Electronic Supplementary Material (ESI) for Chemical Communications

Self-assembly cavitand precisely recognizing hexafluorosilicate: a concerted action of two coordination and twelve CH···F bonds

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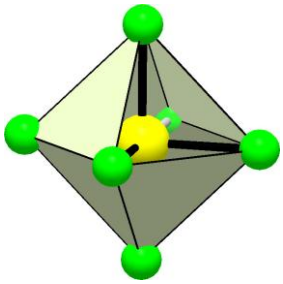

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SUPPORTING INFORMATION

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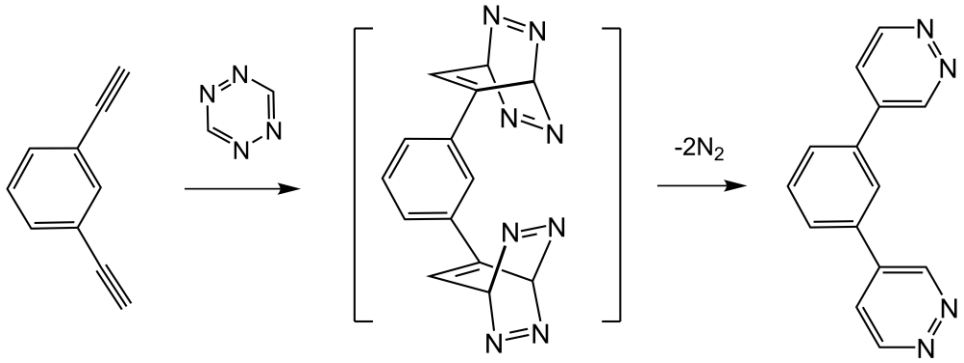
1. Synthesis

1.1. Preparation of the ligand



The organic ligand 1,3-(pyridazin-4-yl)benzene (L) was prepared in a high yield by an inverse electron demand Diels-Alder cycloaddition of 1,3-diethynylbenzene (Aldrich) and 1,2,4,5-tetrazine. The efficient large-scale preparation and purification of 1,2,4,5-tetrazine was descibed previously, in supplementary data for publications [**S1**, **S2**]. For other inverse electron demand cycloadditions of 1,2,4,5-tetrazine see [**S3**].

Synthesis of 1,3-*bis*(pyridazin-4-yl)benzene. A solution of 4.00 g (0.048 mol) 1,2,4,5-tetrazine and 2.50 g (0.020 mol) 1,3-diethynylbenzene in 40 ml of dry 1,4-dioxane was stirred at 90 ºC over a period of 25 h. The reaction proceeded smoothly and the evolution of dinitrogen gas ceased after first 15-16 h. The precipitate was filtered off, washed with 1,4-dioxane and diethyl ether and dried in air. The crude product was dissolved in boiling methanol, the solution was decolorized by 15-20 min reflux with charcoal, then it was filtered and evaporated to a ¼ of the initial volume under reduced pressure yielding 4.00 g (85%) of colorless crystalline product.

^{1}H NMR (400 MHz, dmso-d_6): 9.73 (*s*, 3H), 9.25 (*s*, 1H), 8.43 (*s*, 1H), 8.10 (*dd*, *J* = 5.3, 2.6 Hz, 2H), 8.01 (*dd*, *J* = 7.7, 2.4 Hz, 2H), 7.74 (*dd*, *J* = 7.9, 2.7 Hz, 1H) (See **Figure S1**).

Anal. for (**L**), $C_{14}H_{10}N_4$. Calc. (%): C, 71.77; H, 4.30; N, 23.92. Found: C, 71.60; H, 4.23; N, 24.06%.

1.2. Synthesis of coordination compounds

Complexes $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)\cdot 3CH_3OH$ (**1**), $[\{(SiF_6)_{1-x}(GeF_6)_x\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)_{1-y}(GeF_6)_y\cdot 3CH_3OH$ (**1a**: $x = 0.07$, $y = 0.33$; **1b**: $x = 0.11$, $y = 0.62$), $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)_{1-y}(SnF_6)_y\cdot 3CH_3OH$ (**1c**: $y = 0.50$; **1d**: $y = 0.79$) and $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)(H_2O)](ClO_4)_2\cdot 5.5CHCl_3$ (**3**)

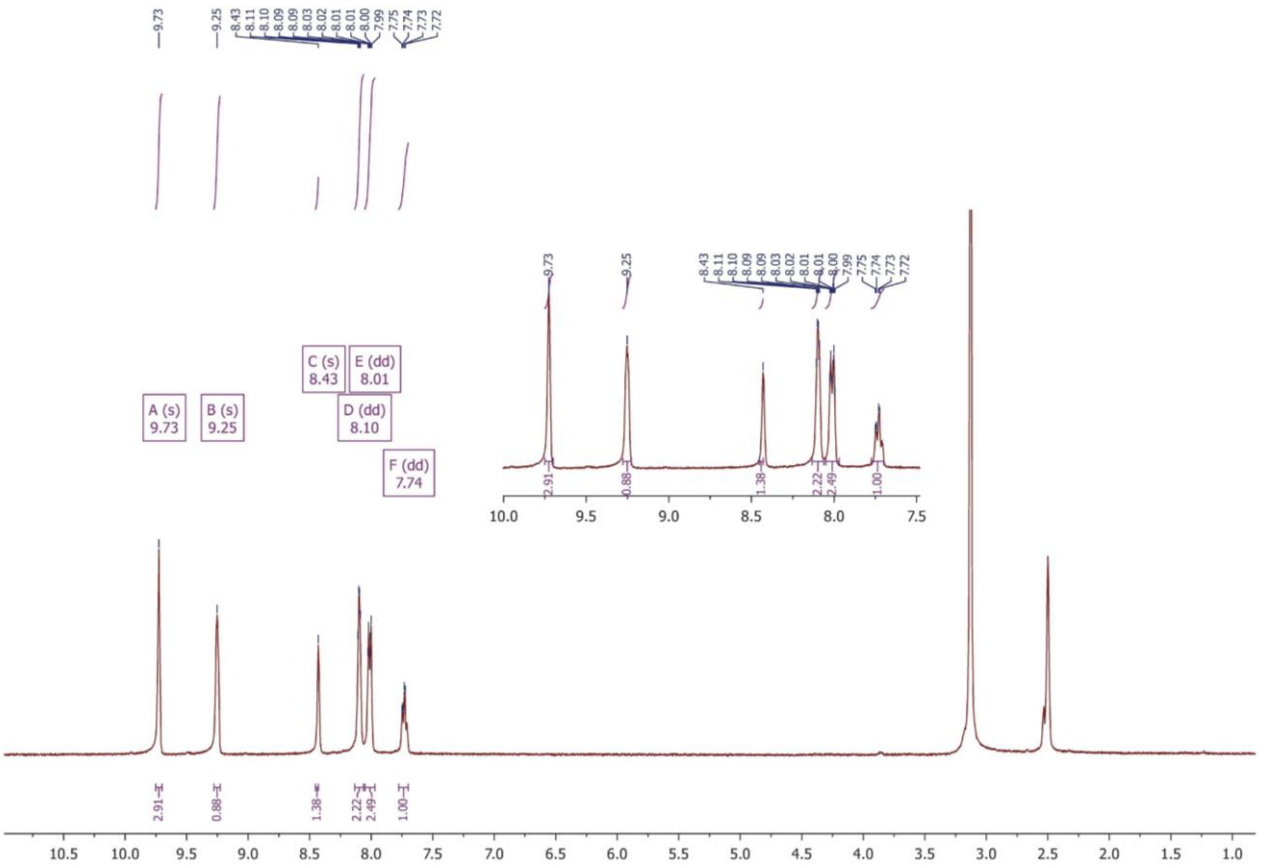


Figure S1. ^{1}H NMR spectrum of 1,3-(pyridazin-4-yl)benzene (dmso-d_6).

were prepared using a layering technique, by slow interdiffusion of the solutions containing the reaction components (methanolic solutions of inorganic salts were layered over chloroform or methanol-chloroform solutions of the ligand). Products of solvothermal synthesis (See Method II) were identical. For the mixed-anion systems, it was possible to obtain the cationic complexes $[\{SiF_6\}\subset Cu_2(L)_4(D)_2]^{2+}$ (D = H_2O, CH_3OH) in the environment of other counter anions. Thus, the reaction of the ligand and 1:1 mixture of $Cu(ClO_4)_2{\cdot}6H_2O$ and $CuSiF_6{\cdot}6H_2O$ led to crystallization of blue-green prisms of the perchlorate salt (**3**). However, the same reactions for $CuSiF_6{\cdot}6H_2O$ utilized in a mixture with copper(II) dithionate $CuS_2O_6{\cdot}6H_2O$ or copper(II) tosylate $Cu(CH_3C_6H_4SO_3)_2{\cdot}6H_2O$ led to crystallization of the entirely fluorosilicate compound (**1**) in lower yields of 20-30%. This method was less efficient also for the preparation of hexafluorophosphate salt (with using of $CuSiF_6{\cdot}6H_2O$ and NBu_4PF_6); it provides only low yields of the desired compound and the reaction products commonly contained mixture of unidentified powdery materials. More suitable method for preparation of $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2](PF_6)_2{\cdot}4CHCl_3$ (**2**) was slightly different and specific for a given compound. As a starting material, we have employed copper(I) salt $CuPF_6{\cdot}4CH_3CN$, which is readily soluble in acetonitrile and gives clear orange solutions when combined with the

bipyridazine ligand. When the solution was stored in a Pyrex tube under contact with air, slow hydrolysis of hexafluorophosphate led to liberation of HF and progressive generation of SiF_6^{2-} ions accompanied by slow air-oxidation of Cu^{I}. Thus the blue-green crystals of the desired $Cu^{II}/SiF_6/PF_6$ compound (**2**) were produced.

Reaction of the ligand and $CuSiF_6{\cdot}6H_2O$ yields blue-green prisms of pure (**1**). At the same time, the reactions performed under indentical conditions (in a polypropylene ware) starting with $CuGeF_6{\cdot}6H_2O$, $CuSnF_6{\cdot}6H_2O$ and $CuTiF_6{\cdot}4H_2O$ resulted only in slow deposition of mixtures of unidentified powdery products. It was not possible to prepare Ge, Sn or Ti analogs of (**1**) varying molar proportions of the components and their concentrations, solvents for reactions and methods of crystallizations. Powdery impurities were formed also for the some mixed systems containing $CuGeF_6{\cdot}6H_2O$ and $CuSiF_6{\cdot}6H_2O$ (with the initial molar ratios of Ge to Si exceeding 2:1). However, with 1:1 or 2:1 initial molar ratios of these two fluorosalts, the reactions proceeded identically to the entirely fluorosilicate system and led to deposition of blue-green crystalline materials (**1a**) and (**1b**). Fluorosilicate complexes, which are identical to the above $[\{SiF_6\}{\subset}Cu_2(L)_4(CH_3OH)_2](SiF_6){\cdot}3CH_3OH$ (**1**), was prepared also by solvothermal technique (See "Method II").

The chloroform solvates (**2**) and (**3**) are unstable; they readily lose solvent in air within few minutes and therefore it was not possible to obtain satisfactory microanalysis data for these compounds. The methanol solvates **1** and **1a-1d** are slightly more stable and lose solvent molecules when exposed to air for 1-2 h. In each case the crystals became opaque and finally gave powdery partially desolvated materials.

Preparation of $[\{SiF_6\}{\subset}Cu_2(L)_4(CH_3OH)_2](SiF_6){\cdot}3CH_3OH$ (1).

Method I. A solution of $CuSiF_6{\cdot}6H_2O$ (13.0 mg, 0.041 mmol) in 3 mL methanol was layered over the solution of ligand L (10.0 mg, 0.043 mmol) in 3 mL chloroform. 6 mL of a chloroform-methanol mixture (1:1 v/v) was introduced as an intermediate layer. Slow interdiffusion of the solutions over 6 d led to crystallization of green-blue crystals of the complex. The yield was 13 mg or 80%, based on the ligand (after complete interdiffusion for a period of 20-25 d).

Anal. for (**1**), $C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_2$. Calc. (%): C, 48.57; H, 4.01; N, 14.86. Found: C, 48.41; H, 4.07; N, 14.69%.

Method II. A mixture of $CuSiF_6{\cdot}6H_2O$ (13.2 mg, 0.042 mmol), the ligand (10.0 mg, 0.043 mmol) and 5 mL of methanol were sealed in Teflon vessel and placed in a steel autoclave, heated at 140 ºC for 24 h, and then cooled to room temperature over a period of 58 h. This afforded green-blue prisms of the product in a yield of 8.2 mg (50%, based on the ligand).

Anal. for (**1**), $C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_2$. Calc. (%): C, 48.57; H, 4.01; N, 14.86. Found: C, 48.39; H, 4.06; N, 14.72%.

Preparation of $[\{(SiF_6)_{1-x}(GeF_6)_x\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)_{1-y}(GeF_6)_y\cdot 3CH_3OH$ (1a, x = 0.07, y = 0.33). In a polypropylene tube, a solution of $CuGeF_6\cdot 6H_2O$ (3.6 mg, 0.01 mmol) and $CuSiF_6\cdot 6H_2O$ (3.1 mg, 0.01 mmol) in 2 mL of methanol was layered over the solution of ligand L (9.8 mg, 0.042 mmol) in 3 mL of chloroform. 6 mL of a chloroform-methanol mixture (1:1 v/v) was introduced as an intermediate layer. Slow interdiffusion of the solutions over 5 d led to crystallization of green-blue crystals of the complex. The product was collected after a period of 20 d, yielding 9 mg (60 %). Crystals of **1b** (x = 0.11, y = 0.62) were prepared similarly, starting with solution of 4.8 mg (0.013 mmol) of $CuGeF_6\cdot 6H_2O$ and 2.1 mg (0.0067 mmol) of $CuSiF_6\cdot 6H_2O$.

Anal. for (**1a**), $C_{61}H_{60}Cu_2F_{12}Ge_{0.40}N_{16}O_5Si_{1.60}$. Calc. (%): C, 48.00; H, 3.96; N, 14.69. Found: C, 47.87; H, 4.01; N, 14.54%.

Anal. for (**1b**), $C_{61}H_{60}Cu_2F_{12}Ge_{0.73}N_{16}O_5Si_{1.27}$. Calc. (%): C, 47.54; H, 3.92; N, 14.55. Found: C, 47.46; H, 3.97; N, 14.51%.

Preparation of fluorostannate(IV) compounds

$[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)_{1-y}(SnF_6)_y\cdot 3CH_3OH$ (**1c**: y = 0.50; **1d**: y = 0.79) was as stated above for **1a**, starting with solution of $CuSnF_6\cdot 6H_2O$ (4.0 mg, 0.01 mmol) and $CuSiF_6\cdot 6H_2O$ (3.1 mg, 0.01 mmol) (**1c**), and solution of 5.3 mg (0.0131 mmol) of $CuSnF_6\cdot 6H_2O$ and 2.1 mg (0.0067 mmol) of $CuSiF_6\cdot 6H_2O$.

Anal. for (**1c**), $C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_{1.50}Sn_{0.50}$. Calc. (%): C, 47.15; H, 3.89; N, 14.43. Found: C, 47.07; H, 3.91; N, 14.32%.

Anal. for (**1d**), $C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_{1.21}Sn_{0.79}$. Calc. (%): C, 46.37; H, 3.83; N, 14.19. Found: C, 46.50; H, 3.78; N, 14.27%.

Preparation of $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2](PF_6)_2\cdot 4CHCl_3$ (2). 9.3 mg (0.025 mmol) of $CuPF_6\cdot 4CH_3CN$ and 11.4 mg (0.049 mmol) of the ligand were dissolved in 9 mL of 2:1 (v/v) acetonitrile-chloroform mixture, containing appr. 1% vol. water. The clear orange solution obtained was placed in a Pyrex tube and slowly evaporated in air to a volume of 3-4 mL over period of 20-22 d. This led to deposition of blue-green crystals of the product (11 mg, 45%). The crystals were washed with some acetonitrile to remove soluble orange-red microcrystalline Cu^I co-product. Compound readily loses chloroform of crystallization in air within few minutes.

Preparation of $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)(H_2O)](ClO_4)_2\cdot 5.5CHCl_3$ (3)

A solution of $CuSiF_6\cdot 6H_2O$ (13.4 mg, 0,043 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (16.0 mg, 0.043 mmol) in 3 mL methanol was layered over the solution of ligand L (10.0 mg, 0,043 mmol) in 3 mL chloroform. 6 mL of a chloroform-methanol mixture (1:1 v/v) was introduced as an

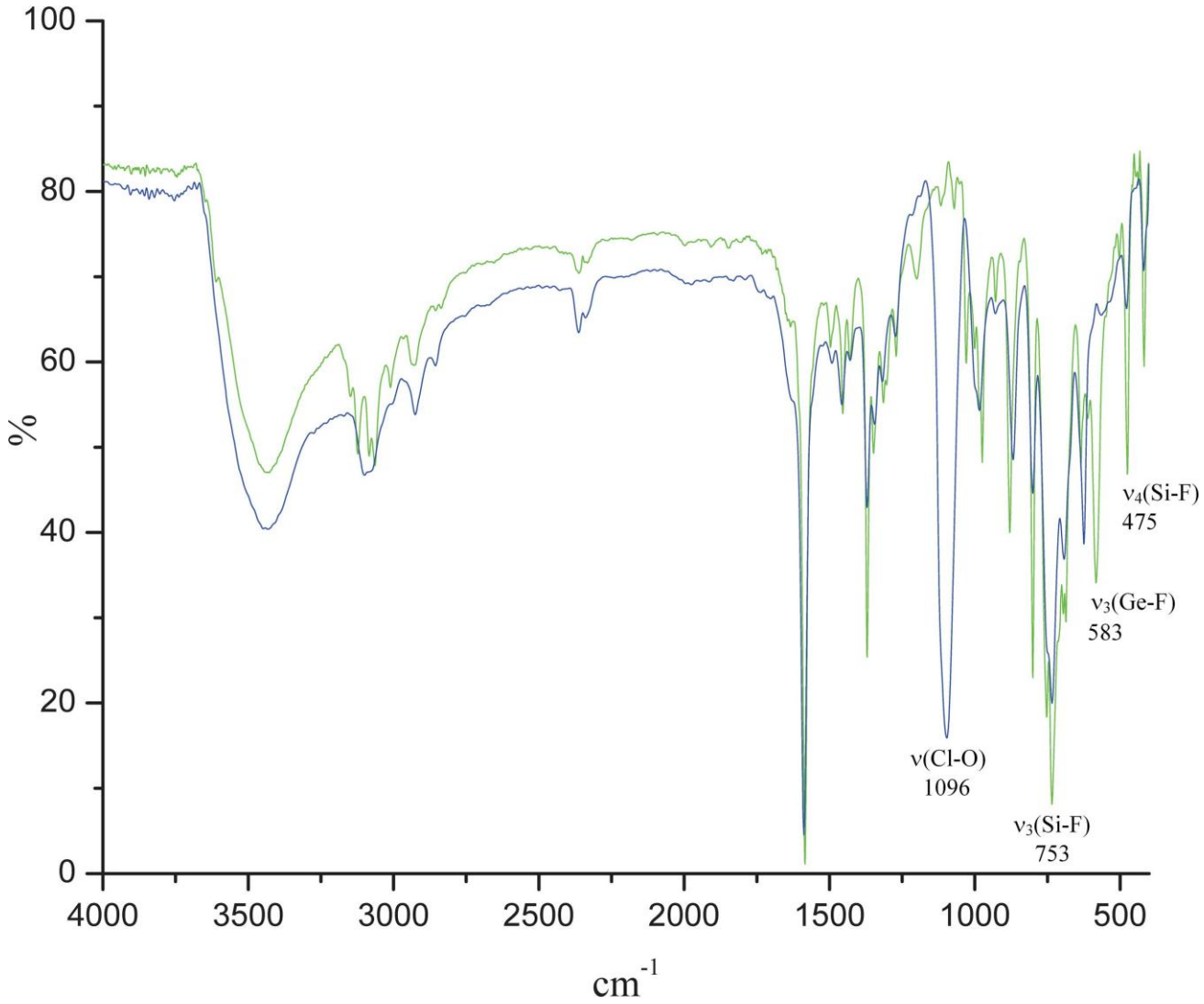


Figure S2. IR spectra (KBr disks, 400-4000 cm^{-1}; Pekin Elmer FTIR spectrometer) of **1a** (marked in green) and **3** (marked in blue).

intermediate layer. Green-blue crystals of the complex grew on the walls of the tube as the solutions slowly interdiffused in a 6 d period (yield 80%, collected after 30 d of the diffusion). The crystals are unstable in air giving powdery desolvated product.

1.3. Appendix: Syntheses of some inorganic salts

All procedures for preparations were performed using a polypropylene ware. Solutions of fluorosilic and fluorogermanic acids were prepared in a standard way, by dissolution of $SiO_2 \cdot xH_2O$ and GeO_2 in 20% aqueous HF (excess 5-10%). After addition of solid copper(II) acetate, **$CuSiF_6 \cdot 6H_2O$** and **$CuGeF_6 \cdot 6H_2O$** were isolated by slow crystallization in a desiccator over conc. H_2SO_4 and solid NaOH (for removal of acetic acid and excess HF). The hydrate compositions of the compounds ($\pm 0.1 H_2O$) were assigned on a basis of trilonometry.

Due to a slow solubility of crystalline SnO_2 and TiO_2 in dilute HF, for preparation of **$CuSnF_6 \cdot 6H_2O$** and **$CuTiF_6 \cdot 4H_2O$**, the starting materials were SnO and K_2TiF_6. This allowed to avoid chloride impurities (which were common for the products obtained from freshly deposited $SnO_2 \cdot xH_2O$ and $TiO_2 \cdot xH_2O$ starting with $SnCl_4$ and $TiCl_4$).

Preparation of $CuSnF_6 \cdot 6H_2O$. 12.00 g of black SnO was dissolved in a mixture of 27 mL of 40% HF and 20 mL water, with stirring. The colorless fluorostannate(II) solution was filtered and then solution of 8.1 mL 34% H_2O_2 in 20 mL water was added dropwise over period of 1 h. To the fluorostannate(IV) solution obtained, 16.00 g of solid $Cu(AcO)_2 \cdot H_2O$ was added, the mixture was stirred for the total dissolution of acetate, the resulting deep-blue solution was filtered and evaporated in a desiccator over conc. H_2SO_4 and solid NaOH until crystallization of large blue prisms of the product. It was washed with few methanol and dried over solid NaOH.

Preparation of $CuTiF_6 \cdot 4H_2O$. 19.94 g K_2TiF_6 was dissolved in 400 mL of hot water and 25% NH_4OH solution was added dropwise to adjust pH=12. The precipitate of $TiO_2 \cdot xH_2O$ was repeatedly washed by decantation with 2 L portions of water in a 3 L beaker. The resulting suspension (in ca. 200 mL water) was dissolved by addition of 42 mL 20% HF, then 13.10 g of solid $Cu(AcO)_2 \cdot H_2O$ was added under stirring. The obtained deep-blue solution was evaporated to a volume of 50 mL on a bath at 50-60^{o}C and then it was left for slow crystallization in a desiccator over conc. H_2SO_4 and solid NaOH. Deep-blue prisms of the product were washed with few methanol and finally dried over solid NaOH.

2. Crystal Structure Determination

The diffraction data were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Measurements for **1**, **1a-1d** and **3** were performed at 173 K on a Bruker APEXII CCD area-detector diffractometer (ω scans). The data were corrected for Lorentz-polarization effects and for the effects of absorption (multi-scans method). Crystallographic measurements for **2** were made at 213 K using a Stoe Image Plate Diffraction System, φ oscillation scans, 0 → 190^o, Δφ = 0.9^o (numerical absorption correction using X-RED and X-SHAPE [**S4**]). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 package [**S5**]. Graphical visualization of the structures was made using the program Diamond 2.1e [**S6**].

2.1. Refinement of $[\{SiF_6\} \subset Cu_2(L)_4(CH_3OH)_2](SiF_6) \cdot 3CH_3OH$ (**1**)

In the framework of complex cation, $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)_2]^{2+}$, the methanol ligands are equally disordered by symmetry, in such a way that the C-atom is common for two components and two components of the disordered O-atom appear to be separated by ca. 1.25 Å. The refined C-O distances were reasonable although certainly shortened due to the disorder (1.28 Å) and therefore no geometry restraints were applied. All atoms of cationic residue, including methanol ligand, were refined anisotropically. The OH-hydrogen was located and then fixed at *d*(O-H) = 0.85 Å and with $U_{iso} = 1.5U_{eq}$(O). The aromatic CH-atoms were added geometrically [$U_{iso} = 1.2U_{eq}$(C)] and two sets of the methyl CH-atoms were added [$U_{iso} = 1.5U_{eq}$(C)] with partial contributions of 0.5 and considering two orientations of methanol O-atoms.

Three unique solvate methanol molecules reside across symmetry elements and are disordered by symmetry over multiple positions. It was impossible to resolve the disordering schemes and therefore the corresponding electron density (218 *e*/cell found, 216 *e*/cell calc.) was modelled using a *Squeeze* routine implemented in *Platon* [**S7**].

2.2. Refinement of $[\{(SiF_6)_{1-x}(GeF_6)_x\}\subset Cu_2(L)_4(CH_3OH)_2](SiF_6)_{1-y}(GeF_6)_y\cdot 3CH_3OH$ (**1a** and **1b**) and $[\{SiF_6\}\subset Cu_2(L)_4(MeOH)_2](SiF_6)_{1-y}(SnF_6)_y\cdot 3MeOH$ (**1c** and **1d**)

These structures are isomorphous to the previous example (**1**) and retain its main features. For the refinement of these structures, we have used common approach including resolution of the disorder for the coordinated methanol ligands (which is similar to the one observed for **1**). The H-atoms of the complex cation were also assigned as stated above.

Similarly to the previous case of (**1**), it was impossible to resolve disorder for two other solvent molecules of methanol and therefore the corresponding electron density was modelled in the same way, using a *Squeeze* routine implemented in *Platon* [**S7**].

Our special attention was connected with attribution of isomorphic substitution of SiF_6^{2-}/GeF_6^{2-} and SiF_6^{2-}/SnF_6^{2-} ions and refinement of partial contribution factors. The substitution was clearly indicated at the early stages by refinement of isotropic thermal parameters, for example for (**1a**), *with two positions refined as Si-atoms*:

	CU1	7	0.641975	0.176638	0.000000	10.50000	0.02562
Encapsulated anion:							
	SI1	6	0.500000	0.000000	0.000000	10.25000	0.01228
	F1	5	0.562195	0.075935	0.000000	10.50000	0.02892
	F2	5	0.424647	0.061531	0.000000	10.50000	0.02899
	F3	5	0.500000	0.000000	-0.082003	10.50000	0.02821
Outer-sphere anion:							
	SI2	6	0.000000	0.000000	0.246474	10.25000	0.00001
	F4	5	0.076665	0.064184	0.246616	11.00000	0.02989
	F5	5	0.000000	0.000000	0.330196	10.25000	0.03007
	F6	5	0.000000	0.000000	0.164751	10.25000	0.03883

and *with two positions refined as Ge-atoms*:

	CU1	7	0.641932	0.176597	0.000000	10.50000	0.02445
Encapsulated anion:							
	GE1	8	0.500000	0.000000	0.000000	10.25000	0.05981
	F1	5	0.562657	0.075563	0.000000	10.50000	0.01724
	F2	5	0.425144	0.061911	0.000000	10.50000	0.01663
	F3	5	0.500000	0.000000	-0.081239	10.50000	0.01772
Outer-sphere anion:							
	GE2	8	0.000000	0.000000	0.246790	10.25000	0.04209
	F4	5	0.076598	0.064552	0.246677	11.00000	0.01790
	F5	5	0.000000	0.000000	0.329413	10.25000	0.02030
	F6	5	0.000000	0.000000	0.165363	10.25000	0.02938

Therefore, in the subsequent refinements, the positions of corresponding central atoms of two hexafluoroanions were treated as “mixed Si/Ge atom”, under common constraints for the positional (EXYZ) and thermal parameters (EADP) of the mixed atom and with the partial contributions set as additional free variables.

For the case of (**1a**) depicted above, the refinement converged at $(SiF_6)_{0.93}(GeF_6)_{0.07}$ for the “encapsulated anion” and $(SiF_6)_{0.67}(GeF_6)_{0.33}$ for the “outer-sphere anion”. In the case of (**1b**) (prepared from SiF_6^{2-}/GeF_6^{2-} = 1:2 mixture), the contributions from germanium were slightly higher for the “encapslated anion” position - $(SiF_6)_{0.89}(GeF_6)_{0.11}$, and appreciably higher for the “outer-sphere” position - $(SiF_6)_{0.38}(GeF_6)_{0.62}$. The refined bond distances were also indicative for the mixed-atom positions, they are actually intermediate between the values for Si-F and Ge-F bonds. For example, in the outer-sphere anion of **1b**, the Si/Ge-F bonds are in the range 1.754(3)-1.757(3) Å (mean 1.756(3) Å) and are significantly longer than similar parameters of Si-F in structure (**1**): 1.678(3)-1.695(3), mean 1.689(3) Å.

In the cases of $[\{SiF_6\}\subset Cu_2(L)_4(MeOH)_2](SiF_6)_{1-y}(SnF_6)_y\cdot 3MeOH$ (**1c** and **1d**), the refinement detected no any contribution from Sn to the position of the encapsulated anion. Attempted refinement of the partial occupancy factors here led to the values of Si: 1.01(1) and Sn: -0.01(1) for **1c**; Si: 1.00(1) and Sn: 0.00(1) for **1d.** Therefore, for the final cycles of the refinement this position was considered as Si atom.

At the same time, as for the Si/Ge series, the isomorphic substitution was relevant for

Table S1 Crystal data for [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)_2$](SiF_6)·3CH_3OH (**1**), [{$(SiF_6)_{1-x}(GeF_6)_x$}⊂$Cu_2(L)_4(CH_3OH)_2$]$(SiF_6)_{1-y}(GeF_6)_y$·3CH_3OH (**1a**: x = 0.07, y = 0.33; **1b**: x = 0.11, y = 0.62), [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)_2$]$(SiF_6)_{1-y}(SnF_6)_y$·3CH_3OH (**1c**: y = 0.50; **1d**: y = 0.79), [{SiF_6}⊂$Cu_2(L)_4(H_2O)_2$]$(PF_6)_2$·4$CHCl_3$ (**2**) and [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)(H_2O)$]$(ClO_4)_2$·5.5$CHCl_3$ (**3**)

	1	**1a**	**1b**	**1c**	**1d**	**2**	**3**
Formula	$C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_2$	$C_{61}H_{60}Cu_2F_{12}Ge_{0.40}N_{16}O_5Si_{1.60}$	$C_{61}H_{60}Cu_2F_{12}Ge_{0.73}N_{16}O_5Si_{1.27}$	$C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_{1.50}Sn_{0.50}$	$C_{61}H_{60}Cu_2F_{12}N_{16}O_5Si_{1.21}Sn_{0.79}$	$C_{60}H_{48}Cl_{12}Cu_2F_{18}N_{16}O_2P_2Si$	$C_{62.5}H_{51.5}Cl_{18.5}Cu_2F_6N_{16}O_{10}Si$
T, K	173	173	173	173	173	213	173
M	1508.51	1526.31	1540.88	1553.81	1580.08	2009.65	2111.69
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group, Z	$I4/m$, 4	$I4/m$, 4	$I4/m$, 4	$I4/m$, 4	$I4/m$, 4	$P2/n$, 2	$P2_1/c$, 4
a/ Å	17.1490(3)	17.1776(8)	17.2531(3)	17.2903(3)	17.3756(4)	12.6120(9)	12.8708(6)
b/ Å	17.1490(3)	17.1776(8)	17.2531(3)	17.2903(3)	17.3756(4)	12.6185(7)	12.5785(5)
c/ Å	20.7268(9)	20.715(2)	20.5377(10)	20.5440(10)	20.5964(9)	25.342(2)	50.263(2)
α/ °	90	90	90	90	90	90	90
β/ °	90	90	90	90	90	99.262(9)	93.272(3)
γ/ °	90	90	90	90	90	90	90
U/ Å^3	6095.5(3)	6112.5(8)	6113.4(3)	6141.7(3)	6218.3(3)	3980.5(5)	8124.1(6)
μ(Mo-Kα)/ mm^{-1}	0.841	1.024	1.175	1.023	1.119	1.088	1.227
D_c/ g cm^{-3}	1.644	1.659	1.674	1.680	1.688	1.677	1.726
θ_{max}/ °	29.11	26.37	26.33	26.39	27.71	27.03	26.02
No. measd reflns.	21088	15148	14347	15247	17174	30828	45147
No. unique reflns.	4216	3195	3208	3236	3744	8401	15944
No. obsvd reflns. I > 2σ(I)]	3037	2031	1978	2078	2894	5041	9456
R_{int}	0.0480	0.0669	0.0705	0.0511	0.0410	0.050	0.089
Parameters refined	223	225	225	224	224	439	1130
$R1$ [I > 2σ(I)]	0.0415,	0.0407,	0.0458	0.0500	0.0354	0.048	0.079
$wR2$ [all data]	0.1048	0.0944	0.1016	0.1513	0.0849	0.127	0.183
Goof on F^2	1.053	0.977	0.960	1.143	1.081	0.845	1.027
Max, min peak/ e Å^{-3}	0.376, -0.611	0.272, -0.486	0.404, -0.622	0.996, -0.517	0.504, -0.674	0.71, -0.54	0.69, -0.86

outer charge-compensation anion. For **1c**, the contributions from two sorts of anions were equal (y = 0.50), while for **1d** the refinement converged at y = 0.79. Higher contribution from Sn in the case of **1d** is indicated also by the bond lengths (mean Si/Sn-F = 1.810(3) Å for **1c**, and 1.902(2) Å for **1d**). In fact, the superposition of two kinds of octahedra (small SiF_6^{2-} and larger SnF_6^{2-}) "sharing" the central atom (Si/Sn) averages the electron density corresponding to F-ligands and therefore the observed bond lengths are artificial and are average between Si-F (1.68 Å) and Sn-F (1.95 Å) (it is not possible to resolve the disorder of so closely separated F-atoms). These effects may be detected through a mean-square displacement amplitude (MSDA) analysis. The parameters ΔMSDA ($<d^2>$, $Å^2$) for the Si/Sn-F bonds are particularly high [F4: 0.0087(16), F5: 0.0133(18); F6: 0.0186(16)], as may be compared with the normal values for the Si-F bonds of the encapsulated SiF_6^{2-} anion [F1: 0.0013(11); F2: 0.0020(10); F3: 0.0008(11)]. This clearly indicates the presence of disorder (which effect is similar to librational effects) involving all these six bonds of the "mixed anion" (**Figure S3**). Note that these pseudo-librational effects led to the generation of many Alerts in the checkcif files.

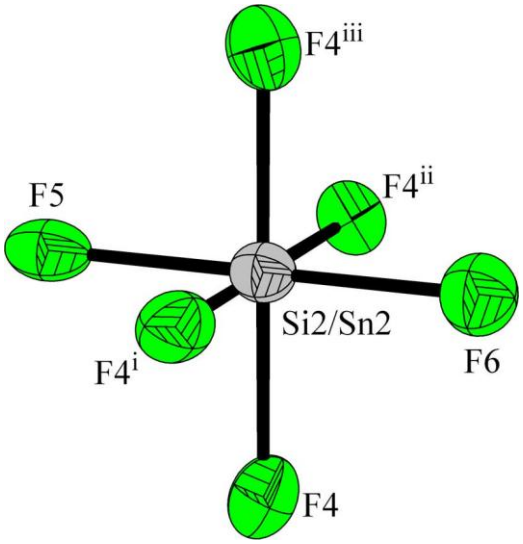


Figure S3. Structure of outer-sphere octahedral anion in **1d**, whith thermal ellipsoids at 50% probability level. Note the directions of the maximum anisotropic displacement parameter of the bonded F atoms, which are nearly parallel to the Si/Sn-F bonds.

2.3. Refinement of $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2](PF_6)_2\cdot 4CHCl_3$ (**2**)

Non-hydrogen atoms for the coordination framework and for non-coordinated PF_6^- anions were refined anisotropically, the CH-hydrogens were added geometrically [$U_{iso} = 1.2U_{eq}$(C)], the OH-hydrogens of aqua ligands were located and then included in calculations with fixed bond lengths [d(O-H) = 0.85 Å] and with $U_{iso} = 1.5U_{eq}$(O).

Two unique solvate chloroform molecules reside in the crystal channels and are badly disordered over several (more than two) overlapping positions. It was not possible to found satisfactory disordering schemes and the consequent refinements led to poorly converged models ($R1 \geq 0.11$). This electron density was successfully modelled using a *Squeeze* routine implemented in *Platon* [S7], giving reasonable parameters corresponding to 8 chloroform molecules per unit cell (in total, 521 *e* / unit cell).

2.4. Refinement of $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)(H_2O)](ClO_4)_2\cdot 5.5CHCl_3$ (**3**)

For the $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)(H_2O)]^{2+}$ portion of the structure, the refinement was standard. All the atoms were refined anisotropically, CH-hydrogen atoms were placed in calculated positions [*d*(C-H) = 0.95 Å], the OH-hydrogen atoms were located and included in calculations with fixed *d*(O-H) = 0.85 Å and $U_{iso} = 1.5U_{eq}$(O). Atoms of two non-coordinated ClO_4^- anions were also refined anisotropically.

The most appreciable problems during the structure refinement were connected with the solvent chloroform molecules. Unlike the previous case, it was possible to resolve disorder in the solvent regions. In total, there are 6 independent $CHCl_3$ molecules, one of which lies across a centre of inversion (referenced by C61 carbon atom) and thus it is equally disordered by symmetry. Two other $CHCl_3$ molecules (C62 and C63) are unequally disordered over two overlapping positions and refinement of thermal parametres in both the cases led to the partial contribution factors 0.60 and 0.40 (**Figure S4**). It was possible to resolve the disorders without restrains in geometry parameters and to refine all solvent atoms anisotropically. To improve the stability of the model, the only constraint applied was uniform displacement parameters assigned to C62A and C62B carbon atoms. The hydrogen atoms were added geometrically and considering partial contributions of the disorder components.

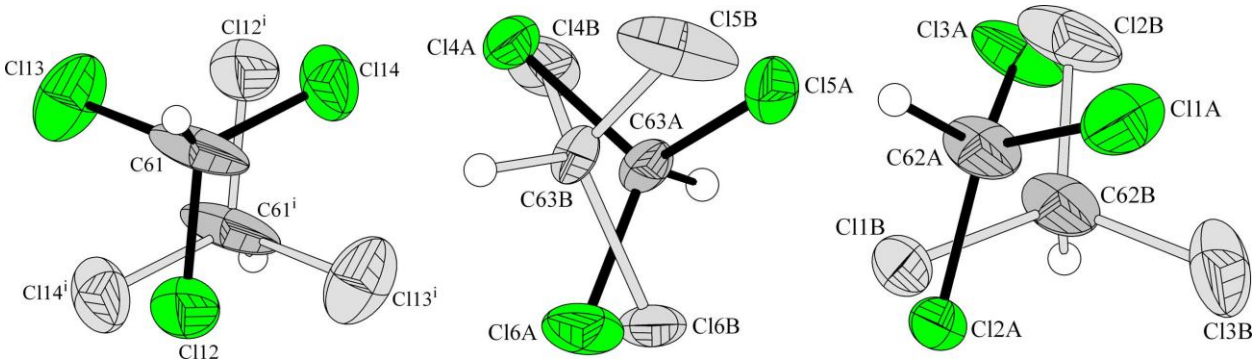


Figure S4. The refined disordering models for chloroform molecules in the structure of (**3**). Thermal elleipsoids are at 30% probability. Symmetry code: (i) 1-*x*, -*y*, 1-*z*.

4. Additional information on crystal structures

4.1. [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)_2$](SiF_6)·3CH_3OH (**1**), **1a-1d**

All the compounds **1, 1a-1d** are isomorphous (Tetragonal, I4/m, Z = 4; **Table S1**). In every case, Cu1 atom lies on a mirror plane; the Si1 and Si2 atoms in **1** (or "Si1/Ge1" and "Si2/Ge2" mixed atoms in **1a**, **1b**; Si1 and "Si2/Sn2" mixed atom in **1c**, **1d**) are at sites with crystallographically-imposed 2/m and 4-fold symmetry, respectively.

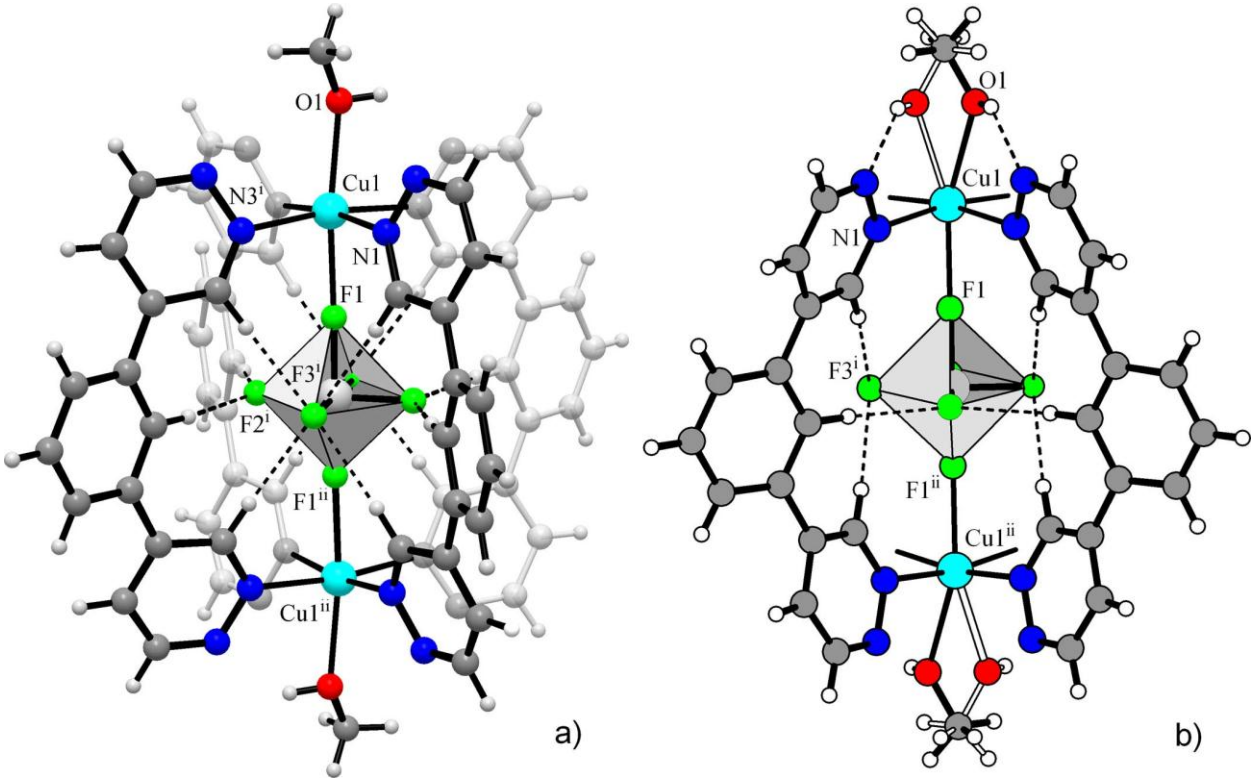


Figure S5. (a) – Structure of the [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)_2$]$^{2+}$ complex cations in (**1**). Note the mode of hydrogen bonding for the encapsulated SiF_6^{2-}. Structure of cationic species in mixed-ion compounds **1a** and **1b** is identical; (b) The refined disordering model for the coordinated methanol ligands. The symmetry codes for the atoms labelled with additional "i" and "ii" characters are: (i) 1-*x*, -*y*, -*z*; and (ii) 1-*x*, -*y*, *z*.

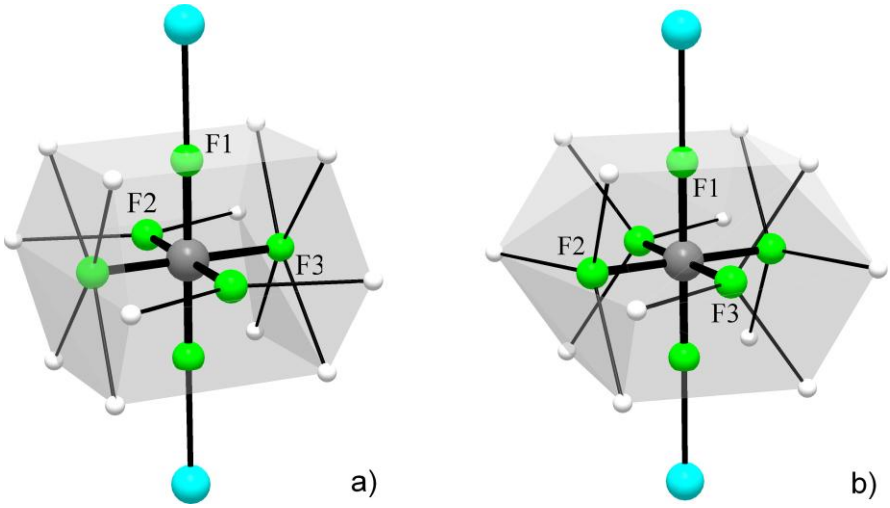


Figure S6. Mode of CH···F hydrogen bonding for the encapsulated anions in **1**, **1a** and **1b** (a) and **2** and **3** (b). Note that in the first case 12 hydrogen bonds are formed by two double and two quadruple equatorial F-acceptors, while in the second case bonding of each F-acceptor is uniform and include three CH···F interactions.

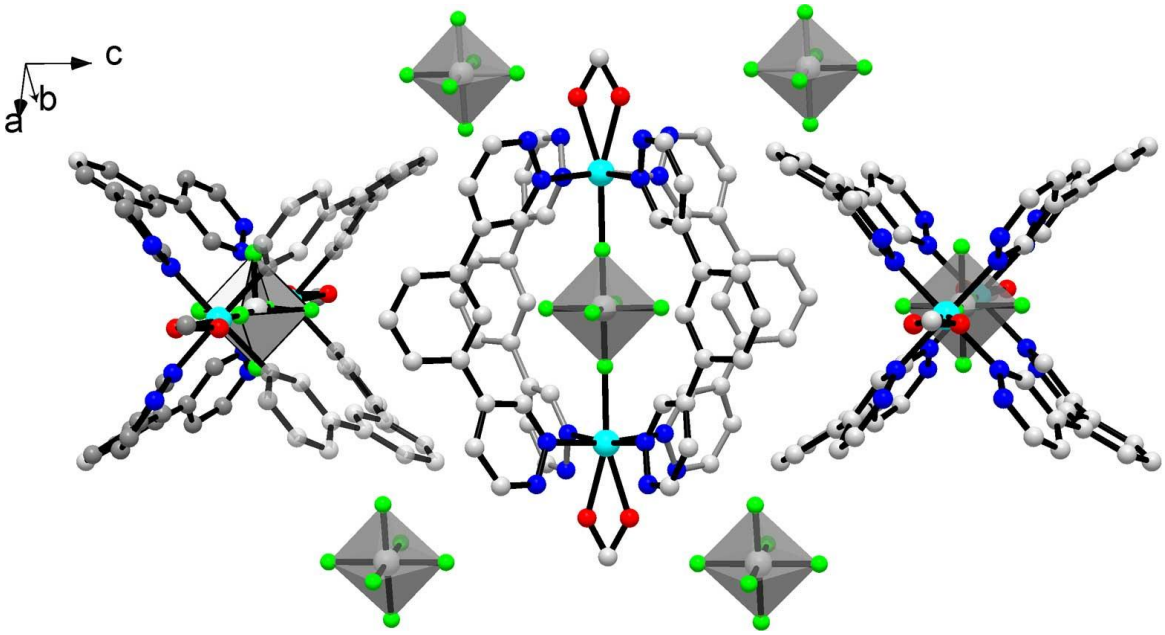


Figure S7. Non-covalent chain along the *c* direction in **1**. Note the orthogonal situation of successive cationic moieties, which provides more tight packing and minimizes the solvent accessible volume.

Table S2.

Geometry of hydrogen bonding in structure [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)_2$](SiF_6)·3CH_3OH (**1**)[a]

Donor (D)	H-atom	Acceptor (A)	D-H/ Å	H···A/ Å	D···A/ Å	∠DH···A/ °
Encapsulated SiF_6^{2-} anion:						
C1	**H1**	F3	0.95	2.31	3.262(2)	174.3
C5	**H5**	F3	0.95	2.26	3.210(2)	176.1
C10	H10	F2	0.95	2.26	3.202(2)	171.5
Outer SiF_6^{2-} anion:						
C3	**H3**	F5 (*y*, -*x*, *z*)	0.95	2.39	3.339(3)	176.6
C7	**H7**	F5 (0.5-*y*, -0.5+*x*, 0.5-*z*)	0.95	2.47	3.290(3)	144.4
C8	**H8**	F6 (0.5-*x*, -0.5-*y*, 0.5-*z*)	0.95	2.21	3.071(3)	150.6

[a] Pyridazine **CH-donors** are marked in bold.

CH···F hydrogen bonding of the encapsulated SiF_6^{2-} anion in (**1**) is slightly different from the one observed for (**2**) and (**3**): of the four "equatorial" fluoride atoms, two F are double acceptors of the bonds from phenylene groups C10-H10, and two fluorides are quadruple acceptors of the bonds from pyridazine donors (two with C1-H1 and two with C5-H5) (Figures Sx, Sx). Bonding of the outer SiF_6^{2-} anions is also interesting: in total, the anion forms 12 CH···F, with F6 as a quadruple acceptor of 4 symmetry related C8-H8···F6 bonds, and each of four symmetry related F5 atoms as acceptors of two bonds (with C3-H3 and C7-H7) (Table S2). It is worth noting that all these bonds utilize CH of pyridazine rings, as the most polarized and acidic. Bonding of the outer SiF_6^{2-} anions are comparable in strength with the bonding of the encapsulated anions, these bonds are also relatively directional. In this view, behaviour of outer SiF_6^{2-} anions is different from those of PF_6^- anions in (**2**), which form set of much weaker and bifurcate bonds.

4.2. [{SiF_6}⊂$Cu_2(L)_4(H_2O)_2$](PF_6)$_2$·4$CHCl_3$ (**2**)

The structure comprises complex cations [{SiF_6}⊂$Cu_2(L)_4(H_2O)_2$]$^{2+}$, which are situated across an inversion centre (with the Si1 atom lying on an inversion centre), and non-coordinated PF_6^- anions (**Figure S8**).

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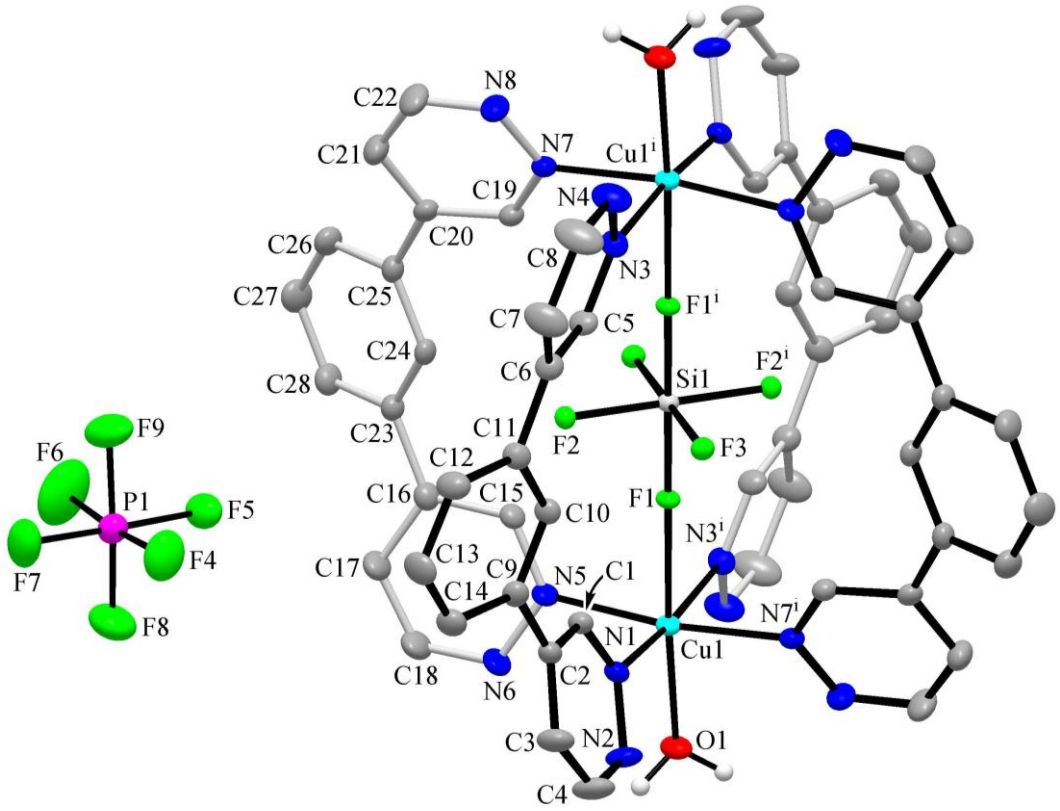

Figure S8. Structure of complex cation and PF_6^- counter anion in $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2](PF_6)_2\cdot 4CHCl_3$ (**2**) showing the atom labeling scheme. Thermal ellipsoids are drawn at 35% probability level and CH-hydrogen atoms omitted for clarity. Symmetry code: (i) -*x*, 1-*y*, -*z*.

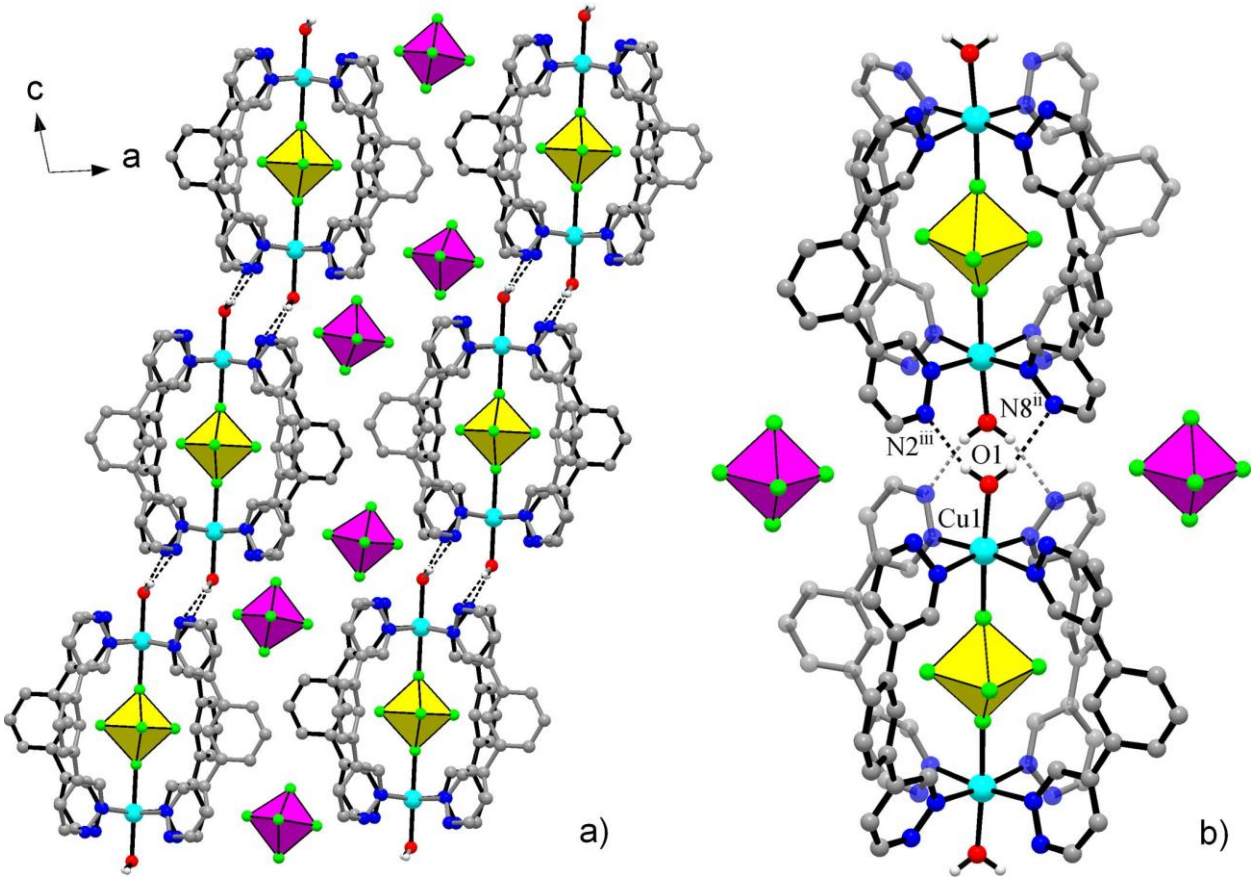

Figure S9. The OH···N hydrogen bonded chains in the structure of (2), with outer PF_6^- anions located between the chains (a) and the mode of the double intermoiety interactions.
(See **Table S3** for the details of symmetry operations involved in the hydrogen bonds shown in **Figure S9b**).

The packing pattern is appreciably different from the one for fluorosilicate (**1**): double OH···N hydrogen bonding (O···N = 2.875(3) and 3.161(4) Å) between the aqua ligands and pyridazine-N acceptors arranges complex cations into the columns (**Figure S7**). Specific shape of the $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$ modules predetermines formation (similarly to clathrates of $MPy_4(NCS)_2$) of very open structure. The solvent accessible area is as large as 1304.0 $Å^3$ per unit cell or 32.8% of the crystal volume, which is populated by disordered $CHCl_3$ molecules. Non-coordinated PF_6^- anions reside in small channels and interact with the framework by means of CH···F bonding (C···F = 3.190(4)-3.511(4) Å). These bonds, however, are longer and less directional than the ones adopted by the encapsulated fluorosilicates (Table S3) and some of such bonds are bifurcate.

Table S3.

Geometry of hydrogen bonding in structure [{SiF_6}⊂$Cu_2(L)_4(H_2O)_2$](PF_6)$_2$·4$CHCl_3$ (**2**)[a]

Donor (D)	H-atom	Acceptor (A)	D-H/ Å	H···A/ Å	D···A/ Å	∠DH···A/ º
Convenient bonding:						
O1	H1W	N2 (0.5-*x*, *y*, 0.5-*z*)	0.85	2.06	2.875(3)	161.3
O1	H2W	N8 (0.5+*x*, 1-*y*, 0.5+*z*)	0.85	2.34	3.161(4)	162.2
Encapsulated SiF_6^{2-} anion:						
C1	**H1**	F2	0.94	2.30	3.237(3)	174.8
C5	**H5**	F2	0.94	2.30	3.236(3)	171.4
C24	H24	F2	0.94	2.23	3.171(3)	175.4
C10	H10	F3	0.94	2.29	3.229(3)	176.1
C15	**H15**	F3 (-*x*, 1-*y*, -*z*)	0.94	2.32	3.257(3)	176.1
C19	**H19**	F3 (-*x*, 1-*y*, -*z*)	0.94	2.30	3.235(3)	177.7
Outer PF_6^- anion:						
C17	**H17**	F4	0.94	2.40	3.332(4)	170.1
C28	H28	F5	0.94	2.60	3.511(4)	163.5
C3	**H3**	F5 (1+*x*, *y*, *z*)	0.94	2.45	3.190(4)	135.4
C21	**H21**	F6 (-1-*x*, 2-*y*, -*z*)	0.94	2.63	3.313(5)	129.9
C21	**H21**	F7 (-1-*x*, 2-*y*, -*z*)	0.94	2.61	3.305(4)	130.7
C7	**H7**	F4 (-*x*, 2-*y*, -*z*)	0.94	2.47	3.391(4)	168.3
C12	H12	F4 (-*x*, 2-*y*, -*z*)	0.94	2.55	3.407(4)	152.1

[a] Pyridazine **CH-donors** are marked in bold.

4.3. [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)(H_2O)$](ClO_4)$_2$·5.5$CHCl_3$ (**3**)

Table S4. Geometry of H-bonding in [{SiF_6}⊂$Cu_2(L)_4(CH_3OH)(H_2O)$](ClO_4)$_2$·5.5$CHCl_3$ (**3**)

Donor (D)	H-atom	Acceptor (A)	D-H/ Å	H···A/ Å	D···A/ Å	∠DH···A/ º
Encapsulated SiF_6^{2-} anion:						
C1	H1	F3	0.95	2.33	3.270(6)	171.8
C5	H5	F3	0.95	2.23	3.175(7)	177.1
C10	H10	F6	0.95	2.23	3.179(6)	178.0
C15	H15	F4	0.95	2.35	3.250(7)	158.6
C19	H19	F4	0.95	2.30	3.236(7)	169.6
C24	H24	F3	0.95	2.26	3.213(7)	175.3
C29	H29	F5	0.95	2.34	3.265(7)	165.0
C33	H33	F5	0.95	2.27	3.219(6)	176.7
C38	H38	F4	0.95	2.22	3.166(7)	177.4
C43	H43	F6	0.95	2.34	3.217(6)	153.6
C47	H47	F6	0.95	2.26	3.211(7)	175.6

C52	H52	F5	0.95	2.27	3.212(7)	172.9

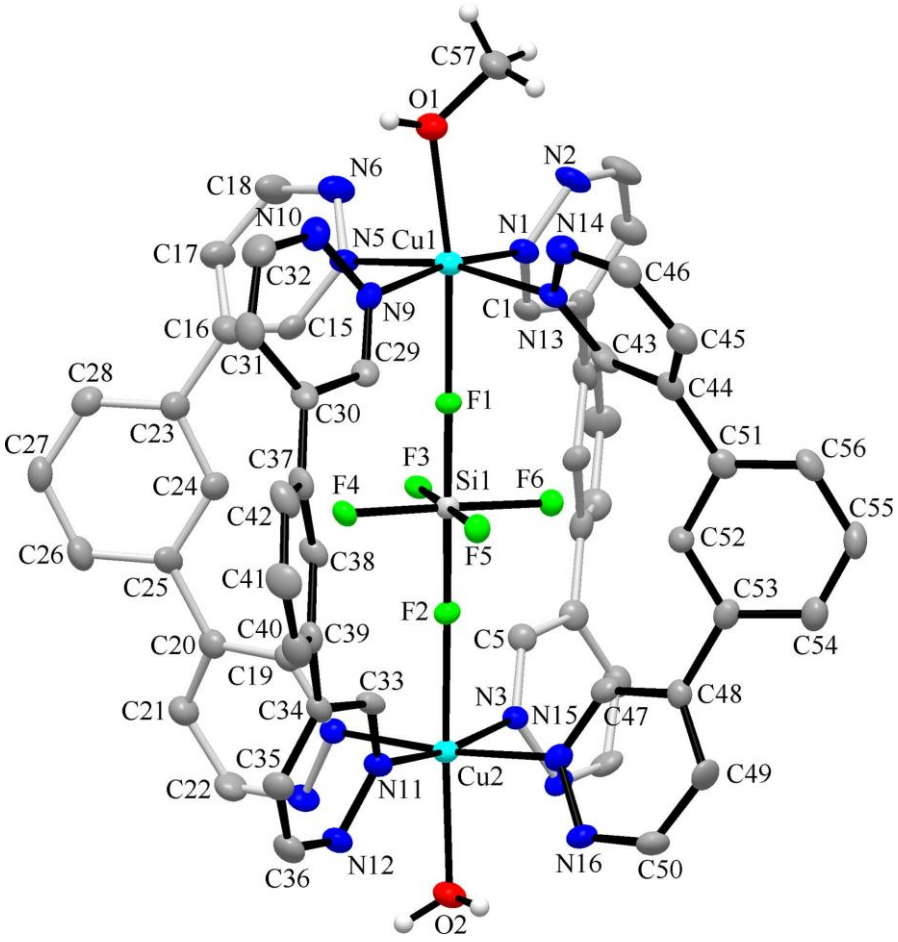

Figure S10. Structure of complex cation in $[\{SiF_6\}\subset Cu_2(L)_4(CH_3OH)(H_2O)](ClO_4)_2\cdot 5.5CHCl_3$ (**3**) showing the atom labeling scheme. Thermal ellipsoids are drawn at 35% probability level and CH-hydrogen atoms omitted for clarity.

5. Computational details

All calculations were carried out using the Turbomole package version 6.4 [**S8**] using the BP86-D3/def2-TZVPD level of theory, which includes the latest available correction for dispersion [**S9**]. All geometries (hosts, guests and complexes) have been fully optimized without symmetry constrains. The interaction energies have been corrected for the Basis Set Superposition Error by using the Boys and Bernardi [**S10**] counterpoise method.

6. Cartesian Coordinates

6.1. $[\{PF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3714122	-0.0747561	3.9867155
F	0.1813046	-0.0475871	1.6114812
F	-0.1697078	1.6266780	0.0669262
F	1.6172934	0.1751284	-0.1754081
O	0.8837615	-0.2207987	6.1232796
H	1.6141009	0.4294169	6.2092927
H	1.3195021	-1.0976735	6.1856324
N	1.7697332	1.4722177	3.7039618
N	2.6276369	1.6541174	4.7036420
N	1.0825756	1.5436577	-3.8450621
N	1.8915063	1.5863796	-4.8963980
N	-1.1005361	1.3730625	3.9402727
N	-1.0430291	2.2306022	4.9494173
N	-1.8918421	1.5099648	-3.5727770
N	-2.1476619	2.3321558	-4.5895993
C	1.8224130	2.2117586	2.5915834
H	1.0344654	2.0244652	1.8713371
C	2.8115280	3.1895695	2.3553459
C	3.7014394	3.3892460	3.4138574
H	4.5130554	4.1147152	3.3498482
C	3.5551091	2.6099562	4.5672848
H	4.2192786	2.7309099	5.4240858
C	1.2877740	2.3065412	-2.7612459
H	0.5378914	2.2310049	-1.9801359
C	2.3971939	3.1656835	-2.6297143
C	3.2204507	3.2457001	-3.7549171
H	4.1035868	3.8856411	-3.7672746
C	2.9157498	2.4473033	-4.8629294
H	3.5283880	2.4633045	-5.7653249
C	2.8780095	3.9167367	1.0675515
C	2.5570855	3.2572822	-0.1327425
H	2.2819647	2.2071899	-0.1088783
C	2.6696646	3.9053178	-1.3734191
C	3.0929862	5.2466100	-1.4033094
H	3.1716155	5.7744439	-2.3548501
C	3.3900626	5.9166677	-0.2153030
H	3.6981349	6.9615199	-0.2465566
C	3.2928058	5.2601776	1.0121386
H	3.5214637	5.8029120	1.9304128
C	-1.9834704	1.5071798	2.9419004
H	-1.9679270	0.7236767	2.1894106
C	-2.8831030	2.5887577	2.8578314
C	-2.8641608	3.4585883	3.9506073
H	-3.5243344	4.3253150	3.9986790
C	-1.9358493	3.2278435	4.9718553
H	-1.8687499	3.8826568	5.8414522
C	-2.5097479	1.6458653	-2.3946131
H	-2.2729847	0.8908066	-1.6537229
C	-3.4228933	2.6840544	-2.1107538
C	-3.6980500	3.5348008	-3.1838662
H	-4.3822959	4.3780549	-3.0845757
C	-3.0466375	3.3056516	-4.4013128
H	-3.2276594	3.9377399	-5.2717961
C	-3.7511676	2.7898016	1.6735389
C	-3.2384001	2.5816197	0.3824700
H	-2.2010870	2.2801172	0.2676322
C	-4.0123675	2.8429738	-0.7619610
C	-5.3343162	3.2951353	-0.5968759
H	-5.9640345	3.4814019	-1.4680509
C	-5.8592321	3.4820362	0.6823317
H	-6.8900529	3.8157478	0.8000719
C	-5.0754411	3.2436687	1.8123475
H	-5.5023855	3.3927107	2.8051960
F	-0.1820172	0.0473848	-1.6113587
F	0.1691081	-1.6268789	-0.0668233
F	-1.6179730	-0.1753705	0.1754844
Cu	-0.3720461	0.0746500	-3.9866080
O	-0.8845854	0.2201595	-6.1231856
H	-1.6151961	-0.4298237	-6.2087700
H	-1.3199790	1.0971752	-6.1858312

N	-1.7701773	-1.4725885	-3.7038705
N	-2.6280322	-1.6547083	-4.7035440
N	-1.0831440	-1.5438145	3.8451150
N	-1.8921201	-1.5867679	4.8964004
N	1.1000615	-1.3729990	-3.9403120
N	1.0429073	-2.2304332	-4.9495512
N	1.8914034	-1.5099835	3.5728204
N	2.1475862	-2.3320954	4.5896063
C	-1.8225770	-2.2122335	-2.5915607
H	-1.0346880	-2.0246927	-1.8713279
C	-2.8113455	-3.1904041	-2.3553458
C	-3.7012885	-3.3902300	-3.4137948
H	-4.5127389	-4.1158825	-3.3497411
C	-3.5552366	-2.6108198	-4.5671886
H	-4.2193846	-2.7319409	-5.4239820
C	-1.2880626	-2.3067708	2.7613015
H	-0.5381469	-2.2310683	1.9802576
C	-2.3972017	-3.1662645	2.6297385
C	-3.2204527	-3.2465769	3.7549260
H	-4.1032903	-3.8869309	3.7673103
C	-2.9161203	-2.4479817	4.8628913
H	-3.5289092	-2.4639991	5.7651852
C	-2.8775643	-3.9175546	-1.0675319
C	-2.5570848	-3.2579064	0.1327671
H	-2.2825371	-2.2076566	0.1088932
C	-2.6693359	-3.9060092	1.3734321
C	-3.0921792	-5.2474557	1.4033308
H	-3.1708038	-5.7752432	2.3548973
C	-3.3888285	-5.9176940	0.2153140
H	-3.6965094	-6.9626612	0.2465753
C	-3.2916637	-5.2612118	-1.0121462
H	-3.5198081	-5.8041053	-1.9304561
C	1.9829408	-1.5069600	-2.9418751
H	1.9671847	-0.7234891	-2.1893626
C	2.8828964	-2.5882585	-2.8578121
C	2.8643537	-3.4579587	-3.9507012
H	3.5248800	-4.3244147	-3.9988587
C	1.9360208	-3.2274182	-4.9719877
H	1.8691503	-3.8822069	-5.8416196
C	2.5093212	-1.6456202	2.3946333
H	2.2720725	-0.8907450	1.6537185
C	3.4228958	-2.6834247	2.1107331
C	3.6983842	-3.5341241	3.1838000
H	4.3828380	-4.3771980	3.0844276
C	3.0469385	-3.3052342	4.4012680
H	3.2282742	-3.9372330	5.2717514
C	3.7510957	-2.7888906	-1.6735640
C	3.2382206	-2.5811186	-0.3824744
H	2.2006935	-2.2803639	-0.2675920
C	4.0124140	-2.8419933	0.7619193
C	5.3346763	-3.2932275	0.5967712
H	5.9645661	-3.4790457	1.4679181
C	5.8596655	-3.4797322	-0.6824645
H	6.8907306	-3.8126682	-0.8002593
C	5.0756594	-3.2418878	-1.8124409
H	5.5026185	-3.3907223	-2.8053164
P	-0.0003474	-0.0001037	0.0000541

6.2. $[\{AsF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3606613	-0.0677551	4.0160341
F	0.1866286	-0.0346532	1.7386176
F	-0.1765600	1.7581696	0.0557703
F	1.7486200	0.1796368	-0.1808448
O	0.9037660	-0.2208571	6.1348808
H	1.6449473	0.4185441	6.2107095
H	1.3284529	-1.1040212	6.1910323
N	1.7621513	1.4879559	3.7167934
N	2.6528688	1.6379645	4.6924787
N	1.0871564	1.5549259	-3.8727392
N	1.9030945	1.5995229	-4.9174736
N	-1.1299451	1.3751362	3.9601180
N	-1.0809593	2.2363875	4.9654923
N	-1.9019781	1.5087213	-3.5891070
N	-2.1515069	2.3398957	-4.5994260
C	1.8062153	2.2355438	2.6082443
H	0.9892647	2.0880465	1.9114474

C	2.8206881	3.1809179	2.3481231
C	3.7428494	3.3488922	3.3842540
H	4.5735072	4.0506194	3.3012444
C	3.6029831	2.5685713	4.5379468
H	4.2915918	2.6660386	5.3782892
C	1.2864731	2.3156971	-2.7851435
H	0.5288103	2.2432877	-2.0113087
C	2.3985761	3.1698863	-2.6410779
C	3.2300126	3.2498359	-3.7605877
H	4.1159658	3.8860220	-3.7643639
C	2.9299910	2.4571951	-4.8740154
H	3.5487774	2.4747245	-5.7721557
C	2.8814195	3.9123325	1.0609164
C	2.5594921	3.2561255	-0.1407688
H	2.2910542	2.2053173	-0.1175048
C	2.6681156	3.9066595	-1.3808408
C	3.0892453	5.2487900	-1.4072566
H	3.1654795	5.7798051	-2.3572313
C	3.3887238	5.9155764	-0.2177832
H	3.6959451	6.9607469	-0.2471047
C	3.2960123	5.2558705	1.0085199
H	3.5279733	5.7952826	1.9280086
C	-2.0075153	1.5051787	2.9552579
H	-1.9906193	0.7177589	2.2069624
C	-2.9055328	2.5873053	2.8583145
C	-2.8927900	3.4624101	3.9471365
H	-3.5523141	4.3301379	3.9862102
C	-1.9729087	3.2349599	4.9768050
H	-1.9119350	3.8932820	5.8442025
C	-2.5210702	1.6414100	-2.4104578
H	-2.2972491	0.8761805	-1.6762449
C	-3.4257906	2.6848890	-2.1184276
C	-3.6926708	3.5456489	-3.1858322
H	-4.3703697	4.3935320	-3.0807929
C	-3.0429057	3.3194811	-4.4048495
H	-3.2189778	3.9586987	-5.2711219
C	-3.7685105	2.7832428	1.6679497
C	-3.2482050	2.5844606	0.3782252
H	-2.2068003	2.2988918	0.2667234
C	-4.0197953	2.8381683	-0.7697096
C	-5.3468988	3.2768962	-0.6094459
H	-5.9747268	3.4582140	-1.4830618
C	-5.8788090	3.4565784	0.6680357
H	-6.9133070	3.7801238	0.7818809
C	-5.0979875	3.2234817	1.8013522
H	-5.5310717	3.3663145	2.7924902
F	-0.1865852	0.0346060	-1.7385453
F	0.1766879	-1.7581708	-0.0557318
F	-1.7485550	-0.1796562	0.1808166
Cu	-0.3607330	0.0678490	-4.0159319
O	-0.9036504	0.2204897	-6.1348832
H	-1.6449536	-0.4187905	-6.2105304
H	-1.3281945	1.1036955	-6.1913379
N	-1.7622794	-1.4880110	-3.7166279
N	-2.6530544	-1.6379811	-4.6922576
N	-1.0870899	-1.5548526	3.8729084
N	-1.9030220	-1.5994610	4.9176436
N	1.1297708	-1.3750964	-3.9602227
N	1.0806541	-2.2363881	-4.9655529
N	1.9021215	-1.5087951	3.5889868
N	2.1517653	-2.3399320	4.5993060
C	-1.8062948	-2.2356258	-2.6081053
H	-0.9892632	-2.0882207	-1.9113789
C	-2.8207999	-3.1809398	-2.3479238
C	-3.7430453	-3.3488715	-3.3839821
H	-4.5736860	-4.0506184	-3.3009554
C	-3.6032394	-2.5685057	-4.5376584
H	-4.2919537	-2.6658768	-5.3779274
C	-1.2864186	-2.3156058	2.7853054
H	-0.5287565	-2.2431762	2.0114679
C	-2.3985673	-3.1697131	2.6412202
C	-3.2300569	-3.2496176	3.7606854
H	-4.1160954	-3.8856882	3.7643959
C	-2.9299638	-2.4570775	4.8741624
H	-3.5486801	-2.4746990	5.7723497
C	-2.8814310	-3.9123572	-1.0607027
C	-2.5594560	-3.2560890	0.1409358
H	-2.2909846	-2.2052646	0.1176353

C	-2.6679690	-3.9066078	1.3810170
C	-3.0890742	-5.2487427	1.4075105
H	-3.1652041	-5.7797474	2.3575023
C	-3.3886475	-5.9155521	0.2180728
H	-3.6958546	-6.9607241	0.2474472
C	-3.2960241	-5.2558927	-1.0082611
H	-3.5280435	-5.7953363	-1.9277195
C	2.0074255	-1.5051315	-2.9554402
H	1.9906266	-0.7176916	-2.2071563
C	2.9054623	-2.5872516	-2.8585555
C	2.8926226	-3.4623573	-3.9473828
H	3.5521867	-4.3300490	-3.9865440
C	1.9726121	-3.2349502	-4.9769371
H	1.9115249	-3.8933175	-5.8442902
C	2.5211397	-1.6414652	2.4103055
H	2.2973208	-0.8761832	1.6761390
C	3.4258146	-2.6849656	2.1181833
C	3.6929507	-3.5455812	3.1856497
H	4.3708661	-4.3932949	3.0806487
C	3.0432516	-3.3194442	4.4046981
H	3.2193855	-3.9586722	5.2709498
C	3.7684469	-2.7832847	-1.6682101
C	3.2480946	-2.5847323	-0.3784692
H	2.2065565	-2.2996647	-0.2669310
C	4.0197895	-2.8381795	0.7694531
C	5.3469038	-3.2768609	0.6091491
H	5.9747818	-3.4580766	1.4827517
C	5.8787837	-3.4565511	-0.6683420
H	6.9132666	-3.7801364	-0.7822041
C	5.0979454	-3.2234728	-1.8016416
H	5.5310296	-3.3662356	-2.7927885
As	0.0000362	-0.0000097	0.0000415

6.3. $[\{SiF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3518881	-0.0765453	3.9302668
Si	0.0002048	-0.0000767	-0.0000671
F	0.1878935	-0.0441729	1.6876771
F	-0.1684795	1.7065369	0.0637560
F	1.6969116	0.1734878	-0.1779936
O	0.9019505	-0.2048083	6.1311738
H	1.6251082	0.4612072	6.1309268
H	1.3651200	-1.0712858	6.1171308
N	1.7543885	1.4649420	3.6889848
N	2.5796027	1.6788009	4.7118732
N	1.0853759	1.5528400	-3.8549374
N	1.8295289	1.6710475	-4.9491821
N	-1.1162538	1.3614889	3.9409317
N	-1.1069399	2.1764929	4.9880854
N	-1.8731009	1.5076734	-3.5771486
N	-2.1763376	2.2860662	-4.6170326
C	1.8336649	2.1719551	2.5576848
H	1.0766942	1.9443269	1.8112367
C	2.8178148	3.1597260	2.3390439
C	3.6802557	3.3856322	3.4138180
H	4.4884987	4.1151092	3.3544314
C	3.5090101	2.6308485	4.5784506
H	4.1505902	2.7722200	5.4492475
C	1.3261301	2.2649348	-2.7454071
H	0.6402818	2.1052793	-1.9162642
C	2.4061088	3.1649889	-2.6445625
C	3.1724196	3.3131542	-3.8014879
H	4.0355303	3.9792807	-3.8295225
C	2.8354727	2.5520932	-4.9248947
H	3.4037118	2.6211980	-5.8535596
C	2.9025957	3.8802651	1.0510571
C	2.5801811	3.2226176	-0.1493982
H	2.2808453	2.1753025	-0.1307417
C	2.6987739	3.8827529	-1.3833082
C	3.1255027	5.2229828	-1.4062079
H	3.1988674	5.7565910	-2.3550325
C	3.4253042	5.8871133	-0.2164850
H	3.7330015	6.9323044	-0.2412423
C	3.3225080	5.2225543	1.0051228
H	3.5452810	5.7591789	1.9285278
C	-1.9577352	1.5235152	2.9120822
H	-1.8853823	0.7838312	2.1161354

C	-2.8754178	2.5913824	2.8487511
C	-2.9010542	3.4241695	3.9686704
H	-3.5727620	4.2815147	4.0238945
C	-2.0045586	3.1678603	5.0104552
H	-1.9716381	3.7944121	5.9026912
C	-2.4524768	1.6717990	-2.3840088
H	-2.1578154	0.9575293	-1.6191651
C	-3.3889779	2.6950817	-2.1202474
C	-3.7035628	3.5094736	-3.2095941
H	-4.4004348	4.3430424	-3.1179927
C	-3.0799080	3.2543474	-4.4349487
H	-3.2926673	3.8562152	-5.3195439
C	-3.7240674	2.8113052	1.6566857
C	-3.1985391	2.6029842	0.3709984
H	-2.1632522	2.2809116	0.2612511
C	-3.9715747	2.8686511	-0.7728136
C	-5.2940256	3.3222177	-0.6155946
H	-5.9192561	3.5038884	-1.4910538
C	-5.8271045	3.5098344	0.6591179
H	-6.8592433	3.8413078	0.7720147
C	-5.0481827	3.2665337	1.7905624
H	-5.4801097	3.4076784	2.7825302
F	-0.1875224	0.0441074	-1.6877983
F	0.1688703	-1.7066723	-0.0638895
F	-1.6965136	-0.1736136	0.1778479
Cu	-0.3515152	0.0764505	-3.9303314
O	-0.9014978	0.2048726	-6.1312640
H	-1.6246686	-0.4611267	-6.1311021
H	-1.3646764	1.0713525	-6.1171080
N	-1.7544163	-1.4646778	-3.6890408
N	-2.5797902	-1.6782070	-4.7118626
N	-1.0847428	-1.5532019	3.8549946
N	-1.8283314	-1.6718756	4.9495716
N	1.1162219	-1.3619275	-3.9409282
N	1.1065945	-2.1771609	-4.9878979
N	1.8736853	-1.5076182	3.5771055
N	2.1769904	-2.2859137	4.6170391
C	-1.8338384	-2.1716937	-2.5577517
H	-1.0766384	-1.9444526	-1.8114168
C	-2.8183551	-3.1590721	-2.3390261
C	-3.6810070	-3.3846001	-3.4137116
H	-4.4895146	-4.1137804	-3.3542667
C	-3.5095740	-2.6298766	-4.5783562
H	-4.1512700	-2.7710149	-5.4491053
C	-1.3259925	-2.2648911	2.7453112
H	-0.6404331	-2.1050213	1.9159701
C	-2.4060674	-3.1648526	2.6446072
C	-3.1718908	-3.3133822	3.8018161
H	-4.0350978	-3.9793781	3.8299606
C	-2.8343018	-2.5528956	4.9254150
H	-3.4019582	-2.6225248	5.8543966
C	-2.9033459	-3.8795905	-1.0510409
C	-2.5804469	-3.2221776	0.1494120
H	-2.2805307	-2.1750299	0.1307471
C	-2.6992193	-3.8823247	1.3833032
C	-3.1265423	-5.2223695	1.4061532
H	-3.1999823	-5.7560365	2.3549372
C	-3.4268334	-5.8862802	0.2164326
H	-3.7350132	-6.9313294	0.2411614
C	-3.3239067	-5.2216788	-1.0051407
H	-3.5470717	-5.7581307	-1.9285514
C	1.9578255	-1.5238780	-2.9121672
H	1.8856335	-0.7840738	-2.1163171
C	2.8754640	-2.5917854	-2.8488249
C	2.9008906	-3.4247075	-3.9686499
H	3.5725883	-4.2820598	-4.0238985
C	2.0041653	-3.1685692	-5.0102760
H	1.9709674	-3.7953459	-5.9023431
C	2.4529568	-1.6718509	2.3839295
H	2.1583065	-0.9575726	1.6190920
C	3.3894120	-2.6951779	2.1201741
C	3.7041142	-3.5094332	3.2095934
H	4.4009237	-4.3430558	3.1180088
C	3.0806047	-3.2541613	4.4349902
H	3.2935095	-3.8558908	5.3196449
C	3.7241681	-2.8117076	-1.6568002
C	3.1987480	-2.6032887	-0.3710793
H	2.1634872	-2.2811557	-0.2612872

C	3.9718241	-2.8689967	0.7726942
C	5.2942141	-3.3227190	0.6153950
H	5.9194817	-3.5044416	1.4908168
C	5.8271874	-3.5104590	-0.6593436
H	6.8592898	-3.8420289	-0.7722952
C	5.0482033	-3.2671574	-1.7907435
H	5.4800189	-3.4084782	-2.7827344

6.4. $[\{GeF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3448747	-0.0747100	3.9817344
F	0.1910345	-0.0381401	1.7920174
F	-0.1701300	1.8191624	0.0577509
F	1.8091677	0.1722148	-0.1812414
O	0.9358746	-0.2133286	6.1580803
H	1.6645150	0.4469913	6.1493421
H	1.3930389	-1.0833363	6.1367175
N	1.7497610	1.4776640	3.7189170
N	2.6099180	1.6640579	4.7178482
N	1.0899439	1.5624295	-3.8851151
N	1.8572185	1.6700430	-4.9638975
N	-1.1391192	1.3617829	3.9693611
N	-1.1314468	2.1923848	5.0037768
N	-1.8902143	1.5070182	-3.6024453
N	-2.1948686	2.2962402	-4.6333518
C	1.8176755	2.1898123	2.5890458
H	1.0316660	1.9980596	1.8639076
C	2.8258832	3.1467165	2.3436545
C	3.7218115	3.3455779	3.3961056
H	4.5480264	4.0527219	3.3159847
C	3.5601357	2.5923124	4.5632704
H	4.2278561	2.7133231	5.4173333
C	1.3203772	2.2728841	-2.7709294
H	0.6126237	2.1316116	-1.9573094
C	2.4134849	3.1543643	-2.6466948
C	3.2032779	3.2905455	-3.7894560
H	4.0771995	3.9430095	-3.8002565
C	2.8753728	2.5363713	-4.9201843
H	3.4612884	2.5983256	-5.8383026
C	2.9033682	3.8681539	1.0541013
C	2.5819015	3.2107457	-0.1468554
H	2.2908331	2.1618735	-0.1276668
C	2.6982756	3.8710561	-1.3811726
C	3.1217857	5.2123678	-1.4030181
H	3.1943216	5.7464813	-2.3516820
C	3.4208602	5.8763912	-0.2128495
H	3.7265063	6.9221997	-0.2374370
C	3.3215155	5.2109348	1.0087703
H	3.5456287	5.7463795	1.9326463
C	-1.9765496	1.5142619	2.9344307
H	-1.9111550	0.7611543	2.1510698
C	-2.8867275	2.5871649	2.8485971
C	-2.9116875	3.4368241	3.9559140
H	-3.5785581	4.2989157	3.9947206
C	-2.0226960	3.1900064	5.0064435
H	-1.9906957	3.8292817	5.8896517
C	-2.4682220	1.6627029	-2.4066937
H	-2.1818771	0.9377391	-1.6494342
C	-3.3999954	2.6868501	-2.1290104
C	-3.7148871	3.5118647	-3.2104423
H	-4.4092745	4.3464553	-3.1093181
C	-3.0956241	3.2654244	-4.4399794
H	-3.3096902	3.8754004	-5.3186891
C	-3.7346904	2.7949573	1.6520259
C	-3.2057674	2.5971300	0.3658629
H	-2.1646100	2.2971560	0.2557632
C	-3.9823352	2.8504980	-0.7787777
C	-5.3117820	3.2832090	-0.6212536
H	-5.9395440	3.4557064	-1.4968100
C	-5.8477637	3.4619557	0.6536045
H	-6.8848541	3.7776506	0.7664590
C	-5.0656605	3.2300013	1.7853625
H	-5.4997789	3.3643167	2.7773933
F	-0.1913982	0.0378134	-1.7921081
F	0.1698770	-1.8194796	-0.0578715
F	-1.8095268	-0.1725317	0.1811438
Cu	-0.3450790	0.0742447	-3.9818011

O	-0.9361937	0.2131831	-6.1581079
H	-1.6650509	-0.4468946	-6.1493384
H	-1.3930712	1.0833408	-6.1366540
N	-1.7501801	-1.4778050	-3.7189511
N	-2.6105587	-1.6639196	-4.7177404
N	-1.0899451	-1.5631170	3.8850359
N	-1.8570078	-1.6709651	4.9639510
N	1.1387800	-1.3623549	-3.9692635
N	1.1310774	-2.1932037	-5.0034764
N	1.8903181	-1.5069735	3.6024471
N	2.1954590	-2.2959225	4.6334199
C	-1.8179932	-2.1900846	-2.5891590
H	-1.0318768	-1.9984756	-1.8640974
C	-2.8262868	-3.1468821	-2.3437082
C	-3.7224487	-3.3454575	-3.3960112
H	-4.5487827	-4.0524548	-3.3158027
C	-3.5608713	-2.5920723	-4.5631155
H	-4.2287235	-2.7129223	-5.4170987
C	-1.3205303	-2.2734306	2.7707918
H	-0.6128965	-2.1320265	1.9570902
C	-2.4135929	-3.1549801	2.6466292
C	-3.2031681	-3.2913870	3.7895138
H	-4.0770223	-3.9439403	3.8003955
C	-2.8751129	-2.5373516	4.9202925
H	-3.4608854	-2.5994408	5.8384930
C	-2.9037113	-3.8684215	-1.0542115
C	-2.5822526	-3.2110941	0.1467875
H	-2.2913123	-2.1621847	0.1276637
C	-2.6985599	-3.8715098	1.3810557
C	-3.1220121	-5.2128440	1.4027969
H	-3.1944049	-5.7470782	2.3514025
C	-3.4211785	-5.8767564	0.2125917
H	-3.7268577	-6.9225574	0.2371072
C	-3.3219089	-5.2111865	-1.0089763
H	-3.5461498	-5.7465203	-1.9328868
C	1.9763751	-1.5144851	-2.9344247
H	1.9109641	-0.7612559	-2.1511877
C	2.8867854	-2.5871784	-2.8485080
C	2.9117086	-3.4371050	-3.9556136
H	3.5787054	-4.2991052	-3.9943033
C	2.0224895	-3.1906846	-5.0060505
H	1.9904662	-3.8301507	-5.8891211
C	2.4683132	-1.6625156	2.4066754
H	2.1815090	-0.9378235	1.6493358
C	3.4005904	-2.6862100	2.1290408
C	3.7159220	-3.5110043	3.2105078
H	4.4105758	-4.3453714	3.1093735
C	3.0966779	-3.2646846	4.4400826
H	3.3112027	-3.8743742	5.3188796
C	3.7349496	-2.7944983	-1.6520006
C	3.2060457	-2.5968293	-0.3658096
H	2.1647400	-2.2973520	-0.2556457
C	3.9828703	-2.8496755	0.7787679
C	5.3125401	-3.2816723	0.6211517
H	5.9405033	-3.4536757	1.4966613
C	5.8484690	-3.4603206	-0.6537443
H	6.8856992	-3.7755317	-0.7666754
C	5.0661215	-3.2288903	-1.7854437
H	5.5001791	-3.3631088	-2.7775153
Ge	-0.0001805	-0.0001728	-0.0000525

6.5. $[\{SnF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3295950	-0.0628429	4.0688944
F	0.2278519	-0.0137823	1.9394098
F	-0.1661782	1.9862101	0.0435311
F	1.9741681	0.1604781	-0.2170148
O	1.0057302	-0.2271174	6.1920266
H	1.7385818	0.4294886	6.1614290
H	1.4557372	-1.1012964	6.1450019
N	1.7384326	1.5173629	3.7757861
N	2.6327600	1.6787592	4.7478663
N	1.0957371	1.5751943	-3.9292853
N	1.8834391	1.6842831	-4.9923553
N	-1.1820555	1.3643277	4.0222539
N	-1.1880437	2.2074139	5.0455845
N	-1.9273990	1.5030034	-3.6375176

N	-2.2375374	2.3033106	-4.6579045
C	1.8013661	2.2255309	2.6411963
H	0.9854710	2.0732044	1.9408196
C	2.8375558	3.1415710	2.3590662
C	3.7654622	3.3163468	3.3881856
H	4.6124219	3.9950293	3.2819082
C	3.6079506	2.5760104	4.5644365
H	4.3006844	2.6796058	5.4006579
C	1.3190153	2.2721556	-2.8027757
H	0.5871134	2.1472572	-2.0084405
C	2.4241165	3.1347506	-2.6467301
C	3.2363522	3.2667737	-3.7748121
H	4.1212923	3.9042613	-3.7632533
C	2.9153855	2.5324193	-4.9203611
H	3.5178196	2.5961240	-5.8275934
C	2.9107163	3.8550663	1.0622540
C	2.5917496	3.1932347	-0.1373742
H	2.3196173	2.1400933	-0.1151013
C	2.7021119	3.8490982	-1.3751741
C	3.1225308	5.1916852	-1.4000119
H	3.1923074	5.7241892	-2.3498308
C	3.4225813	5.8595686	-0.2121323
H	3.7266584	6.9057402	-0.2407698
C	3.3270046	5.1981453	1.0121372
H	3.5522285	5.7363108	1.9342552
C	-2.0048547	1.5092198	2.9725669
H	-1.9412310	0.7419860	2.2030490
C	-2.9059793	2.5874571	2.8556485
C	-2.9395024	3.4526380	3.9510828
H	-3.6003375	4.3201603	3.9673540
C	-2.0709866	3.2124902	5.0200150
H	-2.0495471	3.8623640	5.8957861
C	-2.4951203	1.6580404	-2.4355805
H	-2.2266883	0.9178777	-1.6876140
C	-3.4132168	2.6892555	-2.1379786
C	-3.7291476	3.5261094	-3.2103729
H	-4.4140751	4.3668505	-3.0961568
C	-3.1268299	3.2804643	-4.4486152
H	-3.3453225	3.8974781	-5.3213072
C	-3.7473068	2.7849963	1.6499700
C	-3.2122764	2.6045761	0.3633720
H	-2.1628346	2.3379455	0.2534966
C	-3.9915023	2.8443553	-0.7830530
C	-5.3286079	3.2533066	-0.6260455
H	-5.9579598	3.4164954	-1.5022999
C	-5.8696586	3.4192744	0.6483844
H	-6.9120871	3.7172640	0.7602416
C	-5.0862810	3.1960842	1.7810363
H	-5.5252422	3.3183945	2.7725492
F	-0.2272757	0.0136174	-1.9389148
F	0.1663659	-1.9863773	-0.0427823
F	-1.9737367	-0.1604103	0.2171353
Cu	-0.3296778	0.0633101	-4.0684879
O	-1.0052530	0.2247159	-6.1922219
H	-1.7381079	-0.4318730	-6.1608738
H	-1.4552591	1.0989215	-6.1464749
N	-1.7389349	-1.5177260	-3.7747030
N	-2.6328077	-1.6798928	-4.7470856
N	-1.0952176	-1.5746369	3.9302550
N	-1.8827953	-1.6835021	4.9934262
N	1.1813990	-1.3638051	-4.0228639
N	1.1869699	-2.2069154	-5.0461395
N	1.9284426	-1.5033262	3.6367089
N	2.2379918	-2.3045381	4.6565614
C	-1.8021841	-2.2253506	-2.6398066
H	-0.9865767	-2.0724965	-1.9392294
C	-2.8380067	-3.1418493	-2.3577734
C	-3.7655013	-3.3172961	-3.3871552
H	-4.6123664	-3.9961030	-3.2809206
C	-3.6077567	-2.5774187	-4.5636685
H	-4.3000518	-2.6817279	-5.4001655
C	-1.3186421	-2.2717595	2.8038594
H	-0.5867568	-2.1470697	2.0094763
C	-2.4238974	-3.1342080	2.6480466
C	-3.2360183	-3.2659828	3.7762424
H	-4.1210554	-3.9033371	3.7648579
C	-2.9148240	-2.5315488	4.9216737
H	-3.5171769	-2.5950401	5.8289739

C	-2.9112268	-3.8550120	-1.0607814
C	-2.5919135	-3.1930591	0.1386973
H	-2.3195154	-2.1399966	0.1162108
C	-2.7021884	-3.8486962	1.3766263
C	-3.1229525	-5.1911715	1.4017683
H	-3.1926504	-5.7235153	2.3516824
C	-3.4234564	-5.8591524	0.2140605
H	-3.7278729	-6.9052190	0.2429306
C	-3.3278940	-5.1979671	-1.0103339
H	-3.5533701	-5.7362702	-1.9323085
C	2.0045562	-1.5086979	-2.9734401
H	1.9412685	-0.7414291	-2.2039223
C	2.9057350	-2.5869165	-2.8568822
C	2.9389455	-3.4520464	-3.9523669
H	3.5998567	-4.3195052	-3.9689064
C	2.0699775	-3.2119458	-5.0209369
H	2.0481875	-3.8618198	-5.8966976
C	2.4963734	-1.6578236	2.4348076
H	2.2285097	-0.9170408	1.6872321
C	3.4137298	-2.6895136	2.1365900
C	3.7290407	-3.5272909	3.2084326
H	4.4135052	-4.3683422	3.0937037
C	3.1267712	-3.2820681	4.4467884
H	3.3447717	-3.8998081	5.3190902
C	3.7473243	-2.7844918	-1.6513998
C	3.2123909	-2.6045522	-0.3646973
H	2.1628512	-2.3383825	-0.2545794
C	3.9918938	-2.8441868	0.7815549
C	5.3291231	-3.2526142	0.6242928
H	5.9586121	-3.4157780	1.5004559
C	5.8700536	-3.4181541	-0.6502507
H	6.9125751	-3.7157423	-0.7623145
C	5.0864226	-3.1950674	-1.7827509
H	5.5252730	-3.3170503	-2.7743541
Sn	0.0002672	-0.0000954	0.0002572

6.6. $[\{TiF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3396214	-0.0683677	4.0216356
F	0.1774311	-0.0250613	1.8480868
F	-0.1634865	1.8757053	0.0430200
F	1.8679647	0.1636388	-0.1723422
O	0.9606213	-0.2132354	6.1858025
H	1.6980660	0.4370164	6.1668838
H	1.4058764	-1.0892894	6.1610131
N	1.7458264	1.4834688	3.7407865
N	2.6349913	1.6491487	4.7175079
N	1.0890300	1.5640838	-3.9178291
N	1.8685992	1.6728886	-4.9872016
N	-1.1556802	1.3604842	3.9961233
N	-1.1579324	2.2003546	5.0227558
N	-1.8905225	1.5007854	-3.6260173
N	-2.1882764	2.3071807	-4.6451631
C	1.8025149	2.1946324	2.6089693
H	0.9934386	2.0247954	1.9036651
C	2.8272684	3.1258392	2.3375563
C	3.7524859	3.3045192	3.3682101
H	4.5922913	3.9926685	3.2665589
C	3.6019963	2.5557884	4.5396950
H	4.2928465	2.6616428	5.3772272
C	1.3091765	2.2698375	-2.7981198
H	0.5906464	2.1303526	-1.9936178
C	2.4054205	3.1443113	-2.6563427
C	3.2087425	3.2811231	-3.7899155
H	4.0862786	3.9288329	-3.7874704
C	2.8899814	2.5346614	-4.9281694
H	3.4863020	2.5985725	-5.8394297
C	2.8941020	3.8478140	1.0474766
C	2.5663691	3.1930502	-0.1531653
H	2.2761905	2.1434673	-0.1340007
C	2.6831767	3.8561505	-1.3862476
C	3.1076540	5.1973141	-1.4058427
H	3.1794308	5.7327863	-2.3538089
C	3.4096988	5.8590459	-0.2153320
H	3.7160905	6.9046667	-0.2383847
C	3.3146511	5.1898893	1.0044807
H	3.5441177	5.7211617	1.9295007

C	-1.9864904	1.5016809	2.9537750
H	-1.9147409	0.7428244	2.1766369
C	-2.8971507	2.5719978	2.8498161
C	-2.9311844	3.4323388	3.9488328
H	-3.5991725	4.2941149	3.9738585
C	-2.0506543	3.1967968	5.0088833
H	-2.0266406	3.8443855	5.8862979
C	-2.4673788	1.6440994	-2.4279426
H	-2.1924699	0.9047165	-1.6809545
C	-3.3894083	2.6725200	-2.1350732
C	-3.6963394	3.5162910	-3.2044562
H	-4.3829036	4.3556720	-3.0903233
C	-3.0801989	3.2818362	-4.4377853
H	-3.2892782	3.9060493	-5.3076677
C	-3.7384523	2.7678576	1.6463114
C	-3.2015017	2.5734474	0.3626068
H	-2.1568273	2.2830488	0.2554309
C	-3.9752056	2.8239351	-0.7847247
C	-5.3087005	3.2464011	-0.6328258
H	-5.9327085	3.4160808	-1.5116212
C	-5.8527813	3.4186547	0.6393087
H	-6.8928761	3.7258529	0.7478018
C	-5.0734511	3.1922593	1.7738567
H	-5.5122145	3.3229983	2.7643512
F	-0.1762271	0.0243123	-1.8485033
F	0.1646132	-1.8764845	-0.0434624
F	-1.8667237	-0.1641482	0.1719061
Cu	-0.3386574	0.0678202	-4.0219857
O	-0.9602162	0.2130584	-6.1860106
H	-1.6985130	-0.4362123	-6.1665226
H	-1.4043634	1.0896609	-6.1613431
N	-1.7459375	-1.4829103	-3.7407773
N	-2.6362694	-1.6466950	-4.7167601
N	-1.0878193	-1.5650412	3.9175709
N	-1.8665265	-1.6744197	4.9875106
N	1.1560662	-1.3616329	-3.9962714
N	1.1576520	-2.2020179	-5.0224944
N	1.8920562	-1.5006519	3.6258568
N	2.1903540	-2.3065212	4.6452744
C	-1.8026525	-2.1945652	-2.6092632
H	-0.9926815	-2.0263823	-1.9045725
C	-2.8287373	-3.1241880	-2.3373438
C	-3.7551851	-3.3008614	-3.3672291
H	-4.5960727	-3.9876105	-3.2650393
C	-3.6045307	-2.5518977	-4.5385311
H	-4.2962669	-2.6563055	-5.3755149
C	-1.3087299	-2.2703358	2.7977168
H	-0.5907908	-2.1304641	1.9927693
C	-2.4050160	-3.1448791	2.6563989
C	-3.2074684	-3.2822063	3.7905365
H	-4.0850184	-3.9298940	3.7884801
C	-2.8878564	-2.5362871	4.9288919
H	-3.4834685	-2.6006613	5.8405846
C	-2.8958900	-3.8465226	-1.0474779
C	-2.5667580	-3.1926530	0.1532425
H	-2.2751148	-2.1434893	0.1342425
C	-2.6838953	-3.8560145	1.3861632
C	-3.1101990	-5.1966112	1.4054315
H	-3.1823028	-5.7323566	2.3532150
C	-3.4136864	-5.8575108	0.2148243
H	-3.7214448	-6.9027363	0.2376334
C	-3.3182568	-5.1880433	-1.0047944
H	-3.5488136	-5.7186607	-1.9299210
C	1.9871951	-1.5026084	-2.9541538
H	1.9159529	-0.7433689	-2.1773389
C	2.8973847	-2.5732979	-2.8499021
C	2.9307305	-3.4341926	-3.9484984
H	3.5983075	-4.2962935	-3.9732662
C	2.0499856	-3.1988032	-5.0084100
H	2.0255214	-3.8467610	-5.8855387
C	2.4685686	-1.6443496	2.4276682
H	2.1933042	-0.9053203	1.6804770
C	3.3906488	-2.6727647	2.1348965
C	3.6980422	-3.5160510	3.2045356
H	4.3846476	-4.3554144	3.0905339
C	3.0823546	-3.2811206	4.4379968
H	3.2919709	-3.9048281	5.3081100
C	3.7389357	-2.7689768	-1.6465385

C	3.2022397	-2.5742962	-0.3627741
H	2.1575536	-2.2839718	-0.2554763
C	3.9761644	-2.8245267	0.7844703
C	5.3096841	-3.2468427	0.6323810
H	5.9339637	-3.4160771	1.5110673
C	5.8534804	-3.4194703	-0.6398230
H	6.8935566	-3.7266835	-0.7484510
C	5.0738821	-3.1934844	-1.7742670
H	5.5123734	-3.3246774	-2.7648208
Ti	0.0006293	-0.0003830	-0.0002574

6.7. $[\{AlF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3379317	-0.0680264	3.9081453
F	0.1974500	-0.0227348	1.7896123
F	-0.1724247	1.8339424	0.0437373
F	1.8211225	0.1743260	-0.1907062
O	0.9448828	-0.1935485	6.1960317
H	1.6625210	0.4729638	6.1019912
H	1.4045202	-1.0573286	6.0970890
N	1.7455975	1.4598704	3.6999985
N	2.5803907	1.6708592	4.7172945
N	1.0818778	1.5509652	-3.8810030
N	1.7876947	1.7231857	-4.9948445
N	-1.1329429	1.3554525	3.9579207
N	-1.1758762	2.1439483	5.0258963
N	-1.8596190	1.4917786	-3.5998151
N	-2.1896366	2.2556220	-4.6434966
C	1.8340278	2.1399964	2.5523949
H	1.0715049	1.9104496	1.8048821
C	2.8387849	3.1050507	2.3246739
C	3.7151566	3.3254623	3.3884005
H	4.5392873	4.0353275	3.3099154
C	3.5349756	2.5928713	4.5642089
H	4.1866679	2.7287997	5.4286408
C	1.3452176	2.2159399	-2.7471054
H	0.6925468	2.0034367	-1.8970687
C	2.4103837	3.1350643	-2.6536352
C	3.1473829	3.3300695	-3.8219745
H	4.0026686	4.0065813	-3.8469669
C	2.7894271	2.6073137	-4.9624897
H	3.3332232	2.7154662	-5.9023408
C	2.9262109	3.8202814	1.0370093
C	2.5920735	3.1620789	-0.1598111
H	2.2800170	2.1119664	-0.1433168
C	2.7138489	3.8340385	-1.3875378
C	3.1435265	5.1734693	-1.4070140
H	3.2081319	5.7109682	-2.3545504
C	3.4523859	5.8335366	-0.2180879
H	3.7598011	6.8791682	-0.2391451
C	3.3530369	5.1606192	0.9984310
H	3.5783284	5.6892532	1.9261931
C	-1.9330461	1.5259344	2.8969804
H	-1.8056498	0.8146876	2.0758057
C	-2.8744609	2.5734094	2.8364772
C	-2.9486425	3.3863157	3.9679938
H	-3.6370924	4.2310226	4.0154766
C	-2.0829742	3.1257561	5.0328257
H	-2.0873341	3.7379337	5.9360070
C	-2.4092364	1.6622519	-2.3931241
H	-2.0832046	0.9627026	-1.6201029
C	-3.3565942	2.6771078	-2.1328507
C	-3.6938966	3.4828974	-3.2211229
H	-4.3955295	4.3116801	-3.1215621
C	-3.0902832	3.2236038	-4.4541133
H	-3.3202162	3.8176121	-5.3399823
C	-3.7062263	2.7890113	1.6348523
C	-3.1613705	2.5880638	0.3557043
H	-2.1167922	2.2747318	0.2500094
C	-3.9381184	2.8466388	-0.7873329
C	-5.2694082	3.2776975	-0.6404362
H	-5.8903637	3.4454140	-1.5220259
C	-5.8167183	3.4543987	0.6289601
H	-6.8564079	3.7644076	0.7359361
C	-5.0387500	3.2206943	1.7623621
H	-5.4782964	3.3466276	2.7533582
F	-0.1969924	0.0231143	-1.7896079

F	0.1727286	-1.8335873	-0.0437040
F	-1.8207059	-0.1740579	0.1907190
Cu	-0.3376603	0.0685140	-3.9081307
O	-0.9447391	0.1939014	-6.1960224
H	-1.6620400	-0.4729816	-6.1020372
H	-1.4048255	1.0574397	-6.0970381
N	-1.7452227	-1.4596040	-3.6999904
N	-2.5798155	-1.6708553	-4.7173988
N	-1.0818574	-1.5503103	3.8809653
N	-1.7878220	-1.7223915	4.9947355
N	1.1333367	-1.3548775	-3.9580147
N	1.1761350	-2.1433049	-5.0260537
N	1.8596467	-1.4915609	3.5998660
N	2.1891253	-2.2557351	4.6434813
C	-1.8336618	-2.1396797	-2.5523623
H	-1.0712567	-1.9099808	-1.8047749
C	-2.8382695	-3.1049148	-2.3247124
C	-3.7144409	-3.3255836	-3.3885497
H	-4.5384533	-4.0355890	-3.3101098
C	-3.5342177	-2.5930694	-4.5644015
H	-4.1857155	-2.7292278	-5.4289439
C	-1.3450688	-2.2153927	2.7471059
H	-0.6923500	-2.0029464	1.8970931
C	-2.4101765	-3.1345898	2.6536357
C	-3.1472806	-3.3295061	3.8219222
H	-4.0025305	-4.0060641	3.8468903
C	-2.7894998	-2.6065804	4.9623860
H	-3.3334115	-2.7146169	5.9021837
C	-2.9257852	-3.8200366	-1.0369927
C	-2.5917164	-3.1617467	0.1598000
H	-2.2796388	-2.1116376	0.1432638
C	-2.7135513	-3.8336402	1.3875595
C	-3.1432467	-5.1730626	1.4071024
H	-3.2079160	-5.7104817	2.3546798
C	-3.4520394	-5.8332129	0.2182049
H	-3.7594875	-6.8788337	0.2393160
C	-3.3526009	-5.1603764	-0.9983501
H	-3.5778140	-5.6890714	-1.9260960
C	1.9333183	-1.5256631	-2.8970287
H	1.8060705	-0.8144090	-2.0758377
C	2.8743475	-2.5734852	-2.8364848
C	2.9482927	-3.3864126	-3.9680014
H	3.6364040	-4.2313963	-4.0154418
C	2.0828523	-3.1254655	-5.0329246
H	2.0870939	-3.7375917	-5.9361412
C	2.4093071	-1.6621674	2.3932118
H	2.0837403	-0.9623353	1.6202565
C	3.3560508	-2.6775767	2.1328781
C	3.6927454	-3.4837374	3.2210608
H	4.3938972	-4.3129226	3.1214460
C	3.0891687	-3.2242640	4.4540348
H	3.3186298	-3.8185672	5.3398290
C	3.7059198	-2.7894819	-1.6348003
C	3.1610382	-2.5883805	-0.3556872
H	2.1165401	-2.2747399	-0.2500278
C	3.9376023	-2.8472952	0.7873963
C	5.2687299	-3.2788721	0.6405974
H	5.8895561	-3.4468421	1.5222316
C	5.8160621	-3.4557712	-0.6287664
H	6.8556259	-3.7662242	-0.7356733
C	5.0382716	-3.2217211	-1.7622207
H	5.4778439	-3.3478390	-2.7531808
Al	0.0002368	0.0002139	0.0000028

6.8. $[\{GaF_6\}\subset Cu_2(L)_4(H_2O)_2]^{2+}$

Cu	0.3390671	-0.0682853	3.9590411
F	0.2170179	-0.0175504	1.8646894
F	-0.1716691	1.9208985	0.0404815
F	1.9077826	0.1711931	-0.2099771
O	0.9782772	-0.2037475	6.2154621
H	1.6945299	0.4649752	6.1234246
H	1.4399254	-1.0667547	6.1148843
N	1.7444883	1.4741290	3.7335514
N	2.5980754	1.6761008	4.7366358
N	1.0837742	1.5553412	-3.9012401
N	1.8177441	1.7116226	-4.9989906

N	-1.1439353	1.3540344	3.9863954
N	-1.1866030	2.1569835	5.0433495
N	-1.8786382	1.4924607	-3.6221583
N	-2.2119631	2.2660976	-4.6573394
C	1.8236147	2.1546807	2.5846648
H	1.0462161	1.9397440	1.8500163
C	2.8376298	3.1051298	2.3379850
C	3.7314877	3.3171430	3.3889527
H	4.5624874	4.0173355	3.2967732
C	3.5599449	2.5882934	4.5685380
H	4.2257795	2.7180000	5.4230842
C	1.3357677	2.2192700	-2.7631195
H	0.6594022	2.0287734	-1.9275926
C	2.4164433	3.1178391	-2.6472930
C	3.1815114	3.2957035	-3.8003116
H	4.0492628	3.9566436	-3.8077456
C	2.8348337	2.5770426	-4.9469062
H	3.4006513	2.6728287	-5.8750265
C	2.9183922	3.8161798	1.0464227
C	2.5895986	3.1522365	-0.1489278
H	2.2894522	2.0989796	-0.1309952
C	2.7091260	3.8203879	-1.3790522
C	3.1315470	5.1620862	-1.4021283
H	3.1955863	5.6961886	-2.3517001
C	3.4346680	5.8279925	-0.2147971
H	3.7364423	6.8751985	-0.2391054
C	3.3379999	5.1586203	1.0039847
H	3.5601519	5.6909280	1.9304778
C	-1.9396533	1.5170243	2.9201027
H	-1.8210928	0.7933612	2.1094938
C	-2.8725189	2.5710804	2.8402048
C	-2.9441356	3.3996829	3.9605399
H	-3.6265091	4.2500488	3.9934845
C	-2.0857454	3.1462039	5.0329554
H	-2.0897164	3.7700051	5.9281479
C	-2.4228737	1.6569337	-2.4114509
H	-2.1021013	0.9475204	-1.6469099
C	-3.3633014	2.6742983	-2.1362220
C	-3.7020220	3.4903403	-3.2166252
H	-4.3991265	4.3216410	-3.1066488
C	-3.1069598	3.2371278	-4.4551612
H	-3.3395294	3.8387349	-5.3351959
C	-3.7046765	2.7775212	1.6357452
C	-3.1597199	2.5847076	0.3552061
H	-2.1109014	2.2877866	0.2474378
C	-3.9408741	2.8356002	-0.7869150
C	-5.2766333	3.2517502	-0.6372325
H	-5.9006372	3.4135953	-1.5178209
C	-5.8238617	3.4210726	0.6332192
H	-6.8666913	3.7196804	0.7420970
C	-5.0416634	3.1947252	1.7652778
H	-5.4808723	3.3151240	2.7571732
F	-0.2166050	0.0176154	-1.8648187
F	0.1719950	-1.9207501	-0.0406362
F	-1.9074205	-0.1710393	0.2098282
Cu	-0.3387224	0.0684146	-3.9591340
O	-0.9781106	0.2040435	-6.2155467
H	-1.6945965	-0.4644149	-6.1233751
H	-1.4394375	1.0672208	-6.1149769
N	-1.7444552	-1.4737106	-3.7335544
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N	-1.0832178	-1.5554837	3.9011597
N	-1.8169038	-1.7120291	4.9990641
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N	1.1862805	-2.1573880	-5.0432352
N	1.8791417	-1.4921394	3.6221283
N	2.2125281	-2.2656239	4.6574074
C	-1.8235641	-2.1543655	-2.5847294
H	-1.0459308	-1.9398172	-1.8502083
C	-2.8378578	-3.1044946	-2.3379397
C	-3.7320728	-3.3159971	-3.3887062
H	-4.5633856	-4.0157990	-3.2963687
C	-3.5604832	-2.5871348	-4.5682782
H	-4.2264978	-2.7165642	-5.4227274
C	-1.3353747	-2.2192713	2.7629922
H	-0.6592389	-2.0285247	1.9273324
C	-2.4159666	-3.1179744	2.6472774
C	-3.1807496	-3.2960897	3.8004513

H	-4.0483977	-3.9571634	3.8080083
C	-2.8339172	-2.5775419	4.9470702
H	-3.3995823	-2.6734564	5.8752701
C	-2.9186413	-3.8156810	-1.0464548
C	-2.5893689	-3.1520380	0.1489239
H	-2.2887930	-2.0989116	0.1310618
C	-2.7089442	-3.8203048	1.3789854
C	-3.1318040	-5.1618691	1.4019404
H	-3.1957297	-5.6961355	2.3514260
C	-3.4354718	-5.8274686	0.2145810
H	-3.7376540	-6.8745592	0.2387960
C	-3.3388499	-5.1579350	-1.0041163
H	-3.5615395	-5.6899770	-1.9306340
C	1.9397903	-1.5172405	-2.9202054
H	1.8216095	-0.7933082	-2.1097767
C	2.8722133	-2.5716695	-2.8401411
C	2.9433742	-3.4005742	-3.9602833
H	3.6253475	-4.2512668	-3.9930702
C	2.0850296	-3.1469642	-5.0327003
H	2.0887227	-3.7709251	-5.9277828
C	2.4232440	-1.6568148	2.4113862
H	2.1023396	-0.9475298	1.6467792
C	3.3635826	-2.6742823	2.1362216
C	3.7023180	-3.4902020	3.2167167
H	4.3992877	-4.3216234	3.1067935
C	3.1074391	-3.2367418	4.4552842
H	3.3400935	-3.8382157	5.3353866
C	3.7044635	-2.7781694	-1.6357591
C	3.1597507	-2.5849361	-0.3551823
H	2.1110482	-2.2876639	-0.2473287
C	3.9409768	-2.8358832	0.7868845
C	5.2765975	-3.2524354	0.6370898
H	5.9007076	-3.4142457	1.5176096
C	5.8235847	-3.4221956	-0.6334056
H	6.8663077	-3.7211431	-0.7423711
C	5.0412915	-3.1958528	-1.7653994
H	5.4803109	-3.3166510	-2.7573294
Ga	0.0001754	0.0000853	-0.0000737

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