂O decomposition gradually continues above 800 °C, the highest temperature limit of the instrument used. For the other complexes, a final plateau appears at slightly below or slightly above 600 °C and approximate mass loss calculations indicate that the final residue is CuO. For example, the final residue in 17-(nhexane) is 10.1% of the original mass, while the theoretical value for CuO is 8.9%. The small discrepancies observed in most cases are presumably due to the assumption that the original samples at 20 °C contained all the amount of the lattice solvent found through crystallography.

Conclusions

The Cu(II)/HL/BF₄ reaction system shows a remarkable competence to form solvatomorphs. The complexes are crystallized as solvated forms from a large number of polar protic, polar aprotic and non-polar solvents. The solvents included are $\rm H_2O + Me_2CO$ (1), MeOH (2), EtOH (3), 1-PrOH (4), 2-PrOH (5), 1-BuOH (6), iso-BuOH (7), *tert*-BuOH (8), 1-PeOH (9), DMF (10), Me₂CO (11), THF (12), 1,4-dioxane (13), EtOAc (14), Et₂O (15), DIPE (16) and *n*-hexane (17). They all crystallize in the $P\bar{1}$ space group with Z=1, except 1·2Me₂-CO·2H₂O (in $P2_1/c$, Z=2) and 8·1.33(*tert*-BuOH) (in $P\bar{1}$, Z=3). The initially used 4-phenylimidazole ligand is present in all complexes as its 5-phenylimidazole tautomeric form. There

are two solvent molecules per [Cu(BF₄)₂(HL)₄] unit (with full or partial site occupancy due to disorder), except for solvatomorphs 1.2Me₂CO·2H₂O, 8.1.33(tert-BuOH) and 14-17 (in which the solvents are located on inversion centres, presumably to fit more efficiently in the unit cell since they are large and elongated). The $[Cu(BF_4)_2(HL)_4]$ host molecules in the solvatomorphs have similar conformations with a few minor differences in the orientation of the aromatic rings, most likely to facilitate the formation of the H-bonding synthons and accommodate the included solvents. All solvent molecules reside in channels, except for compounds 8-1.33(tert-BuOH) and 11-1.2Me₂CO (with a highly disordered HL ligand) in which the solvents are found in lattice pockets. The void space of the channels (or lattice pockets), calculated after the removal of the solvent molecules, ranges from 16.0% to 30.1% of the unit-cell volume. It follows that the [Cu(BF₄)₂(HL)₄] host framework of the seventeen structures can readily incorporate solvent molecules containing two to six light non-H atoms (C, O, N).

At the supramolecular level, the large number of the solvatomorphs with a variety of solvents (with respect to their H-bond functionalities, size and shape) allows for interesting conclusions to be drawn. The molecular self-assembly is clearly directed by robust synthons formed by the N-H/BF₄ donor/ acceptor groups of the [Cu(BF₄)₂(HL)₄] host molecules. Depending on the H-bond capabilities of the solvents included three distinct cases show up: i) the polar protic solvents (compounds 1-9) participate in the formation of N-H···O_{solvent}-H···F motifs and, together with the other N-H···F synthons, lead to compact 2D layers; ii) the polar aprotic solvents (compounds 10-13) are, perforce, only terminally linked through N-H···O_{solvent} interactions and, thus, the remaining N-H/BF₄ groups can only form 1D tapes via N-H···F synthons; however, 1,4-dioxane (13), due to its centrosymmetrically-related oxygen atoms O and O*, is an exception participating in N-H···O-//-O1*···H-N motifs, which together with the other N-H.F interactions form 2D layers; and iii) the non-polar solvents (compounds 14-17) are not engaged in any strong H-bonding motif and the N-H/BF₄ groups form directly 2D layers via N-H···F synthons. In all three cases the 1D or 2D constructions are further stabilized in 3D by means of weak interactions (e.g. $\pi \cdots \pi/C-H \cdots \pi/C-H \cdots O/C-H \cdots F$). All the N-H and O-H donor groups of the ligands and the solvents, respectively, and most of the fluorine acceptor atoms of the BF4 ions are engaged in synthon formation in the course of the crystallization process. Finally, the packing organization of the 'failed' structures 18 and 19.0.8MeNO2, corroborates the structure-directing role of the robust N-H···F synthon conserved among all seventeen solvatomorphs studied.

It seems that in the present series of solvatomorphs, the solvents have a distinct role in the formation of self-assembled structures, either by interfering with the otherwise expected synthon by forming alternative associations, or by connecting terminally to donor groups of the guest molecule, or by simply residing in channels participating only in structurally non-important weak interactions.

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Work currently in progress in our laboratory involves the synthetic and structural study of the related Cu(II)/HL/ClO₄, $Cu(\Pi)/HL/PF_6$, $Cu(\Pi)/HL/CF_3SO_3$ and Cu(II)/HL/SiF₆²⁻ systems in order to study the effect of solvatomorphism as a function of the weakly coordinating anion, and the extensions of this type of chemistry in other, non-Jahn-Teller distorted divalent metals, e.g. Mn(II), Co(II), Ni(II) and Zn(II).

Author contributions

MD: synthesis, X-ray structure analysis, IR/microanalyses, writing; NP, CP, AT: data collection/X-ray crystallography/TGA; DP: mechanistic studies, writing; VN, SPP: conceptualization, supervision, data curation, writing/draft preparation, project administration.

Conflicts of interest

There are no conflicts to declare.

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