

Dinuclear Copper(II) Complexes of Two Homologous Pyrazine-Based Bis(terdentate) Diamide Ligands

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The 1:1 reactions of the new bis(terdentate) diamide ligand *N,N'*-bis(2-pyridylmethyl)pyrazine-2,5-dicarboxamide (H_2L^1) and its higher homologue *N,N'*-bis[2-(2-pyridyl)ethyl]pyrazine-2,5-dicarboxamide (H_2L^2) with $Cu(BF_4)_2 \cdot 4H_2O$ in the absence of added base have consistently afforded dicopper(II) complexes of the doubly deprotonated ligands $(L^1)^{2-}$ and $(L^2)^{2-}$. The complex $[Cu^{II}_2(L^2)(H_2O)_2(MeCN)_2](BF_4)_2$ (**2a**) has been structurally characterised. Subsequently, reactions employing a correct stoichiometric 2:1 metal-to-ligand ratio in MeCN have afforded bulk samples of the dinuclear complexes. The compounds $[Cu^{II}_2(L^1)(MeCN)_2(H_2O)_2](BF_4)_2 \cdot H_2O$ (**1a**· H_2O) and $[Cu^{II}_2(L^2)(H_2O)_4](BF_4)_2 \cdot 2H_2O$ (**2b**· $2H_2O$) have been structurally characterised. While complex **1a**· H_2O of the lower ligand homologue exhibits very weak antiferromagnetic spin coupling ($J = -0.24 \text{ cm}^{-1}$), complex **2b** of the higher ligand homologue exhibits very weak ferromagnetic spin coupling ($J = +0.67 \text{ cm}^{-1}$). EPR studies have been carried out on polycrystalline powders and frozen DMF solutions of

1a· H_2O and **2b**· $2H_2O$. The EPR spectra of the polycrystalline powders indicate the presence of dipolar broadening and weak intermolecular exchange, while those of the frozen DMF solutions are characteristic of dipolar-coupled Cu^{II} pairs within the dinuclear molecules, with no evidence of intra- or intermolecular exchange. The spectral simulations confirm that the binuclear structure and the Cu...Cu distances are retained in frozen solution. Dinuclear SiF_6^{2-} containing compounds, $[Cu^{II}_2(L^1)(H_2O)_4](SiF_6)$ (**1b**) and $\{[Cu^{II}_2(L^1)(H_2O)_2(\mu-SiF_6)] \cdot 4H_2O\}_\infty$ (**1c**· $4H_2O$), were obtained serendipitously, in nearly quantitative yield, by the 2:1 reaction of $Cu(BF_4)_2 \cdot 4H_2O$ with H_2L^1 in H_2O . The unexpected SiF_6^{2-} anions were generated in the course of the reaction by partial hydrolysis of the BF_4^- anions employed, thus forming traces of HF which reacted with the glassware.

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Introduction

For the formation of grid-type complexes relatively rigid ligand systems with a repeating linear array of bi- or terdentate binding pockets are necessary.^[1] With regard to advanced materials, grid-type complexes containing octahedral rather than tetrahedral metal ions are expected to give rise to a broader range of potentially useful properties. The design of ligands with terdentate rather than bidentate binding pockets is therefore desirable. Grid-type complexes of relatively simple pyrimidine-bridged bis(terdentate) ligands, which exhibit intriguing electronic^[2] or magnetic properties,^[3] for example, have been reported by Lehn and co-workers. The use of amide-based ligands for the formation of grid-type complexes offers advantages over other

systems as amides can usually be synthesised relatively easily. Apart from their ability to coordinate to metal ions, amide groups also reduce the degrees of freedom in a given ligand system.^[4]

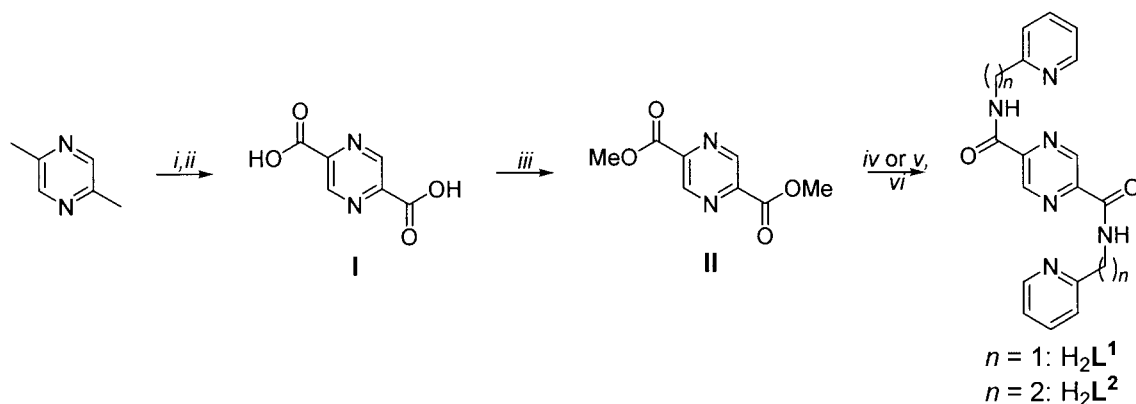
The two homologous pyrazine-based diamide ligands *N,N'*-bis(2-pyridylmethyl)pyrazine-2,5-dicarboxamide (H_2L^1) and *N,N'*-bis[2-(2-pyridyl)ethyl]pyrazine-2,5-dicarboxamide (H_2L^2) are relatively rigid, bis(terdentate) chelates with antiparallel coordinate vectors, and in theory they should be able to form $[2 \times 2]$ grid-type complexes of octahedral transition metal ions. Indeed, we have recently reported a cobalt(III) $[2 \times 2]$ grid-type complex of the doubly deprotonated ligand $(L^2)^{2-}$.^[5] Likewise, copper(II)^[6] and nickel(II)^[7] $[2 \times 2]$ grid-type complexes of the ligand *N,N'*-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide (H_2L^3), which is isomeric to the lower ligand homologue H_2L^1 , have been reported recently. However, it has been found that attempts to isolate similar copper(II) $[2 \times 2]$ grid-type complexes of either H_2L^1 or H_2L^2 , in the presence of base, consistently produced amorphous solids, which analysed as $[CuHL]^n$ (1 equivalent of base per ligand strand) and $[Cu_xL_x]$ (2 equivalents of base per ligand strand) species.^[8] These rather intractable solids have not been further characterised. In contrast, in the absence of added base, reactions

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Scheme 1. Synthesis of the ligands H_2L^1 and H_2L^2 . Reagents and conditions: (i) SeO_2 , pyridine/ H_2O , (10:1), reflux; (ii) H_2O , filtration; (iii) SOCl_2 , MeOH, reflux; (iv) 2.2 equiv. 2-(aminomethyl)pyridine, MeOH, 80–90°, open flask; (v) 2.2 equiv. 2-(2-aminoethyl)pyridine, MeOH, 80–90°C, open flask; (vi) filtration.

of copper(II) with these ligands consistently resulted in the isolation of crystalline samples of dinuclear complexes of a single ligand strand, of the type $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{co-ligand})_n]^{2+}$ or $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{co-ligand})_n]^{2+}$, which are related to the dinuclear copper(II) complexes obtained by Fleischer and co-workers with the isomeric ligand N,N' -bis[2-(2-pyridyl)ethyl]pyrazine-2,3-dicarboxamide (H_2L^4).^[9,10] In this paper, we report the synthesis of the homologous diamide ligands H_2L^1 and H_2L^2 and describe the X-ray crystal structures of the five dinuclear copper(II) complexes $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**1a**· H_2O), $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_4](\text{SiF}_6)$ (**1b**), $\{[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_2(\mu\text{-SiF}_6)] \cdot 4\text{H}_2\text{O}\}_\infty$ (**1c**· $4\text{H}_2\text{O}$), $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{H}_2\text{O})_2(\text{MeCN})_2](\text{BF}_4)_2$ (**2a**) and $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{H}_2\text{O})_4(\text{BF}_4)_2] \cdot 2\text{H}_2\text{O}$ (**2b**· $2\text{H}_2\text{O}$). The magnetic properties and EPR data of **1a**· H_2O and **2b** are also presented.

Results and Discussion

Ligand Syntheses

The ligand precursor, dimethyl pyrazine-2,5-dicarboxylate (**II**),^[11,12] was synthesised, by modifying the literature procedure, from commercially available 2,5-dimethylpyrazine in a one-pot two-step procedure (Scheme 1). The first step consisted of the oxidation of the α -methyl groups with SeO_2 in aqueous pyridine to afford pyrazine-2,5-dicarboxylic acid (**I**).^[11–13] The diacid **I** was not isolated in pure form as the crude product could be esterified with MeOH and SOCl_2 yielding analytically pure diester **II** as a crystalline material.

The potentially bis(terdentate) diamide ligands H_2L^1 and H_2L^2 were obtained by reacting the diester **II** with 2-(aminomethyl)pyridine or 2-(2-aminoethyl)pyridine, respectively, in a 1:2.2 molar ratio (Scheme 1). The reactions were carried out in MeOH solutions in open flasks, thus allowing most of the solvent to evaporate. The ligands H_2L^1 and H_2L^2 were obtained by filtration in ca. 80 and 70% yield, respectively, as colourless solids. Both compounds proved to be virtually insoluble in all common solvents at room temperature, but some solubility was observed in CHCl_3

and CH_2Cl_2 at room temperature and in MeOH, MeCN and DMF at reflux. However, the poor solubility of these two ligands did not preclude successful complexations being carried out (see below).

Dinuclear Copper(II) Complexes

Complexations of H_2L^1 and H_2L^2 with $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ in a metal-to-ligand ratio of 1:1 in MeCN resulted in the isolation of 2:1 complexes of the doubly deprotonated ligands. Single crystals of $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{H}_2\text{O})_2(\text{MeCN})_2](\text{BF}_4)_2$ (**2a**) suitable for an X-ray crystal structure determination were obtained by the vapour diffusion of Et_2O into the 1:1 MeCN reaction solution (Figure 1, Table 1, Table 2, Table 3 and Table 4).

Complex **2a** features two crystallographically independent but chemically very similar centrosymmetric dinuclear molecules. In each molecule the doubly deprotonated ligand acts as an $(\text{N}_3)_2$ bis(terdentate) chelate. Each copper(II) centre is in a distorted N_4O square-pyramidal coordination environment ($\tau^{[14]} = 0.24, 0.41$). The coordination sphere is made up of the equatorially coordinating N_3 terdentate coordination site of the deprotonated amide ligand, an H_2O co-ligand in the remaining equatorial position and a MeCN co-ligand at the apex. As observed in related amide complexes,^[6,7,10,15–18] the Cu– N_{amide} distances of **2a** [Cu(1)–N(2) 1.936(2) Å and Cu(2)–N(12) 1.929(2) Å] are shorter than the Cu– $\text{N}_{\text{heterocycle}}$ distances [Cu– N_{py} : Cu(1)–N(3) 2.011(3) Å, Cu(2)–N(13) 1.992(3) Å; Cu– N_{pz} : Cu(1)–N(1) 2.027(2) Å, Cu(2)–N(11) 2.021(2) Å]. The canting angles, formed between the mean plane of the pyridine ring and the mean plane of the pyrazine ring, are 33.4(1)° and 39.5(1)° for the two independent molecules Cu(1) and Cu(2), respectively. The intramolecular Cu···Cu distances [Cu(1)···Cu(1A) 6.784(2) Å and Cu(2)···Cu(2B) 6.756(2) Å] across the pyrazine bridge are about 0.1 Å shorter than that found in a related dicopper(II) complex of the chemically related ligand N,N' -bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide (H_2L^3).^[7] In complex **2a** the independent dinuclear subunits are $\text{O}_{\text{water}}\cdots\text{H}\cdots\text{O}_{\text{amide}}$ intermolecularly hy-

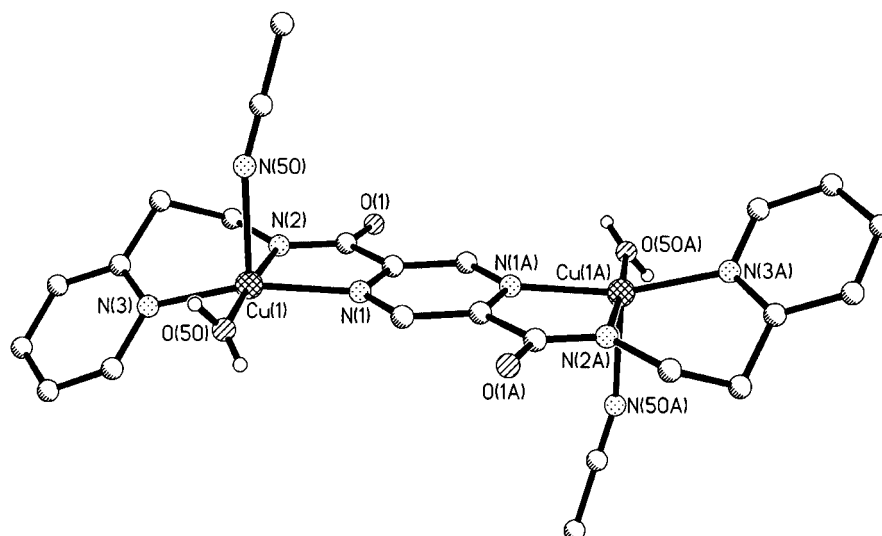


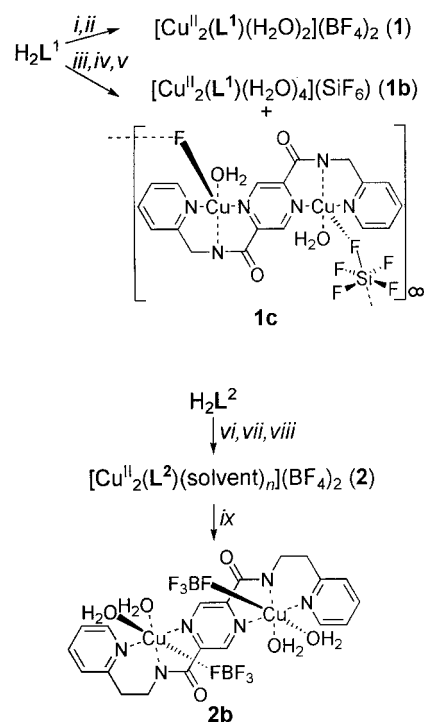
Figure 1. Molecular structure of one of the two independent cations, $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{H}_2\text{O})_2(\text{MeCN})_2]^{2+}$, of complex **2a**. Hydrogen atoms, except those of the H_2O co-ligands, have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) $1 - x$, $2 - y$, $1 - z$.

drogen-bonded, forming a 2D ribbon-like structure [$\text{O}_{\text{water}} \cdots \text{O}_{\text{amide}}$ 2.598 Å and 2.595 Å]. Parallel ribbons are connected through $\text{O}_{\text{water}} - \text{H} \cdots \text{F} - \text{BF}_2 - \text{F} \cdots \text{H} - \text{O}_{\text{water}}$ hydrogen bonds (Figure S1, Supporting Information; $\text{O}_{\text{water}} \cdots \text{F}$ 2.738 Å and 2.801 Å).

As reactions, in the absence of base, employing metal-to-ligand ratios of 1:1 consistently afforded 2:1 products, the complexations of H_2L^1 and H_2L^2 were repeated using 2:1 molar metal-to-ligand ratios to isolate bulk materials (Scheme 2).

Vapour diffusion of Et_2O into the reaction solution containing the lower ligand homologue H_2L^1 and $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ in a 1:2 molar ratio in MeCN afforded the dinuclear compound $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (**1**) in 60% yield as a dark turquoise microcrystalline solid (Scheme 2). Single crystals of $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**1a**· H_2O) (Figure 2, Table 1, Table 2, Table 3 and Table 4) suitable for an X-ray crystal structure determination were obtained by slow evaporation of the reaction solution.

The copper(II) coordination sphere in the centrosymmetric dinuclear complex in **1a**· H_2O is N_4O square-pyramidal, exhibiting only a slight distortion from the perfect geometry ($\tau^{[14]} = 0.06$). As in **2a**, the doubly deprotonated $(\text{N}_3)_2$ bis-(terdentate) ligand $(\text{L}^1)^{2-}$ in **1a**· H_2O encapsulates each copper(II) ion in an equatorial manner. Again, the copper(II) coordination sphere is completed by a MeCN and an H_2O co-ligand. Compared to complex **2a**, however, these co-ligands have switched their positions, so that in complex **1a**· H_2O the H_2O co-ligand coordinates axially and the MeCN co-ligand coordinates in the equatorial position. Owing to the increase in ligand rigidity due to the methylene instead of the ethylene linkers, the ligand backbone of complex **1a**· H_2O is much flatter than that in **2a**, showing a mean deviation of only 0.048 Å from the mean plane made up of all non-hydrogen atoms of the ligand, and a maximum deviation of only 0.082(4) Å for $\text{C}(10)_{(4-yy)}$. The



Scheme 2. Synthesis of the complexes **1**, **1b**, **1c**, **2** and **2b**. Reagents and conditions: (i) 2 equiv. $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$, MeCN, room temp.; (ii) Et_2O (vapour diffusion); (iii) 2 equiv. $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$, H_2O , room temp.; (iv) 2 equiv. NEt_3 ; (v) slow evaporation; (vi) 2 equiv. $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$, MeCN, 60 °C; (vii) room temp., 10 h; (viii) filtration; (ix) MeCN/EtOH (1:1) (slow evaporation).

$\text{Cu} \cdots \text{Cu}$ distance of the equivalent copper(II) centres [$\text{Cu}(1) \cdots \text{Cu}(1\text{A})$ 6.811(3) Å] is slightly longer than that found in complex **2a**. A stair-like chain structure is formed through hydrogen bonding of the axial H_2O co-ligand to the amide oxygen atom of a neighbouring dinuclear subunit [$\text{O}_{\text{water}} \cdots \text{O}_{\text{amide}}$ 2.714 Å]. The H_2O co-ligand forms a second

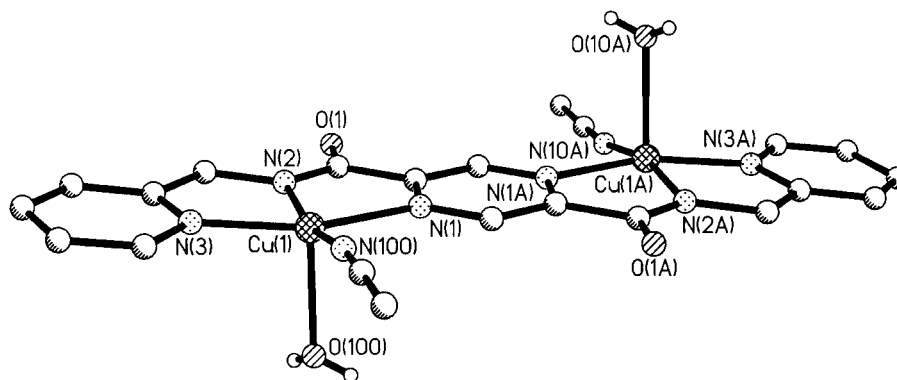


Figure 2. Molecular structure of $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{MeCN})_2(\text{H}_2\text{O})_2]^{2+}$, the cation of complex **1a**·H₂O. Hydrogen atoms, except those of H₂O co-ligands, have been omitted for clarity. Symmetry operation used to generate equivalent atoms: (A) $2 - x, 1 - y, 1 - z$.

Table 1. Crystallographic data for the complexes **1a**·H₂O, **1b**, **1c**·4H₂O, **2a** and **2b**·2H₂O.

	1a ·H ₂ O	1b	1c ·4H ₂ O	2a	2b ·2H ₂ O
Molecular formula	C ₂₂ H ₂₆ B ₂ Cu ₂ F ₈ N ₈ O ₅	C ₁₈ H ₂₂ Cu ₂ F ₆ N ₆ O ₆ Si	C ₁₈ H ₂₆ Cu ₂ F ₆ N ₆ O ₈ Si	C ₂₄ H ₂₈ B ₂ Cu ₂ F ₈ N ₈ O ₄	C ₂₀ H ₃₀ B ₂ Cu ₂ F ₈ N ₆ O ₈
<i>M_r</i> [g mol ^{−1}]	783.21	687.59	723.62	793.24	783.20
<i>T</i> [K]	150(2)	200(2)	200(2)	168(2)	168(2)
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	8.29650(10)	21.1697(3)	8.00020(10)	9.312(3)	7.898(16)
<i>b</i> [Å]	10.0428(2)	7.55260(10)	8.96160(10)	13.156(4)	8.101(20)
<i>c</i> [Å]	10.1034(2)	15.1687(2)	10.2285(2)	13.802(4)	11.19(3)
α [°]	74.5940(10)	90	71.3330(10)	106.649(4)	84.98(6)
β [°]	69.3420(10)	94.4300(10)	77.7600(10)	101.489(4)	80.11(6)
γ [°]	84.3250(10)	90	69.0230(10)	99.121(4)	85.62(8)
<i>V</i> [Å ³]	759.37(2)	2418.02(6)	644.760(17)	1545.0(8)	701(3)
<i>Z</i>	1	4	1	2	1
ρ_{calcd} [g cm ^{−3}]	1.713	1.889	1.864	1.705	1.855
μ [mm ^{−1}]	1.498	1.904	1.796	1.471	1.628
<i>F</i> (000)	394	1384	366	800	396
Crystal colour and shape	green block	green block	green block	green block	green block
Crystal size [mm ³]	0.38 × 0.26 × 0.08	0.20 × 0.15 × 0.08	0.40 × 0.20 × 0.08	0.50 × 0.40 × 0.35	0.70 × 0.20 × 0.10
θ range [°]	2.10/25.48	0.96/27.16	2.11/26.42	1.59/26.37	2.53/26.38
Reflections collected	6914	14503	6211	19871	3172
Independent reflections	2803 [<i>R</i> _{int} = 0.0235]	2637 [<i>R</i> _{int} = 0.0380]	2598 [<i>R</i> _{int} = 0.0359]	6216 [<i>R</i> _{int} = 0.0432]	2497 [<i>R</i> _{int} = 0.1674]
Completeness to θ	99.5%	98.0%	98.5%	98.3%	87.4%
Data/restraints/parameters	2803/0/226	2637/0/189	2598/0/205	6216/0/451	2497/0/232
GO _F on <i>F</i> ²	1.046	1.072	1.129	1.027	1.108
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.1210	<i>R</i> ₁ = 0.0625, <i>wR</i> ₂ = 0.1683	<i>R</i> ₁ = 0.0277, <i>wR</i> ₂ = 0.0766	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.1127	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.1250
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0507, <i>wR</i> ₂ = 0.1244	<i>R</i> ₁ = 0.0728, <i>wR</i> ₂ = 0.1771	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0775	<i>R</i> ₁ = 0.0538, <i>wR</i> ₂ = 0.1194	<i>R</i> ₁ = 0.0542, <i>wR</i> ₂ = 0.1302
Largest diff. peak/hole [e·Å ^{−3}]	1.294/−1.364	2.622/−0.858	0.694/−0.524	1.212/−0.758	0.750/−0.728

hydrogen bond, to the BF₄[−] anion [O_{water}...F 2.745 Å]. The amide oxygen atom is also involved in another hydrogen bond, to the H₂O solvate molecule [O_{amide}...O_{solvate} 2.907 Å] (Figure S2, Supporting Information).

The 2:1 molar reaction of Cu(BF₄)₂·4H₂O with the higher ligand homologue H₂L² in MeCN afforded the complex [Cu^{II}₂(L²)(solvent)_{*n*}](BF₄)₂ (**2**) in ca. 50% yield in the form of a bottle-green microcrystalline solid, that precipitated from the reaction mixture after several hours of stirring (Scheme 2). Recrystallisation of complex **2** from MeCN/EtOH (1:1) afforded single crystals of [Cu^{II}₂(L²)(H₂O)₄(BF₄)₂·2H₂O (**2b**·2H₂O) suitable for an X-ray

crystal structure determination (Figure 3, Table 1, Table 2, Table 3 and Table 4).

The overall molecular structure of the centrosymmetric molecule of complex **2b**·2H₂O is very similar to that of complex **2a**. The major difference is the N₃O₂F distorted octahedral coordination environment about the copper(II) ions in **2b**·2H₂O, the two axial positions being elongated and occupied by an H₂O and a BF₄[−] co-ligand. The Cu–F_{ax} distance [Cu(1)–F(13B) 2.598(3) Å] is, as expected, somewhat longer than the Cu–O_{ax} distance [Cu(1)–O(60) 2.516(5) Å]. Although BF₄[−] ions are commonly regarded as “non-coordinating” a number of structures with coordi-

Table 2. Selected distances [Å] for the complexes **1a**·H₂O, **1b**, **1c**·4H₂O, **2a** and **2b**·2H₂O.

	1a ·H ₂ O ^[a]		1b ^[a]		1c ·4H ₂ O ^[a]	
Cu–N _{am}	Cu(1)–N(2)	1.906(3)	Cu(1)–N(2)	1.904(4)	Cu(1)–N(2)	1.912(2)
Cu–N _{py}	Cu(1)–N(3)	1.999(3)	Cu(1)–N(3)	2.007(5)	Cu(1)–N(3)	2.012(2)
Cu–N _{pz}	Cu(1)–N(1)	2.044(3)	Cu(1)–N(1)	2.030(4)	Cu(1)–N(1)	2.052(2)
Cu–L _{eq}	Cu(1)–N(100)	1.972(3)	Cu(1)–O(20)	1.949(4)	Cu(1)–O(10)	1.951(2)
Cu–L _{ax}	Cu(1)–O(100)	2.201(3)	Cu(1)–O(30)	2.271(5)	Cu(1)–F(1)	2.235(1)
Cu···Cu	Cu(1)···Cu(1A)	6.811(3)	Cu(1)···Cu(1A)	6.775(1)	Cu(1)···Cu(1A) (intra)	6.827(1)
					Cu(1)···Cu(1B) (inter)	7.166(1)
	2a ^[a]		2b ·2H ₂ O ^[a]			
Cu–N _{am}	Cu(1)–N(2)	1.936(2)	Cu(1)–N(2)	1.946(4)		
	Cu(2)–N(12)	1.929(2)				
Cu–N _{py}	Cu(1)–N(3)	2.011(3)	Cu(1)–N(3)	1.981(4)		
	Cu(2)–N(13)	1.992(3)				
Cu–N _{pz}	Cu(1)–N(1)	2.027(2)	Cu(1)–N(1)	2.021(4)		
	Cu(2)–N(11)	2.021(2)				
Cu–L _{eq}	Cu(1)–O(50)	1.972(2)	Cu(1)–O(50)	1.961(4)		
	Cu(2)–O(60)	1.996(2)				
Cu–L _{ax}	Cu(1)–N(50)	2.321(3)	Cu(1)–O(60)	2.516(5)		
	Cu(2)–N(60)	2.299(3)	Cu(1)–F(13B)	2.598(3)		
Cu···Cu	Cu(1)···Cu(1A)	6.784(2)	Cu(1)···Cu(1A)	6.764(1)		
	Cu(2)···Cu(2B)	6.756(2)				

[a] Symmetry operations used to generate equivalent atoms: **1a**·H₂O: (A) $2 - x, 1 - y, 1 - z$. **1b**: (A) $1 - x, 2 - y, 1 - z$. **1c**·4H₂O: (A) $-x, -y - 1, -z$; (B) $-x, -y, -z$. **2a**: (A) $1 - x, 2 - y, 1 - z$; (B) $-x, 2 - y, -z$. **2b**·2H₂O: (A) $1 - x, 1 - y, 1 - z$; (B) $x - 1, y, z$.

Table 3. Selected bond angles [°] for the complexes **1a**·H₂O, **1b**, **1c**·4H₂O, **2a** and **2b**·2H₂O.

	1a ·H ₂ O		1b		1c ·4H ₂ O	
N _{pz} –Cu–N _{am}	N(1)–Cu(1)–N(2)	81.1(1)	N(1)–Cu(1)–N(2)	81.6(2)	N(1)–Cu(1)–N(2)	81.27(7)
N _{pz} –Cu–N _{py}	N(1)–Cu(1)–N(3)	161.7(1)	N(1)–Cu(1)–N(3)	162.9(2)	N(1)–Cu(1)–N(3)	163.58(7)
N _{pz} –Cu–L _{eq}	N(1)–Cu(1)–N(100)	95.9(1)	N(1)–Cu(1)–O(20)	92.0(2)	N(1)–Cu(1)–O(10)	97.53(7)
N _{pz} –Cu–L _{ax}	N(1)–Cu(1)–O(100)	94.5(1)	N(1)–Cu(1)–O(30)	96.4(2)	N(1)–Cu(1)–F(1)	87.19(6)
N _{am} –Cu–N _{py}	N(2)–Cu(1)–N(3)	81.9(1)	N(2)–Cu(1)–N(3)	82.2(2)	N(2)–Cu(1)–N(3)	82.40(7)
N _{am} –Cu–L _{eq}	N(2)–Cu(1)–N(100)	165.2(1)	N(2)–Cu(1)–O(20)	161.0(2)	N(2)–Cu(1)–O(10)	163.68(8)
N _{am} –Cu–L _{ax}	N(2)–Cu(1)–O(100)	103.5(1)	N(2)–Cu(1)–O(30)	106.2(2)	N(2)–Cu(1)–F(1)	105.31(6)
N _{py} –Cu–L _{eq}	N(3)–Cu(1)–N(100)	99.0(1)	N(3)–Cu(1)–O(20)	101.7(2)	N(3)–Cu(1)–O(10)	97.68(7)
N _{py} –Cu–L _{qx}	N(3)–Cu(1)–O(100)	95.8(1)	N(3)–Cu(1)–O(30)	93.4(2)	N(3)–Cu(1)–F(1)	98.75(6)
L _{eq} –Cu–L _{ax}	N(100)–Cu(1)–O(100)	95.8(1)	O(20)–Cu(1)–O(30)	92.2(2)	O(10)–Cu(1)–F(1)	90.84(6)
	2a		2b ·2H ₂ O ^[a]			
N _{pz} –Cu–N _{am}	N(1)–Cu(1)–N(2)	82.1(1)	N(1)–Cu(1)–N(2)	81.1(2)		
	N(11)–Cu(2)–N(12)	82.3(1)				
N _{pz} –Cu–N _{py}	N(1)–Cu(1)–N(3)	161.2(1)	N(1)–Cu(1)–N(3)	173.5(1)		
	N(11)–Cu(2)–N(13)	175.7(1)				
N _{pz} –Cu–L _{eq}	N(1)–Cu(1)–O(50)	93.5(1)	N(1)–Cu(1)–O(50)	91.4(2)		
	N(11)–Cu(2)–O(60)	93.7(1)				
N _{pz} –Cu–L _{ax}	N(50)–Cu(1)–N(1)	91.4(1)	N(1)–Cu(1)–O(60)	85.5(2)		
	N(60)–Cu(2)–N(11)	84.9(1)	N(1)–Cu(1)–F(13B)	91.6(1)		
N _{am} –Cu–N _{py}	N(2)–Cu(1)–N(3)	92.3(1)	N(2)–Cu(1)–N(3)	95.0(2)		
	N(12)–Cu(2)–N(13)	94.3(1)				
N _{am} –Cu–L _{eq}	N(2)–Cu(1)–O(50)	175.6(1)	N(2)–Cu(1)–O(50)	165.7(1)		
	N(12)–Cu(2)–O(60)	51.4(1)				
N _{am} –Cu–L _{ax}	N(2)–Cu(1)–N(50)	92.8(1)	N(2)–Cu(1)–O(60)	102.0(2)		
	N(12)–Cu(2)–N(60)	102.8(1)	N(2)–Cu(1)–F(13B)	91.4(1)		
N _{py} –Cu–L _{eq}	N(3)–Cu(1)–O(50)	91.9(1)	N(3)–Cu(1)–O(50)	93.5(2)		
	N(13)–Cu(2)–O(60)	90.5(1)				
N _{py} –Cu–L _{qx}	N(3)–Cu(1)–N(50)	106.9(1)	N(3)–Cu(1)–O(60)	90.3(2)		
	N(13)–Cu(2)–N(60)	93.3(1)	N(3)–Cu(1)–F(13B)	93.7(1)		
L _{eq} –Cu–L _{ax}	N(50)–Cu(1)–O(50)	87.1(1)	O(50)–Cu(1)–O(60)	89.5(2)		
	O(60)–Cu(2)–N(60)	105.0(1)	O(50)–Cu(1)–F(13B)	76.5(1)		
L _{ax} –Cu–L _{ax}			O(60)–Cu(1)–F(13B)	165.7(1)		

[a] Symmetry operations used to generate equivalent atoms: **2b**·2H₂O: (B) $x - 1, y, z$.

Table 4. Selected hydrogen bond lengths [$\text{\AA}$] for the complexes **1a**·H₂O, **1b**, **1c**·4H₂O, **2a** and **2b**·2H₂O.

	1a ·H ₂ O ^[a]		1b ^[a]		1c ·4H ₂ O ^[a]	
O _{amide} ...O _{co-lig.}	O(1B)...O(100)	2.714	O(1A)...O(20)	2.603(7)	O(1C)...O(10)	2.662
O _{amide} ...O _{solv.}	O(1)...O(110)	2.907				
O _{co-lig.} ...O _{solv.}			O(20)...F(11)	2.760(7)	O(10)...O(50)	2.571
O _{co-lig.} ...F _{anion}	O(100)...F(11)	2.745	O(20)...F(12)	2.792(7)		
			O(30)...F(11B)	3.169(7)		
			O(30)...F(13C)	3.377(7)		
O _{solv.} ...O _{solv.}					O(50)...O(60)	2.670
O _{solv.} ...F _{anion}					O(50)...F(2D)	2.736
					O(60)...F(3E)	2.714
					O(60)...O(1F)	2.845
	2a ^[a]		2b ·2H ₂ O ^[a]			
O _{amide} ...O _{co-lig.}	O(10B)...O(50)	2.598	O(1D)...O(60)	2.828		
	O(1)...O(60)	2.595	O(1E)...O(60)	2.747		
O _{amide} ...O _{solv.}						
O _{co-lig.} ...O _{solv.}						
O _{co-lig.} ...F _{anion}	O(50)...F(11)	2.738	O(50)...F(12C)	2.771		
	O(60)...F(12C)	2.801				
O _{solv.} ...O _{solv.}			O(50)...O(70)	2.620		
			O(60F)...O(70)	2.794		
O _{solv.} ...F _{anion}			O(70)...F(11)	2.756		

^[a] Symmetry operations used to generate equivalent atoms: **1a**·H₂O: (B) $-x + 1, -y + 1, -z + 1$; **1b**: (A) $x, y - 1, z$; (B) $1 - x, y, 0.5 - z$; (C) $-x + 1, y + 1, -z + 0.5$; **1c**·4H₂O: (C) $x + 1, y, z$; (D) $-x + 1, -y - 1, -z$; (E) $x, y - 1, z$; (F) $x + 1, y - 1, z$; **2a**: (B) $x + 1, y, z + 1$; (C) $x, y, z - 1$; **2b**·2H₂O: (C) $-x + 2, -y + 1, -z + 2$; (D) $x + 1, y, z$; (E) $x + 1, -y + 2, -z + 1$; (F) $-x + 2, -y + 1, -z + 1$.

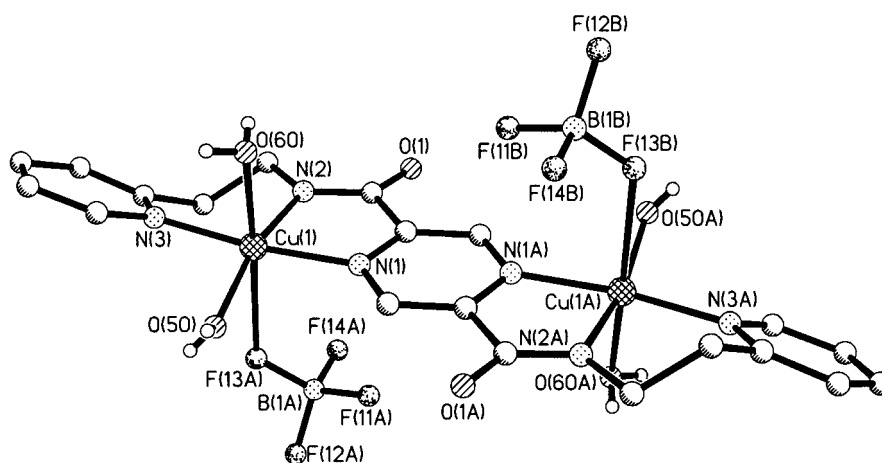


Figure 3. Molecular structure of the complex $[\text{Cu}^{\text{II}}_2(\text{L}^2)(\text{H}_2\text{O})_4(\text{BF}_4)_2]$ (**2b**·2H₂O). The H₂O solvates and hydrogen atoms, except those of H₂O co-ligands, have been omitted for clarity. Symmetry operations used to generate equivalent atoms: (A) $1 - x, 1 - y, 1 - z$; (B) $x - 1, y, z$.

nated BF_4^- ions are known.^[19,20] In copper(II) complexes with coordinated BF_4^- ions, Cu–F distances between 2.07 $\text{\AA}$ ^[21] and 2.85 $\text{\AA}$ ^[22] have been observed, but mostly the distances lie in the range 2.40–2.71 $\text{\AA}$. In complex **2b**·2H₂O a 3D network is formed by hydrogen bonds, involving the amide oxygen atoms, both H₂O co-ligands, the BF_4^- co-ligands and the H₂O solvates (Figure S3, Supporting Information).

Dinuclear copper(II) compounds unexpectedly incorporating SiF_6^{2-} as counterions were obtained by reacting $\text{Cu}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ with the lower ligand homologue H_2L^1 , in a 2:1 metal-to-ligand ratio, using H₂O as the solvent and a glass vial as the reaction and crystallisation vessel (slow

evaporation of the solvent in air). Reactions carried out without base resulted in the isolation of blue-green crystal blocks, along with yellow crystals which, on the basis of elemental and IR analyses, are believed to be $(\text{H}_4\text{L}^1)(\text{BF}_4)_2$. The blue-green crystal blocks were identified as a mixture of the complexes $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_4](\text{SiF}_6)_2$ (**1b**) and $\{[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_2(\mu\text{-SiF}_6)] \cdot 4\text{H}_2\text{O}\}_\infty$ (**1c**·4H₂O) by X-ray crystallography (Figure 4 and Figure S4, Supporting information, Table 1, Table 2, Table 3 and Table 4). The formation of the yellow crystals could be prevented by the addition of two equivalents of NEt_3 as a base (Scheme 2), which also resulted in an increased yield (ca. 70–80% yield) of the desired SiF_6^{2-} compounds. The occurrence of SiF_6^{2-}

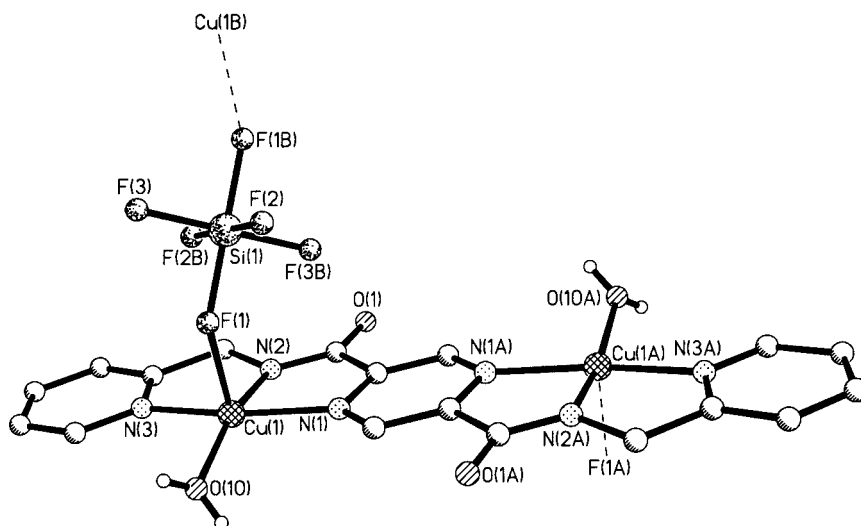


Figure 4. View of the $[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_2(\mu\text{-SiF}_6)]$ subunit of the polymeric chain structure of the cation of complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$, emphasising the coordination environment about Cu(1). Hydrogen atoms, except those of H_2O co-ligands, have been omitted for clarity. Symmetry operations used to generate equivalent atoms: (A) $-x, -y - 1, -z$; (B) $-x, -y, -z$.

ions in these compounds, rather than BF_4^- ions, was unexpected but was readily confirmed by the negative ion ESI mass spectrum, which showed a peak at $m/z = 123.0$ corresponding to the SiF_5^- anion, and the IR spectrum, which showed an intense broad split band (with peaks at 780 and 750 cm^{-1}) typical of the SiF_6^{2-} ion. It has been reported that SiF_6^{2-} anions can arise in compounds originally containing BF_4^- ions as partial hydrolysis of the latter in the presence of moisture can generate traces of HF, which then react with the glassware to form SiF_6^{2-} ions.^[23–27]

The molecular structure of the hexafluorosilicate complex $\mathbf{1b}$ (Figure S4, Supporting Information, Table 1, Table 2, Table 3 and Table 4) is very similar to the structure of the analogous tetrafluoroborate complex $\mathbf{1a} \cdot \text{H}_2\text{O}$. In the centrosymmetric complex $\mathbf{1b}$ an N_3O_2 distorted square-pyramidal coordination environment about the copper(II) ion is achieved by equatorially and axially coordinated H_2O co-ligands ($\tau_{\text{Cu}(1)}^{[14]} = 0.03$). Hydrogen bonding, involving the amide oxygen atom and the equatorial H_2O co-ligand of two neighbouring subunits [$\text{O}_{\text{amide}} \cdots \text{O}_{\text{water}} 2.603\text{ Å}$] and both of the H_2O co-ligands with the SiF_6^{2-} anions [$\text{F}_{\text{anion}} \cdots \text{O}_{\text{water}} 2.760\text{--}3.377\text{ Å}$], is also a feature of this structure.

The related compound $\mathbf{1c} \cdot 4\text{H}_2\text{O}$, obtained from the same reaction mixture, features bridging SiF_6^{2-} co-ligands. The coordination environment about the copper(II) ion is therefore best described as N_3OF square-pyramidal (Figure 4; $\tau^{[14]} = 0.00$).

A polymeric chain structure is formed by the SiF_6^{2-} bridges, which connect two apical positions of two neighbouring dinuclear subunits (Figure 5). The first crystal structure of a chain compound containing bridging SiF_6^{2-} co-ligands, $[\text{Co}^{\text{II}}(\text{viz})_4(\text{SiF}_6)]_\infty$ ($\text{viz} = N$ -vinylimidazole), was reported in 1982 by Reedijk and co-workers.^[28] Even now polynuclear compounds with bridging SiF_6^{2-} ions are not very common and all reported compounds incorporate six-coordinate me-

tal ions and mononuclear subunits.^[24,29–31] To the best of our knowledge, complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$ is the first polymeric chain compound incorporating square-pyramidal metal ions bridged by SiF_6^{2-} ions and, at the same time, it is the first polymeric compound featuring discrete dinuclear subunits that are bridged by SiF_6^{2-} ions. The Cu–F bond length in complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$ [Cu(1)–F(1) $2.235(1)\text{ Å}$] is around 0.3 Å shorter than in the dimeric complexes $[\{\text{Cu}^{\text{II}}(\text{Hsabh})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ ($\text{H}_2\text{sabh} = \text{salicylaldehyde benzoylhydrazone}$) (2.522 Å)^[32] or $[\{\text{Cu}^{\text{II}}(\text{Hspca})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ ($\text{H}_2\text{spca} = N^3$ -salicyloylpyridine-2-carboxamidrazon) (2.528 Å)^[25] the only crystal structures reported to date that contain square-pyramidal copper(II) ions bridged by the apical positions by SiF_6^{2-} ions. The intermolecular Cu $\cdots$ Cu distance in complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$ is $7.166(1)\text{ Å}$ and thus is in between the distances reported for $[\{\text{Cu}^{\text{II}}(\text{Hsabh})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ (6.04 Å)^[32] and $[\{\text{Cu}^{\text{II}}(\text{Hspca})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ (7.951 Å)^[25]. The Cu–F–Si angle in complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$ is only $130.45(7)^\circ$ and is thus smaller than in both $[\{\text{Cu}^{\text{II}}(\text{Hsabh})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ (144.0°)^[32] and $[\{\text{Cu}^{\text{II}}(\text{Hspca})(\text{H}_2\text{O})\}_2(\text{SiF}_6)] \cdot 2\text{H}_2\text{O}$ (140.1°)^[25] and considerably smaller than in the six-coordinate polymeric chain structures, where the M–F–Si angles range from 152° to 180° .^[24,28,33] In complex $\mathbf{1c} \cdot 4\text{H}_2\text{O}$ the parallel polymeric strands are interconnected through hydrogen bonds involving the equatorial H_2O co-ligand and the amide oxygen atom [$\text{O}(10) \cdots \text{O}(1\text{C}) 2.662\text{ Å}$]. Furthermore, the two H_2O solvates per asymmetric unit are involved in a network of hydrogen bonds involving all non-coordinated fluorine atoms of the SiF_6^{2-} ligand and the equatorial H_2O co-ligand (Figure 5).

In all of the above structures the Cu–N_{ligand} bond lengths follow the same general trend, specifically Cu–N_{am} < Cu–N_{py} < Cu–N_{pz} (Table 2). Another general, and expected, trend is that in each case on deprotonation and coordination to copper(II) the ν_{CO} band of the free ligand moves to

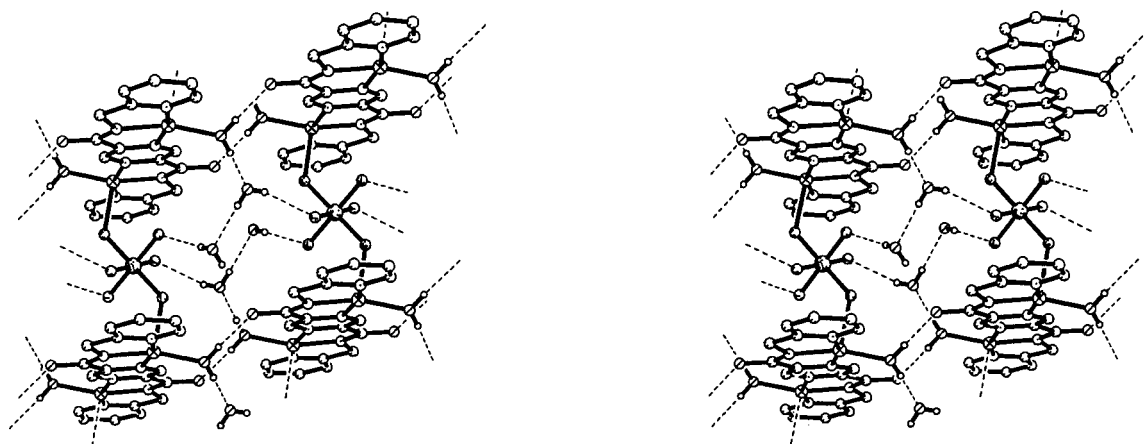


Figure 5. Stereo view of a section of the 3D structure of $\{[\text{Cu}^{\text{II}}_2(\text{L}^1)(\text{H}_2\text{O})_2(\text{SiF}_6)] \cdot 4\text{H}_2\text{O}\}_\infty$ (**1c**·4H₂O). Hydrogen atoms not involved in hydrogen bonds have been omitted for clarity.

lower energy [1681 cm^{-1} for H_2L^1 to $1628\text{--}1634\text{ cm}^{-1}$ for the complexes of $(\text{L}^1)^{2-}$; 1659 cm^{-1} for H_2L^2 to 1607 cm^{-1} for the complexes of $(\text{L}^2)^{2-}$].

Magnetic and EPR Studies

The temperature dependence of the magnetic susceptibility was measured for the two complexes **1a**·H₂O and **2b** over the range 300–4.2 K. The plots of the temperature dependence of μ_{eff} and χ_{m} are given in the Figures S5–S8 (Supporting Information).

Complex **1a**·H₂O showed Curie-like behaviour at higher temperatures ($\mu_{\text{eff}} = 1.91\text{ }\mu_{\text{B}}$) and only at temperatures below 5 K a small, rapid decrease was observed. Consequently, χ_{m} increased and no maximum was observed in the plot χ_{m} vs. T . The best fit to the Bleaney–Bowers equation^[34] was obtained from the parameters $J = -0.24\text{ cm}^{-1}$, $g = 2.2$, $TIP = 60 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$. Setting J at zero gave a calculated line that did not reproduce the decrease in μ_{eff} values below 5 K. Calculations of μ_{eff} using the thermodynamic form of susceptibility, applicable to low temperature/high field combinations, rather than the Bleaney–Bowers equation, show that the small decrease is partly, but not wholly, due to Zeeman level depopulation (saturation) effects in the field used (1 T). Nevertheless, the antiferromagnetic coupling interaction was less than that (-7.5 cm^{-1}) of a related dicopper(II) complex of the isomeric ligand N,N' -bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide (H_2L^3).^[7] In the 2,3-dicarboxamide compound, an internal $\text{O}\cdots\text{H}\cdots\text{O}=\text{C}$ hydrogen-bond was present in the $(\text{HL}^3)^-$ form of the bridging ligand and the terminal ligands to each copper(II) centre were different to those in **1a**·H₂O. However, the Cu $\cdots$ Cu distances, τ values and *trans-axial* copper(II) geometries were very similar in both cases (vide infra). DFT calculations made on the 2,3-dicarboxamide complex yielded spin densities and spin populations on the pyrazine N-donor atoms compatible with weak antiferromagnetic superexchange coupling of the $\text{Cu}^{\text{II}}(\text{d}_{x^2-y^2})$ orbitals across the pyrazine ring.^[7] Thus, while **1a**·H₂O and this 2,3-dicarboxamide analogue are both very weakly antiferromag-

netically coupled, there is no clearly identifiable feature which explains this difference in J values. For complex **2b** the χ_{m} values follow Curie behaviour while μ_{eff} is constant at $1.86\text{ }\mu_{\text{B}}$ down to 50 K, then increases to $1.92\text{ }\mu_{\text{B}}$ at 4 K. Fitting to a dinuclear model gave $g = 2.14$ and $J = +0.67\text{ cm}^{-1}$. The observed very weak ferromagnetic spin coupling was unexpected, as the main difference between the complexes **2b** and **1a**·H₂O is only the more flexible ethylene containing ligand arm and weak Cu–F coordination in complex **2b**. Furthermore, antiferromagnetic spin coupling has been observed for various copper(II) complexes of the ligands N,N' -bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide (H_2L^3)^[7] and N,N' -bis[2-(2-pyridyl)ethyl]pyrazine-2,3-dicarboxamide (H_2L^4),^[35] which are isomeric to H_2L^1 and H_2L^2 , respectively.

The EPR spectrum of a polycrystalline powder of **1a**·H₂O at 120 K shows a strong resonance near $g = 2$, with no hyperfine structure being resolved on the parallel feature (Figure S9, Supporting Information). Simulations give $g_{\parallel} = 2.24$ and $g_{\perp} = 2.06$. An extremely weak resonance of similar shape is observed at $g \approx 4$ (Figure S10, Supporting Information). The spectrum of a polycrystalline powder of **2b**·2H₂O at both 260 K and 150 K (Figure S11, Supporting Information) shows an asymmetric resonance near $g = 2$, with the features associated with $g_{\parallel}$ being unresolved and tailing off to low field. The g -values are estimated as $g_{\parallel} = 2.23$ and $g_{\perp} = 2.05$. Again, a weak resonance is observed near $g = 4$ (Figure S12, Supporting Information). None of the polycrystalline powder spectra showed a dependence on temperature between 120 K and 295 K. The appearance of the resonances in the $g \approx 2$ and $g \approx 4$ regions is indicative of the presence of dipolar and weak exchange interactions between the copper(II) ions.^[36] The former give rise to spectral broadening while the latter result in exchange narrowing, as is observed here. The effect of the different magnitudes of exchange interaction on the spectra is shown by the collapse of the hyperfine interaction in **1a**·H₂O and the smearing out of the differences in g -value due to a larger exchange interaction in **2b**·2H₂O.

The observation of resonances at $g \approx 4$ in the polycrystalline powder systems is additional evidence for interaction between the copper(II) ions. These resonances are not due to Fe^{III} impurities in either the cavity background or in the powders themselves. Although in a three-dimensional extended lattice the $g \approx 4$ resonances are expected to be smeared out unless $E_d, E_{ex} \ll E_0$,^[37] this inequality does not hold in the present case, where the Zeeman energy $E_0 \approx 0.3 \text{ cm}^{-1}$, the dipolar coupling energy $E_d \approx 0.01 \text{ cm}^{-1}$ and E_{ex} is -0.24 cm^{-1} for **1a**·H₂O and $+0.67 \text{ cm}^{-1}$ for **2b**·2H₂O. However, this condition is relaxed for low-dimensional magnetic systems. Thus the observation of resonances near $g = 4$ for both complexes implies the existence of low-dimensional intermolecular exchange interactions in the solid state.^[37,38]

The EPR spectra of **1a**·H₂O and **2b**·2H₂O in frozen DMF solution (ca. 1 mM) at 130 K were identical and showed well resolved resonances at $g \approx 2$ and $g \approx 4$ as shown in Figure 6 and Figure 7 respectively. These resonances are typical of those observed for many dinuclear copper(II) complexes in dilute frozen solution^[36] and are attributed to the coupling of two copper(II) ions, each with electron spin $S = 1/2$, by dipole–dipole and exchange interactions to give a triplet state ($S = 1$) and a singlet state ($S = 0$). The resonances in the $g \approx 2$ region are due to the $\Delta M_s = 1$ transitions within the triplet state and those near $g \approx 4$ (“half field”) to the “forbidden” or $\Delta M_s = 2$ transitions between the $M_s = \pm 1$ levels of the triplet state.

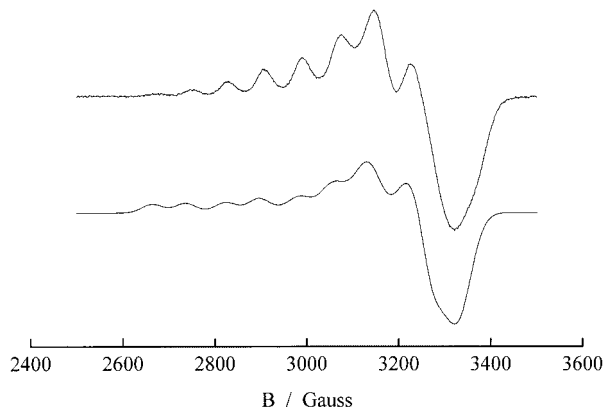


Figure 6. EPR spectrum in the $g = 2$ region of **2b**·2H₂O in frozen DMF solution at 130 K (approximately 1 mM). Experimental spectrum (top): microwave frequency 9.424 GHz; microwave power 2 mW; 100 kHz modulation amplitude 1 G; receiver gain 2.0×10^4 ; scan time 167 s; time constant 82 ms. Simulated spectrum (bottom): computed using the parameters referred to in the text.

The spectra can be simulated as shown in Figures 6 and 7 with the following spin Hamiltonian parameters $g_{\parallel} = 2.290 (\pm 0.005)$, $g_{\perp} = 2.080 (\pm 0.005)$, $A_{\parallel} = 170 (\pm 5) \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 5 (\pm 5) \times 10^{-4} \text{ cm}^{-1}$. A Cu^{II}...Cu^{II} distance of $6.9 (\pm 0.1) \text{ \AA}$ is obtained with the inter-nuclear vector in the xy plane of the magnetic axes of the copper(II) ions (to within 15°), i.e. perpendicular to the z or symmetry axis of the individual ions. The best fit of experimental and simulated spectra is found with an isotropic exchange interaction $J = 0$. The uncertainties, given in parentheses, repre-

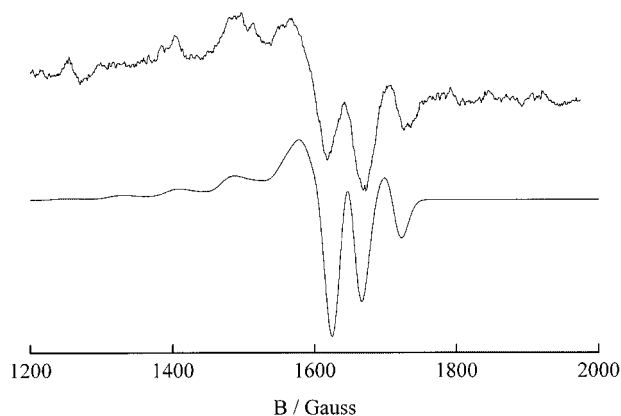


Figure 7. Half-field portion of EPR spectrum of **2b**·2H₂O in frozen DMF solution at 130 K. Experimental spectrum (top): microwave frequency 9.424 GHz; microwave power 10 mW; 100 kHz modulation amplitude 10 G; receiver gain 5.0×10^5 ; scan time 84 s; time constant 328 ms; average of 17 scans. Simulated spectrum (bottom): computed using the parameters referred to in the text.

sent the range of parameters for which acceptable agreement is found between experimental and simulated spectra. There is no inherent contradiction between the value of $J = 0$ found from the simulation of the frozen solution spectra and the small values of J found by magnetic susceptibility measurements, as the latter may arise from intermolecular interactions in the solid state. Intermolecular exchange is not expected to be significant in dilute frozen solution.

The spin Hamiltonian parameters from the simulation of the frozen solution spectra can be taken as being those of the individual copper(II) ions and give $g_{av} = 2.14$. This value may be compared with the values of g_{av} from the solid-state powder spectra of 2.12 (**1a**·H₂O) and 2.11 (**2b**·2H₂O) and from magnetic susceptibility of 2.20 (**1a**·H₂O) and 2.14 (**2b**·2H₂O). The g values of the solid-state powder spectra and those from magnetic susceptibility measurements are subject to significant sources of uncertainty. Nevertheless, the magnetic susceptibility and EPR measurements show that the copper(II) ions retain the Cu^{II}($d_{x^2-y^2}$) orbital ground state even in solution, consistent with the distorted square pyramidal or octahedral coordination shown by the X-ray crystallographic analysis.

Conclusions

The pyrazine-based bis(terdentate) diamide ligands H₂L¹ and H₂L² can be used for the formation of grid-type metal complexes.^[5] However, it has been found that on complexation with Cu(BF₄)₂·4H₂O both ligands prefer to form dicopper(II) complexes of the type [Cu^{II}₂(L¹)(co-ligand)₄]²⁺ or [Cu^{II}₂(L²)(co-ligand)₄]²⁺ featuring doubly deprotonated ligands and varying co-ligands. Unlike their isomeric ligands *N,N'*-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide (H₂L³)^[6] and *N,N'*-bis[2-(2-pyridyl)ethyl]pyrazine-2,3-dicarboxamide (H₂L⁴)^[35] where the addition of base is required to even monodeprotonate the ligand for complexation, no additional base is required to form complexes of

the doubly deprotonated ligand species (L^1)²⁻ and (L^2)²⁻. All of the complexes described in this paper, except compound **2b**·2H₂O, feature distorted square-pyramidal coordination spheres for the copper(II) ions. A distorted octahedral coordination sphere with BF₄⁻ coordination is observed in complex **2b**·2H₂O. In all cases the central pyrazine ring bridges the metal ions. Very weak antiferromagnetic spin coupling is observed in magnetic studies on complex **1a**·H₂O which features N₄O five-coordinate copper(II) ions, whereas very weak ferromagnetic spin coupling is observed in studies of complex **2b**, which features N₃O₂F six-coordinate copper(II) ions. X-band EPR studies confirm the very weak exchange coupling in the solid state. The frozen solution spectra are interpreted in terms of dipolar coupling with no intramolecular exchange and intra-cluster Cu...Cu separations similar to those obtained by crystallography. Serendipitous formation of SiF₆²⁻ ions, and the almost quantitative crystallisation of the corresponding SiF₆²⁻ compounds **1b** and **1c**·4H₂O, has been observed when reacting H₂L¹ with Cu(BF₄)₂·4H₂O in H₂O as the solvent and using a glass vial as both the reaction and crystallisation vessel. Complex **1c**·4H₂O was found to be a rare example of a structure featuring five-coordinate dicopper(II) subunits bridged by SiF₆²⁻ ions.

Experimental Section

General Remarks: Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago. Melting points were determined with a Gallenkamp melting point apparatus in open-glass capillaries and are uncorrected. ¹H and ¹³C NMR spectra were recorded with a Varian INOVA-300 or with a Varian INOVA-500 spectrometer at 25 °C. Chemical shifts are given relative to tetramethylsilane (TMS). IR spectra were recorded with a Perkin–Elmer Spectrum BX FT-IR spectrophotometer over the range 4000–400 cm⁻¹. UV/Vis/NIR spectra were recorded with a Varian CARY 500 Scan UV/Vis/NIR spectrophotometer over the range 200–1400 nm. Molar conductivities were measured using 1 mM solutions with a Suntex SC-170 conductivity meter. ESI mass spectra were recorded with a MicroMass LCT spectrometer. For all compounds MeCN was used as the solvent. Magnetic data were recorded over the range 300–4.2 K using a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 T. Single-crystal X-ray data were collected with a Bruker SMART CCD area detector diffractometer ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97^[39,40] and refined against F^2 using full-matrix least-squares techniques with SHELXL-97.^[41] Continuous wave (CW) EPR spectra were obtained with a Bruker ESP380FT/CW X-band spectrometer at Monash University, using the standard rectangular TE₀₁₂ cavity. Temperatures below room temperature (295 K) down to 120 K were achieved with a Bruker nitrogen flow insert in the cavity. The microwave frequency was measured with an EIP microwave 548A frequency counter and the g factors were determined by proton NMR and with reference to the F⁺ line in CaO (2.0001 ± 0.0001).^[42] Spectrum simulations were performed with either the Bruker SIMFONIA software or (for Figure 6 and Figure 7) with the SOPHE software described by Griffin and co-workers.^[43]

Dimethyl Pyrazine-2,5-dicarboxylate (II): A solution of 2,5-dimethylpyrazine (8.11 g, 75.0 mmol) in pyridine/H₂O (10:1) (165 mL) was

treated with solid SeO₂ (37.5 g, 337.5 mmol) and the resulting suspension was refluxed for 18 hours. The resulting dark red-brown mixture was evaporated to dryness under reduced pressure. H₂O (250 mL) was added and the solid elemental selenium was filtered off. After evaporation of the red solution to dryness, the resulting dark red brown solid was taken up in MeOH (150 mL), treated with SOCl₂ (3.5 mL) and refluxed for 8 hours. The resulting suspension was then filtered whilst hot and the solid was washed with CH₂Cl₂ (5 × 20 mL). The combined organic layers were reduced in volume under reduced pressure (to ca. 100 mL) to give the product in the form of pale yellow-orange feathery crystals. The solid was filtered off and washed with ice-cold MeOH (20 mL) to give 8.98 g (45.8 mmol, 61%) of analytically pure **II**. M.p. 167–168 °C. C₈H₈N₂O₄ (196.16): calcd. C 48.98, H 4.11, N 14.28; found C 49.24, H 3.87, N 14.25. TLC (SiO₂, CH₂Cl₂/10% MeOH): R_f = 0.83. ¹H NMR (300 MHz, CDCl₃): δ = 9.39 (s, 2 H, pzH), 4.07 (s, 6 H, CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 163.6 (pzCO), 145.6 (pzH), 145.3 (pzCO), 53.6 (OCH₃) ppm. IR (KBr, disk): $\tilde{\nu}$ = 3549, 3472, 3417, 3077, 3015, 2960, 2853, 1720, 1637, 1618, 1472, 1431, 1359, 1279, 1202, 1181, 1144, 1020, 959, 824, 759, 616 495, 466, 425 cm⁻¹.

N,N'-Bis(2-pyridylmethyl)pyrazine-2,5-dicarboxamide (H₂L¹): A suspension of **II** (1.96 g, 10.0 mmol) in MeOH (70 mL) was treated with a solution of 2-(aminomethyl)pyridine (2.38 g, 22.0 mmol) in MeOH (30 mL) and the resulting solution was kept in an open flask at 80–90 °C for 4 hours, allowing most of the solvent to evaporate. Filtration of the resulting suspension gave 2.92 g (8.38 mmol, 84%) of H₂L¹ in the form of an analytically pure colourless powder. M.p. 205–206 °C. C₁₈H₁₆N₆O₂ (348.36): calcd. C 62.06, H 4.63, N 24.12; found C 61.94, H 4.66, N 24.30. TLC (SiO₂, CH₂Cl₂/10% MeOH): R_f = 0.60. ¹H NMR (500 MHz, CDCl₃): δ = 9.39 (s, 2 H, 2 × pzH), 8.88 (t, J = 5.0 Hz, 2 H, 2 × NH), 8.62 (ddd, ³ $J_{6,4}$ = 5.0, ⁴ $J_{6,4}$ = 2.0, ⁵ $J_{6,3}$ = 1.0 Hz, 2 H, 2 × 6-pyH), 7.69 (dt, ³ $J_{4,5}$ = ³ $J_{4,3}$ = 7.5, ⁴ $J_{4,6}$ = 2.0 Hz, 2 H, 2 × 4-pyH), 7.34 (td, ³ $J_{3,4}$ = 7.5, ⁴ $J_{3,5}$ = ⁵ $J_{3,6}$ = 1.0 Hz, 2 H, 2 × 3-pyH), 7.23 (ddd, ³ $J_{5,4}$ = 7.5, ³ $J_{5,6}$ = 5.0, ⁴ $J_{5,3}$ = 1.0 Hz, 2 H, 2 × 5-pyH), 4.82 (d, J = 5.0 Hz, 4 H, 2 × pyCH₂) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 162.6 (pzCO), 156.0 (2-py), 149.5 (6-py), 146.4 (pzCO), 142.4 (pzH), 136.9 (4-py), 122.6 (5-py), 122.1 (3-py), 44.7 (CH₂) ppm. IR (KBr, disk): $\tilde{\nu}$ = 3458, 3417, 3338, 2922, 1681, 1572, 1522, 1461, 1434, 1363, 1325, 1208, 1177, 1027, 997, 902, 758, 726, 648, 504, 460 cm⁻¹.

N,N'-Bis[2-(2-pyridyl)ethyl]pyrazine-2,5-dicarboxamide (H₂L²): This compound was synthesised in an analogous manner to the preparation of H₂L¹, using 2-(2-aminoethyl)pyridine (2.69 g, 22.0 mmol) instead of 2-(aminomethyl)pyridine. Yield: 2.68 g (7.12 mmol, 71%). M.p. 225–227 °C. C₂₀H₂₀N₆O₂ (376.42): calcd. C 63.82, H 5.36, N 22.33; found C 63.51, H 5.42, N 22.69. TLC (SiO₂, CH₂Cl₂/10% MeOH): R_f = 0.70. ¹H NMR (500 MHz, CDCl₃): δ = 9.28 (s, 2 H, 2 × pzH), 8.59 (d, J = 5.0 Hz, 2 H, 2 × 6-pyH), 8.54 (s, 2 H, 2 × NH), 7.62 (dt, ³ $J_{4,5}$ = ³ $J_{4,3}$ = 7.8, ⁴ $J_{4,6}$ = 2.0 Hz, 2 H, 2 × 4-pyH), 7.20–7.16 (m, 4 H, 2 × 3-pyH and 2 × 5-pyH), 3.92 (q, J = 6.5 Hz, 4 H, 2 × NHCH₂), 3.13 (t, J = 6.5 Hz, 4 H, 2 × pyCH₂) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 162.5 (pzCO), 159.1 (2-py), 149.5 (6-py), 146.4 (pzCO), 142.2 (pzH), 136.7 (4-py), 123.5 (3-py), 121.8 (5-py), 38.8 (HNCH₂), 37.0 (pyCH₂) ppm. IR (KBr, disk): $\tilde{\nu}$ = 3369, 3092, 3036, 3013, 1985, 2973, 1659, 1590, 1569, 1535, 1475, 1461, 1441, 1367, 1321, 1286, 1263, 1196, 1169, 1049, 1036, 1017, 993, 951, 884, 857, 763, 745, 654, 633, 614, 512, 494, 472, 449 cm⁻¹.

[Cu^{II}₂(L¹)(H₂O)₂](BF₄)₂ (I): A solution of Cu(BF₄)₂·4H₂O (149 mg, 482 μmol) in MeCN (10 mL) was added to a hot (60 °C) solution of H₂L¹ (84.0 mg, 241 μmol) in MeCN (10 mL). The re-

sulting dark bottle-green solution was left at this temperature for 10 minutes and was then cooled to room temperature. By vapour diffusion of Et₂O into the reaction mixture, 106 mg (155 μmol, 64%) of complex **1** were obtained in the form of a dark turquoise solid. Single crystals of [Cu^{II}₂(L¹)(MeCN)₂(H₂O)₂](BF₄)₂·H₂O (**1a**·H₂O) suitable for X-ray analysis were obtained by slow evaporation of the reaction solution, obtained as described above. [Cu^{II}₂(L¹)(H₂O)₂](BF₄)₂ (C₁₈H₁₈B₂N₆O₄F₈Cu₂) (683.08): calcd. C 31.65, H 2.66, N 12.30; found C 31.86, H 2.23, N 12.30. IR (KBr, disk): $\tilde{\nu}$ = 3424, 3110, 2897, 1634, 1567, 1485, 1449, 1436, 1416, 1361, 1350, 1335, 1288, 1214, 1190, 1167, 1083, 1062, 923, 772, 743, 715, 656, 635, 585, 556, 533, 521, 465, 415 cm⁻¹. ESI-MS (pos, MeCN): *m/z* (fragment) = 571.5 ([Cu^ICu^{II}(L¹)(H₂O)(MeCN)₂]⁺), 531.7 ([Cu^ICu^{II}(L¹)(H₂O)(MeCN)]⁺), 450.7 ([Cu^{II}(HL¹)(MeCN)]⁺), 276.9 ([Cu^{II}₂(L¹)(MeCN)₂]²⁺), 237.9 ([Cu^I₂(H₂L¹)]²⁺), 225.9 ([Cu^{II}(H₂L¹)(MeCN)]²⁺). UV/Vis/NIR (MeCN): λ_{max} (ϵ) = 212 (34 100), 261 (20 500), 349 (4200), 641 nm (204 M⁻¹cm⁻¹). A_m (MeCN) = 231 Ω⁻¹mol⁻¹cm².

[Cu^{II}₂(L¹)(H₂O)₄](SiF₆) (**1b**) and {[Cu^{II}₂(L¹)(H₂O)₂(μ-SiF₆)·4H₂O]_∞ (**1c**·4H₂O): Solid H₂L¹ (40.1 mg, 115 μmol) was treated with a solution of Cu(BF₄)₂·4H₂O (71.1 mg, 230 μmol) in H₂O (5 mL) and the resulting dark bottle green solution was further treated with a solution of NEt₃ (23.3 mg, 230 μmol) in H₂O (3 mL). The resulting blue-green solution was transferred into a sample vial (SAMCO specimen tubes, soda glass, 75 × 25/26 mm, ISO 9002) and was left to slowly evaporate. After 4 weeks 66 mg (96 μmol, 83%) of huge blue-green crystal blocks were isolated by filtration. The crystal blocks analysed as [Cu^{II}₂(L¹)](SiF₆)·4H₂O. Single crystals suitable for X-ray crystal structure determinations, [Cu^{II}₂(L¹)(H₂O)₄](SiF₆) (**1b**) and {[Cu^{II}₂(L¹)(H₂O)₂(μ-SiF₆)·4H₂O]_∞ (**1c**·4H₂O), were selected from these blocks before filtration. [Cu^{II}₂(L¹)](SiF₆)·4H₂O (C₁₈H₂₂N₆O₆F₆SiCu₂) (687.58): C 31.44, H 3.23, N 12.22; found C 31.45, H 3.23, N 12.08. IR (KBr, disk): $\tilde{\nu}$ = 3442, 3084, 2872, 1628, 1563, 1481, 1449, 1407, 1352, 1289, 1214, 1193, 1163, 1111, 1083, 1060, 1026, 981, 961, 923, 780, 750, 651, 556, 512, 472, 417 cm⁻¹. ESI-MS (pos, MeCN): *m/z* (fragment) = 451.1 ([Cu^{II}(L¹)(MeCN)₂]⁺), 349.2 ([H₃L¹]⁺). ESI-MS (neg, MeCN): *m/z* (fragment) = 123.0 ([SiF₆]⁻).

[Cu^{II}₂(L²)(solvent)_n](BF₄)₂ (**2**): This compound was synthesised in an analogous manner to the preparation of complex **1**, using H₂L² (75.3 mg, 200 μmol) instead of H₂L¹. After 10 hours stirring at room temperature complex **2** could be filtered off as a microcrystalline solid. Yield: 74.2 mg (104 μmol, 52%). Single crystals of [Cu^{II}₂(L²)(H₂O)₄](BF₄)₂·2H₂O (**2b**·2H₂O) suitable for X-ray crystal structure analysis were obtained by recrystallisation of compound **2** from MeCN/EtOH, 1:1. Single crystals of [Cu^{II}₂(L²)(H₂O)₂](MeCN)₂(BF₄)₂ (**2a**) suitable for X-ray crystal structure analysis were obtained by vapour diffusion of Et₂O into the reaction filtrate of an analogous 1:1 molar reaction of ligand to Cu(BF₄)₂·4H₂O. [Cu^{II}₂(L²)(MeCN)_{0.5}(H₂O)](BF₄)₂ (C₂₁H_{21.5}B₂N_{6.5}O₃F₈Cu₂) (713.65): calcd. C 35.34, H 3.04, N 12.76; found C 34.94, H 3.26, N 13.30. IR (KBr, disk): $\tilde{\nu}$ = 3423, 1607, 1539, 1484, 1445, 1400, 1336, 1307, 1254, 1210, 1083, 1034, 869, 770, 688, 626, 590, 533, 521 cm⁻¹. ESI-MS (pos, MeCN): *m/z* (fragment) = 1058.7 ([Cu^{II}₂(HL²)(MeCN)(H₂O)₃]⁺). UV/Vis/NIR (MeCN): λ_{max} (ϵ) = 261 (26 400), 346 (2930), 647 nm (113 M⁻¹cm⁻¹). A_m (MeCN) = 186 Ω⁻¹mol⁻¹cm².

Supporting Information: (See also footnote on the first page of this article) A PDF file (5 pages) with supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the authors. It contains a view of the extended 3D structures of complexes **2a**, **1a**·H₂O and **2b**·2H₂O (Figures S1–S3), a view of

the molecular structure of complex **1b** (Figure S4), the curves for the molar magnetic susceptibilities and effective magnetic moments of complexes **1a** and **2b** over the range 300–4.2 K (Figures S5–S8), the EPR spectra in *g* = 2 and in low-field regions of powdered samples of **1a**·H₂O and **2b**·2H₂O (Figures S9–S12) and some background information on the effect on EPR spectra of dipole–dipole and exchange interactions. CCDC-252079 (for **1a**·H₂O), -252080 (for **1b**), -252081 (for **1c**·4H₂O), -252082 (for **2a**) and -252083 (for **2b**·2H₂O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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