Two Examples of Novel and Unusual Double-Layered, Two-Dimensional Cu^{II} Compounds with Bridging 1,3-Bis(1,2,4-triazol-1-yl)propane

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The synthesis and characterisation of two new polymeric Cu^{II} complexes is described, i.e. {[Cu(btp)$_2$(CH$_3$CN)(H$_2$O)]-(CF$_3$SO$_3$)$_2$}$_n$ (**1**) and {[Cu(btp)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$}$_n$ (**2**), in which btp = [1,3-bis(1,2,4-triazol-1-yl)propane]. Compound **1** crystallizes in space group $P2_1/c$ with a = 11.9337(15) Å, b = 20.108(6) Å, c = 12.748(6) Å, β = 92.247(14)°, and Z = 4. Compound **2** crystallizes in space group $Pna2_1$ with a = 18.770(8) Å, b = 12.648(8) Å, and c = 12.019(8) Å. The structures refined to $R1$ values of 0.0683 for **1** and 0.0846 for **2**. In both structures the Cu^{II} ions are linked by the bridging ligands, resulting in two-dimensional networks. Two such curved layers are arranged on top of each other with center-to-center of layer distances of 2.12 Å in **1** and 1.98 Å in **2**. Such double layers are separated from each other by 10.05 Å in **1** and 9.385 Å in **2**. The space between the double layers is occupied with interstitial anions. No significant interaction between Cu^{II} ions is observed by EPR and magnetic susceptibility measurements. The compounds form a new class of a lattice engineered system held together by the Cu^{II} ions. – The coordination geometry of the copper ions is distorted octahedral, with the equatorial plane formed by the N4 nitrogens of the four triazole groups and the axial sites occupied by solvent molecules; acetonitrile and water in structure **1** and two acetonitrile molecules in structure **2**. The two structures are related by a group–subgroup relationship, which appears to be the first such case in supramolecular chemistry. – The Cu–N vibrations in the FIR region are found at 274 cm^{-1} for **1**, and at 276 cm^{-1} for **2**. The ligand-field maxima are observed at about 16·10^3 cm^{-1}, with a shoulder at about 12·10^3 cm^{-1}. The ν_{CN} stretching vibrations of the acetonitrile molecules are found at 2303 and 2261 cm^{-1} for **1**, and at 2313, 2294, 2278, and 2260 cm^{-1} for **2**.

Introduction

Metal complexes with supramolecular features in their structure have recently aroused much interest as materials with potentially new electronic, optical, magnetic, or catalytic properties.[1] Given the strong preference of Cu^{II} for square-planar based geometries, bridging ligands would be almost ideally suited for building a square 2-dimensional lattice. Well-known classical cases are structures like (cation)$_2$CuCl$_4$[2] (cation = organic substituted ammonium). Such 2D systems also allow the coordination of weak axial ligands, like in some clathrate compounds.[3]

When bridging ligands are large, cavities result which need to be filled to form a stable lattice. and This can be accomplished by, for instance, the counter anions and/or guest molecules, or by the formation of interpenetrating lattices.[1a] With proper vertical stacking of such 2D systems, supramolecular systems with channels might result, in which the anions and/or guest molecules could move or migrate. A totally different way of packing would be a case where layers occur in pairs, and be organized in such a way that a corner of a lattice grid in one 2D lattice cell, lies above the cavity of the other cell, filling it up with its axial ligand. In such a case double-layers of 2D lattices result, which as such can be separated by counter anions and solvent/guest molecules. Such systems, when properly stabilized with strongly bridging ligands, would have the axial ligand sites of the copper ions accessible for ligand exchange and/or – more importantly – catalytic reactions, with the reagents transported through the spaces [slabs] between the double-layers.

For Cu^{II} a number of 2D and 3D frameworks are already known with N,N'-bidentate spacers.[4] In most cases the spacer molecules are rigid heterocyclic ligands;[4a,5] however, only a few structures are known in which the 2D or 3D frameworks consist of two heterocyclic donors linked by spacers of variable length, like in the compound Cu^I[(1,4-bis(4-pyridyl)butadiyne],[4b] and Cu^{II} and Mn^{II} compounds with [(1,2-bis(imidazol-1′-yl)alkane] ligands.[6]

Recently, a new class of ligands, [bis(1,2,4-triazol-1-yl)-alkanes], was developed in our laboratories and characterised by X-ray diffraction. A variety of new types of polymeric 2D and 3D frameworks with Fe^{II} and Mn^{II} were found.[7]

We now wish to report the first case of two examples of such lattice-engineered systems using Cu^{II}, and generating double layers of a 2D system. By the using the ligand [1,3-bis(1,2,4-triazol-1-yl)propane] (abbreviated btp), we synthe-

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sized two compounds, i.e. $Cu(btp)_2(CH_3CN)(H_2O)](CF_3SO_3)_2$ (**1**) and $[Cu(btp)_2(CH_3CN)_2](ClO_4)_2$ (**2**), from which crystal structures were obtained.

Results and Discussion

Description of the Crystal Structures

The structures of both compounds are depicted in Figures 1 and 2, respectively, together with the numbering scheme and relevant bond length and bond angle information. In both structures, the coordination polyhedra of the Cu^{II} ions are distorted octahedra, in which the equatorial plane is formed by the N4 nitrogens of the triazole groups, with Cu−N distances of 2.009(4)−2.020(3) Å in **1** and 1.974(12)−2.039(12) Å in **2**. The axial positions in the octahedra are occupied by weaker ligands, i.e. solvent molecules, acetonitrile and water in **1**, and two acetonitrile molecules in **2**. The axial distances in **1** are 2.399(4) Å for Cu−N and 2.462(4) Å for Cu−O. In **2** the axial Cu−N distances are 2.260(15) and 2.665(15) Å, the latter at a semi-coordination distance.

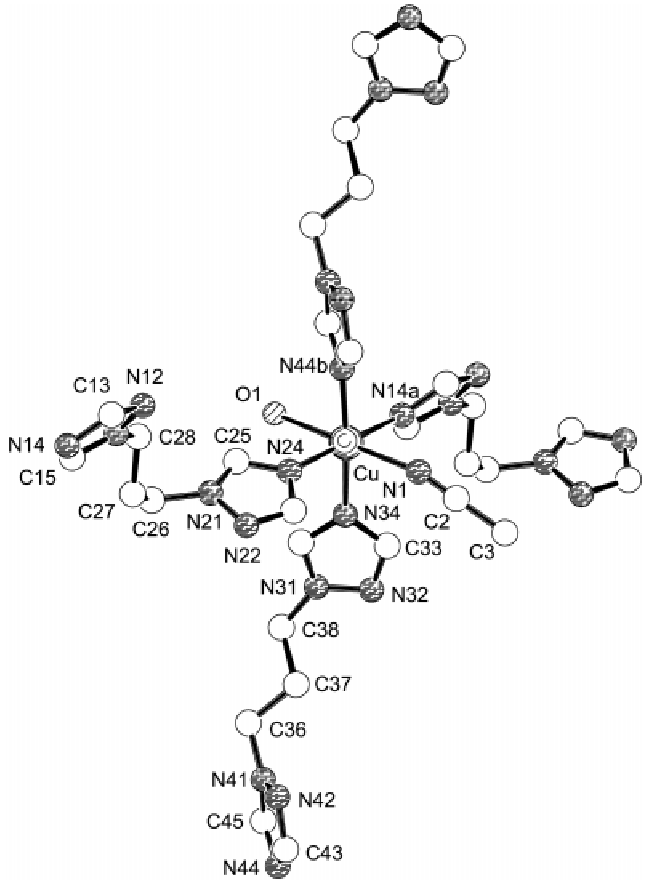

Figure 1. Coordination environment of the Cu atom in $\{[Cu(btp)_2(CH_3CN)(H_2O)](CF_3SO_3)_2\}_n$ (Structure **1**) with atom-labelling scheme. Hydrogen atoms and triflate anions are omitted for clarity. Symmetry operations: *a* = *x* − 1, *y*, *z*; *b* = *x*, *y*, *z* − 1. Bond length [Å] and angles [°]: Cu−O1 2.462(4); Cu−N1 2.399(4); Cu−N14a 2.013(3); Cu−N34 2.020(3); Cu−N44b 2.011(3); Cu−N24 2.010(3); N24−Cu−N44b 91.05(13); N24−Cu−N14a 178.51(14); N44b−Cu−N14a 90.04(13); N24−Cu−N34 89.11(13); N44b−Cu−N34 175.17(15); N14a−Cu−N34 89.72(13); N24−Cu−N1 91.93(14); N44b−Cu−N1 93.12(14); N14a−Cu−N1 89.02(14); N34−Cu−N1 91.70(14); N24−Cu−O1 90.43(14); N44b−Cu−O1 88.44(13); N14a−Cu−O1 88.59(13); N34−Cu−O1 86.73(13); N1−Cu−O1 177.14(13).

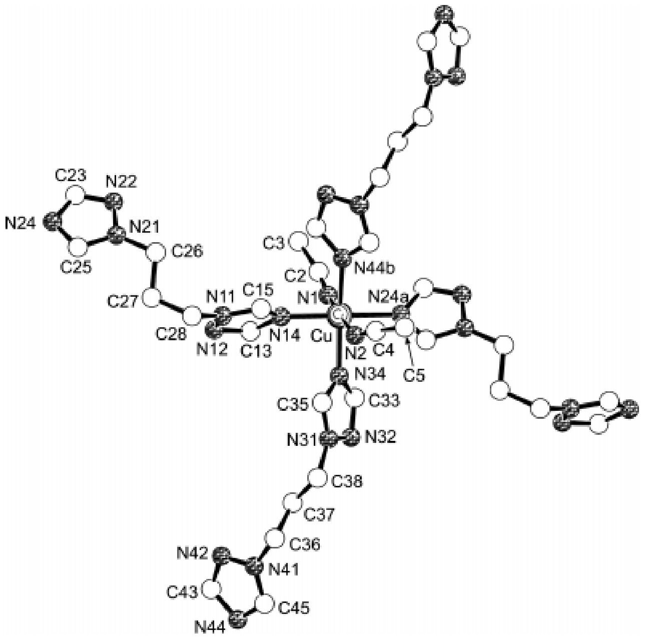

Figure 2. Coordination environment of the Cu atom in $\{[Cu(btp)_2(CH_3CN)_2](ClO_4)_2\}_n$ (structure **2**) with atom-labelling scheme. Hydrogen atoms and perchlorate anions are omitted for clarity. Only one configuration of the disordered acetonitrile (N1−C3) is shown. Symmetry operations: *a* = *x*, *y*, *z* + 1; *b* = *x*, *y* + 1, *z*. Bond length [Å] and angles [°]: Cu−N1 2.261(15); Cu−N14 1.974(13); Cu−N34 2.029(14); Cu−N24a 2.040(13); Cu−N44b 2.009(14); Cu−N2 2.665(15); N14−Cu−N44b 90.6(5); N14−Cu−N34 89.9(5); N44b−Cu−N34 169.0(5); N14−Cu−N24a 178.0(5); N44b−Cu−N24a 89.1(5); N34−Cu−N24a 90.1(5); N14−Cu−N1 90.1(5); N44b−Cu−N1 92.7(6); N34−Cu−N1 98.3(6); N24a−Cu−N1 91.9(5); N14−Cu−N2 91.0(5); N44b−Cu−N2 84.5(5); N34−Cu−N2 84.5(5); N24a−Cu−N2 87.0(5); N1−Cu−N2 177.0(5).

In both structures, the Cu^{II} ions are linked by the btp ligands, building up polymers to a two-dimensional network. In **1**, this 2D sheet is situated parallel to the crystallographic *a,c* plane. A second layer with no bonding interaction to the first one, is situated 2.12 Å above it. So in fact these two layers, shown in Figure 3, should be considered as a double layer. The double layers are stacked in the crystallographic *b* direction with a distance of *b*/2 = 10.054 Å. The space between the sets of double layers is filled up with the triflate anions as shown in Figure 4. The crystal structure of **1** is further stabilized by H-bonding between the water molecule and oxygens of the triflate anion [O1···O2 2.780(6) Å and O1···O5 2.855(5) Å].

The situation in **2** is quite similar. Here the 2D sheets are located parallel to the crystallographic *b,c* plane, and stacked in the *a* direction. The distance within the double layer is even smaller (1.98 Å). Because perchlorate anions are smaller than triflate anions the distance between the double layers is shortened to 9.385 Å (= *a*/2).

The cell parameters of both structures differ slightly, which must be caused by the different anions. The reason

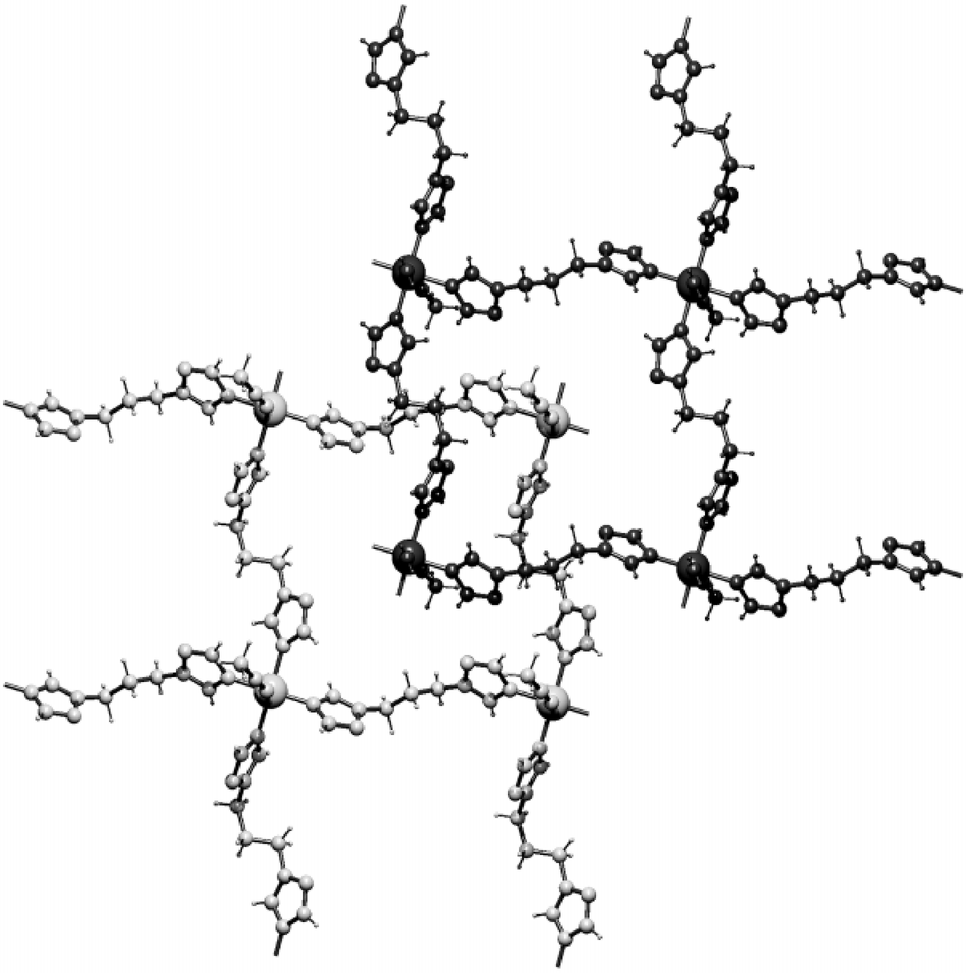

Figure 3. View along the crystallographic b-axis on one double layer in structure **1**

for changing the orientations of the unit cell in **1** and **2** was to achieve the standard setting of the space groups. The space groups $P2_1/c$ for **1** and $Pna2_1$ for **2** are both subgroups of the same super-group; *Pnma.* While such "family tree" relations are well-known in other areas of inorganic chemistry, such as in perovskite-like structures,[8] to our knowledge, this is the first case of such a group−subgroup relationship in supramolecular coordination chemistry.

The shortest Cu−Cu distances are 8.753(3) Å in **1** and 8.946(4) Å in **2**. These distances are shorter than observed in $[(Cu(bim)_{2.5})(ClO_4)_2 \cdot 2\,MeOH]$ [bim = 1,2-bis(imidazol-1′-yl)ethane],[6a] one of the few compounds that also have an alkane chain as a spacer, in which the Cu−Cu distance is 12.55 Å. In fact, this confirms the importance of this family of ligands in adjusting the metal-metal distance. With other metals like Fe^{II} and Mn^{II}, this type of ligand [bis(1,2,4-triazol-1-yl)alkanes] leads to a variety of 2D and 3D structures.[7]

Ligand Field Spectra

The d-d transitions in the UV-Vis-NIR absorption spectra for both Cu compounds are found at about $16 \cdot 10^3$ cm^{-1}, with a shoulder at about $12 \cdot 10^3$ cm^{-1} (See Table 1). These values agree with ligand field transitions for copper square-planar or square-planar based CuN_4 or a CuN_4X_2 chromophore.[9]

EPR and Magnetic Properties

The EPR measurements on **1** and **2** reveal the normal parameters (see Table 1) for a Cu^{II} isolated spin $S = {}^1/_2$,[9a] as almost no Cu−Cu interaction is present due to the large distances between the Cu centres. The $A_{//}$ value of ca. 17 mT (measured as a frozen solution at 77 K) is consistent with a $CuN_4(X)_{1-2}$ (X = N,O) geometry around the copper ion.[9] Magnetic susceptibility data recorded down to 40 K indicate a magnetic moment of 1.8 B.M., below which a slight decrease is observed down to 5 K, which is at best in agreement with a very weak exchange coupling.

Infrared Spectra

In the infrared spectrum the vibrations of the acetonitrile molecules are found at 2261 and 2303 cm^{-1} for compound

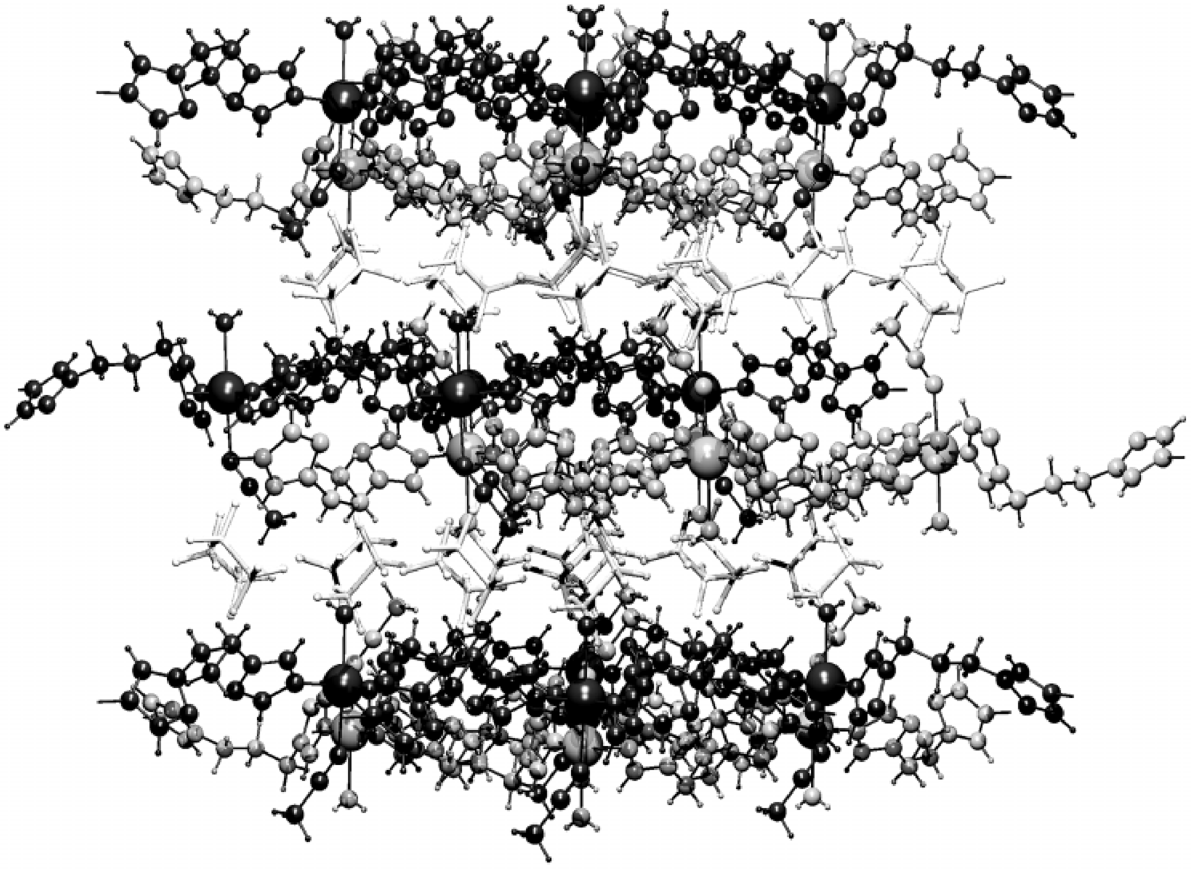

Figure 4. Stacking of the double layers in structure **1** in the direction of the crystallographic *b* axis. The double layers are separated by the triflate anions. (View along [1.0.1])

Table 1. UV-VIS-NIR, EPR, and FIR spectral data[a] for Cu^{II} compounds with btp

Compound	UV-VIS-NIR $[10^3\ cm^{-1}]$	EPR values, (powder, room temp.) $g_{\perp}$, $g_{//}$	EPR values, 77 K[b] $g_{\perp}$, $g_{//}$, $A_{//}$ [mT]	MIR $[cm^{-1}]$ ν_{CN}	FIR $[cm^{-1}]$ ν_{Cu-N}
1, $\{[Cu(btp)_2(CH_3CN)(H_2O)](CF_3SO_3)_2\}_n$	ca.12.0 (sh) 16.1	2.07, ca.2.4 (vw)	2.06, 2.27, 17.3	2303 (w), 2261 (m)	274
2, $\{[Cu(btp)_2(CH_3CN)_2](ClO_4)_2\}_n$	ca.12.0 (sh) 16.8	2.07, ca.2.4 (vw)	2.06, 2.30, 16.4	2313 (w), 2278 (m) 2294 (vw), 2260 (m,sh)	276

[a] Abbreviations: vbr = very broad, vw = very weak, sh = shoulder. − [b] Frozen solution in DMSO/MeOH (1:1)

1, which contains only one coordinated acetonitrile molecule. In compound **2**, which has two acetonitrile molecules, with one short distance of 2.260(15) Å and one long Cu−N distance of 2.665(15) Å, the vibrations are found at 2313 and 2278 cm^{-1} for the first and at 2294 and 2260 cm^{-1} for the second acetonitrile molecule. In each case, the bands at lower frequencies are assigned to the C≡N stretching vibration and those at higher frequencies to the $\nu_3+\nu_4$ combination band mixed with C≡N stretch.[10] In the far-infrared region, the Cu−N vibrations are clearly visible as strong broad peaks at 274 cm^{-1} for **1** and at 276 cm^{-1} for **2**, which is comparable with Cu−N vibrations given in the literature.[11]

In summary, the compounds presented herein are a first step in a new series of supramolecular compounds, and we are currently working on the use of metal ions other than Cu^{II}, as well as changing the anions and axial ligands to synthesizing materials that can be used as host/guest molecules and can be active in catalytic processes.

Experimental Section

General: C, H, N, and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. − Ligand field spectra were obtained on a Perkin−Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. − X-band EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. − FTIR spectra were obtained on a Bruker 113v infrared spectrophotometer as KBr disks (4000−400 cm^{-1}, mirror velocity 0.166 cm/s, resolution 2 cm^{-1}), or as polyethylene mulls (600−100 cm^{-1}, mirror velocity 0.099 cm/sec, resolution 2 cm^{-1}, Mylar 3.5 μ beam splitter). − Magnetic susceptibilities were measured in the temperature range 5−300 K with a Manics DSM-8 susceptometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of the Ligand. − 1,3-Bis(1,2,4-triazol-1-yl)propane: A modified literature procedure[12] was followed. To a solution of 0.5 mol 1*H*-1,2,4-triazole in 200 mL of absolute ethanol, an equimolar amount of metallic sodium was added in small portions, while cooling in ice and stirring vigorously. When the formation of sodium triazolate was completed, 0.22 mol of 1,3-dichloropropane was added, while still cooling and stirring. The solution was then heated under reflux for 7 days. After cooling to room temperature the precipitate of sodium chloride was filtered off. The ethanol filtrate was evaporated to a small volume, while the desired product separated. The compound was recrystallized from absolute ethanol (yield 64%). − ^{1}H NMR data ([D_6]DMSO, TMS as a standard): δ = 2.29 (q, 2 H), 4.18 (t, 4 H), 7.97 (s, 2 H), 8.52(s, 2 H).

Compounds 1 and 2: 1.2 mmol of hydrated Cu^{II} salt and 1.2 mmol of the ligand were each dissolved in 10 mL of water/acetonitrile (1:1). The Cu^{II} salt solution was then added slowly to the ligand solution and filtered to remove any undissolved material. After a few days the blue-green products separated and were isolated by filtration and dried in air (yield 70%). − Elemental analysis: for $Cu(btp)_2(CH_3CN)(H_2O)](CF_3SO_3)_2$: found (calc) (%) 27.82 (28.73) C, 3.24 (3.24) H, 22.43 (21.81) N, 14.67 (14.66) F, 8.18 (8.34) Cu. For $[Cu(btp)_2(CH_3CN)_2](ClO_4)_2$: found (calc) (%) 29.25 (30.84) C, 3.59 (3.74) H, 27.21 (27.98) N, 10.22 (10.12) Cl, 9.24 (9.07) Cu.

X-ray Data Collection and Structure Determination: The single crystal X-ray diffraction work was done at 150 K on an Enraf−Nonius CAD4T diffractometer with rotating anode and Mo-*Kα* radiation (graphite monochromator, λ = 0.71073 Å). Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry. No absorption correction was considered necessary. The structures were solved with automated Patterson methods and subsequent phase refinement techniques (DIRDIF[13a]). Refinement was done with SHELXL97.[13b] In **1** the non-hydrogen atoms of the acetonitrile molecule were refined as a rigid group; the hydrogens of the water molecule were refined freely with isotropic displacement parameters. All other hydrogens were located in the difference map and were not refined. In **2** the copper and chlorine were refined with anisotropic displacement parameters. All other non-hydrogen atoms were refined freely with isotropic displacement parameters; one of the acetonitrile molecules is disordered. The hydrogen atoms were in calculated positions and not refined. All other calculations were performed with the PLATON package.[13c] Crystallographic data and information about the structure determination are given in Table 2.

Colour pictures of Figures 3 and 4 are available as supplementary material (also on http://www.cryst.chem.uu.nl/structures/s1725a/s1725a.html)

Tables with atomic coordinates of all atoms, anisotropic thermal parameters, bond lengths and angles, and tables of observed and calculated structure factors are available from one of the authors (A.L.S.)

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115865 for structure **1** and CCDC-115866 for structure **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336−033, E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and details of the structure determination

Crystal data	**1**	**2**
Formula	$C_{18}H_{25}CuF_6N_{13}O_7S_2$	$C_{18}H_{26}Cl_2CuN_{14}O_8$
Formula weight	777.17	700.97
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
a [Å]	11.9337(15)	18.770(8)
b [Å]	20.108(6)	12.648(8)
c [Å]	12.748(6)	12.019(8)
β [°]	92.247(14)	90
V [$Å^3$]	3056.7(17)	2853(3)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.689	1.632
F(000)	1580	1436
μ [mm^{-1}]	0.95	1.02
Crystal size [mm]	0.65 × 0.23 × 0.23	0.15 × 0.10 × 0.10
Crystal colour	blue	blue
$(\sin\nu/\lambda)_{max}$	0.649	0.572
Refl.collected/ uniques	16416/7015	4595/2358
Restraints	0	32
Parameters	432	208
Goodness-of-fit on F^2	1.032	0.976
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0683, 0.1722	0.0846, 0.1860
Final *R*1, *wR*2 [all data]	0.0992, 0.1920	0.1707, 0.2189
Max. diff. peak and hole [e/$Å^3$]	2.483, −0.868	0.719, −0.755

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[14] The angles around the Cu^{II} ions are only slightly deviating from a perfect octahedron [N14−Cu−N24b = 178.51(12) and N34−Cu−N44b = 175.17(14)° for **1**; N14−Cu−N24c −178.0(6) and N34−Cu−N44d = 169.0(5)° for **2**]. The octahedron can therefore be considered as extended along the C_4 axis or as tetragonally distorted.

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