Supramolecular Architectures of Copper(II) Perchlorate Complexes of *cis,trans*-1,3,5-Triaminocyclohexane Assembled Exploiting the Delicate Balance Between Weak and Strong Interactions

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

The complexation of copper(II) perchlorate with *cis,trans*-1,3,5-triamino-cyclohexane (*trans*-tachH) yields four related mononuclear complexes, [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·(H$_2$O) (**1**), [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·2MeOH (**2**), [Cu(*trans*-tachH)$_2$(ClO$_4$)](ClO$_4$)$_3$ (**3**) and [Cu(*trans*-tach)(*trans*-tachH)(ClO$_4$)$_2$](ClO$_4$)·H$_2$O (**4**). These complexes only differ with respect to ligand protonation, solvent coordination / content, and counterion binding, yet these small differences manifest as vast differences in the supramolecular structures, and we also show that certain crystalline phases of these four compounds persist for different lengths of time in the mother liquor.

Key words: Self-assembly, Stoichiometry Control, Coordination Complexes, Supramolecular Chemistry, Hydrogen Bonding Networks

Introduction

Understanding and controlling the self-assembly of coordination compounds based upon coordinatively flexible metal ions is a formidable problem [1]. This is because the available structural parameter space is large and only can be explored by the subtle and complex manipulation of the variables, not to mention the lack of determinism associated with the crystallisation process [2, 3]. The use of ligand systems that can both take part in well defined strong and weak interactions simultaneously (*e. g.* metal ion coordination and hydrogen bonding) can help to explore this parameter space. In this respect we have been investigating the coordination chemistry of *cis,cis*- and *cis,trans*-1,3,5-triaminocyclohexane (tach), see Fig. 1 [4]. The *cis,cis*- and the *cis,trans*-tach, ligands (here named as *cis*-tach and *trans*-tach, respectively) have convergent and non-convergent coordination modes. In the case of *trans*-tach there are two different sites capable of coordination and hydrogen-bonding interactions, compared to *cis*-tach. Amino-based ligands with cyclohexane backbones generally have been well investigated [5 – 8]. Further, the structural rigidity of the ring is coupled to a conformational isomerisation (‘ring-flipping’) which occurs rapidly in solution and can provide the ligand

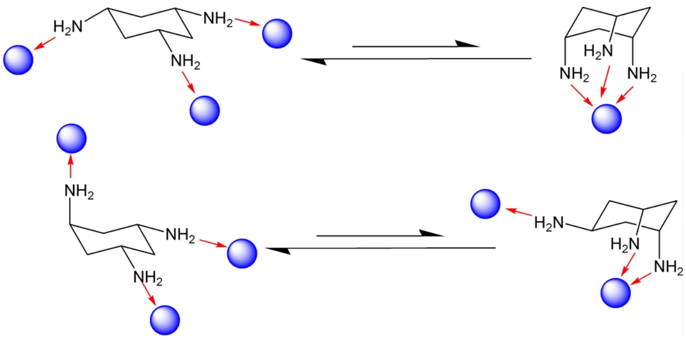

Fig. 1. (Top) The available coordination modes of *cis*-tach in the open (left) and ring-flipped (right) conformations. (Bottom) The available coordination modes of *trans*-tach in the open (left) and ring-flipped (right) conformations.

with two potentially quite different coordination sites [9 – 11].

In previous work based upon the coordination chemistry of *cis*- and *trans*- tach, not only have we been able to construct infinite networks with interesting topologies [4, 12, 13], but also we have been able to assemble topologically interesting coordination polymers based upon silver *cis*- and *trans*- tach [14] and $\{Cu_3Cl\}$ [15] clusters. In the case of the $\{Cu_3Cl\}$ clusters, these are arranged into a 3D hydrogen-bonding network, containing 1D magnetic chains, which give a material with very interesting magnetic properties [16]. Further, *trans*-tach has proved to be a useful ligand in the synthesis of many different cluster types including mononuclear complexes, infinite chains and discrete clusters. Amongst the most interesting have been a family of mixed metal $\{M_{12}\}$ clusters of nickel(II) and cobalt(II), which were constructed using the complementary reaction parameters of pH and Ni:Co ratio to yield a series of discrete clusters from $\{Ni_{12}\}$ to $\{Co_{12}\}$ where the individual clusters in the range contained a mixture of metals equivalent to the starting stoichiometries, and the series exhibits a stepwise magnetic transition from ferromagnetic to antiferromagnetic behaviour [17, 18].

Herein, we report the formation of four copper(II) perchlorate *trans*-tach clusters, isolated from similar reaction / crystalisation conditions but with different coordination modes and degree of protonation: [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·(H$_2$O) (**1**), [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·2MeOH (**2**), [Cu(*trans*-tachH)$_2$(ClO$_4$)](ClO$_4$)$_3$ (**3**) and [Cu(*trans*-tach)(*trans*-tachH)(ClO$_4$)$_2$](ClO$_4$)·H$_2$O (**4**) (see Fig. 2 for a summary of the structures), and we outline the intricate supramolecular architectures and also explain the relationship between the different compounds using crystallisation evidence.

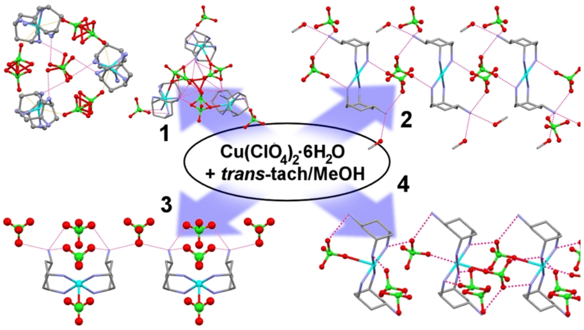

Fig. 2. Summary of compounds **1** – **4**. Colour scheme: chlorine atoms are in light green, oxygen atoms in red, carbon atoms in grey, nitrogen atoms in blue and copper atoms in light blue. *Inter*-complex hydrogen-bonding interactions are shown as pink dashed lines (colour online).

Results and Discussion

When copper(II) is complexed with *trans*-tach in the absence of bridging ligands such as acetate, the result is often the formation of simple clusters [11]. When copper(II) perchlorate is added to a solution of *trans*-tach in methanol which has been previously adjusted to pH = 7.7 *via* the addition of dilute perchloric acid, diffusion of diethyl ether yields four different compounds with subtly different primary structures, as a result of protonation state and solvation, and radically different crystallographic packing motifs. Furthermore, we observe that the crystalline forms of these compounds are not all stable and can convert over time in the mother liquor from one form to another.

*Structure analysis of [Cu(trans-tachH)$_2$](ClO$_4$)$_4$·H$_2$O (**1**)*

The first compound to crystallise from the solution is invariably the species [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·(H$_2$O), (**1**) where all pendant *trans*-amino groups are protonated, which crystallises in large purple hexagonal plate crystals after approximately 1 h, but re-dissolves shortly thereafter indicating the transient and meta-stable aspects of compound **1**, and this is also reflected in the isolated yield which is < 1 %. In

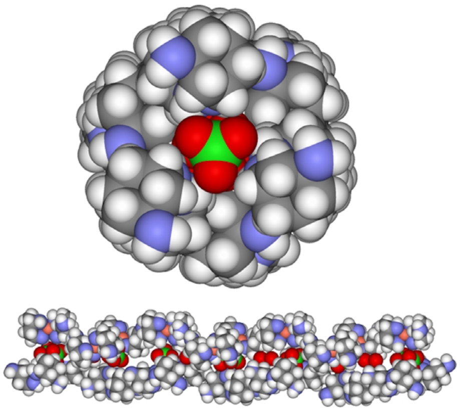

Fig. 3. View down the crystallographic *c* axis of the structure of compound **1** (top), and a view of the hydrogen-bonded chain that runs parallel the *ac* plane (bottom). Colour scheme: chlorine atoms are in green, oxygen atoms in red, carbon atoms in grey, nitrogen atoms in blue, and hydrogen atoms in white (colour online).

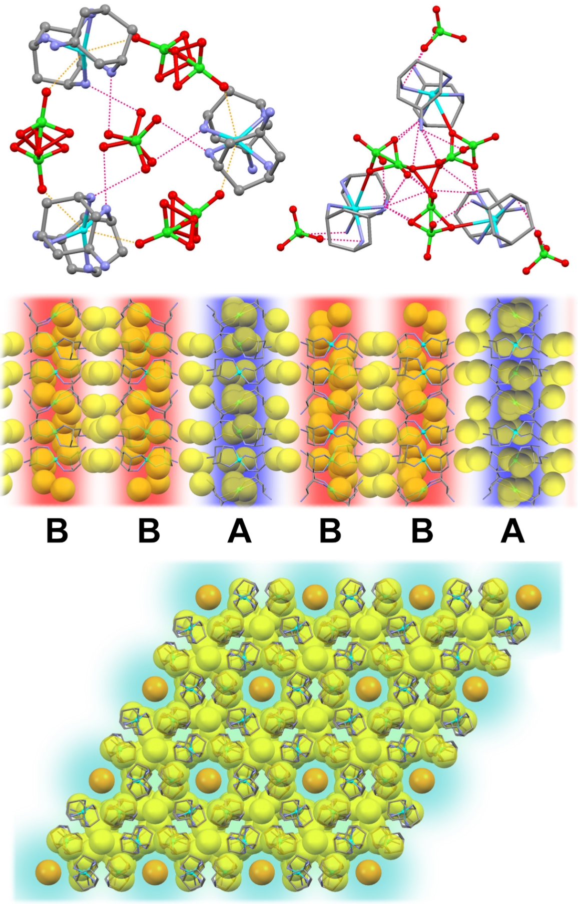

Fig. 4. (Top left) The trimeric 'ring' subunit of **1** illustrating the hydrogen-bonding interactions (pink dashed lines) between the amino groups of *trans*-tach and the disordered perchlorate anions. (Middle) Illustration of the molecular packing of **1**, viewed along the crystallographic *a* axis. Ring trimer units are highlighted in blue ('A' layer) and triangular trimers are highlighted in red ('B' layer), and (bottom) viewed along the crystallographic *c* axis emphasising the tube-like arrangement through the blue 'ring' trimers. Colour scheme: chlorine atoms are in light green, oxygen atoms in red, carbon atoms in grey, nitrogen atoms in blue and copper atoms in light blue. In the packing figures, perchlorate anions are shown as yellow spheres. *Inter*-compound hydrogen-bonding interactions are shown as pink dashed lines (colour online).

compound **1**, the copper(II) ions are found located in two separate coordination environments, where each of the copper(II) ions is ligated by two *trans*-tach groups, and these are arranged in an *anti* configuration with respect to each other. One of the units forms part of a hydrogen-bonded trimer of highly distorted octahedral Cu^{II} ions arranged around three perchlorate anions to form a triangular motif, and the other a highly distorted trimer of octahedral Cu^{II} centres, templated around a further perchlorate counterion to give a ring configuration. The most remarkable aspect of this structure is that a supramolecular ion-channel is formed around the perchlorate ions giving a hexagonal motif with a 78 Å unit cell *c* axis, see Figs. 3 and 4. It is also worth noting that this structure crystallises in the hexagonal chiral space group $P6_322$.

The real interest in this structure, however, does not concern the primary structure, but the plethora of supramolecular interactions which interlink the various monomeric copper(II) *bis*-tach coordination complexes. The 'triangle' trimer is stabilised by hydrogen bonding between the disordered perchlorate anions coordinated in the axial position of the Cu^{II} and the pendant *trans*-amino groups of the three ligands which are positioned with the 'tail' group pointing to the centre of the 'triangle' ($d(N\cdots O)$ range 2.863(7)–3.034(8) Å). Further hydrogen-bonding interactions occur between the axially coordinated perchlorate groups and the *cis*-amino groups of the other three *trans*-tach ligands (whose pendant amino groups point to the outside of the 'triangle'). The axially coordinated perchlorate groups are each disordered over two positions, where two are directed towards the outside of the triangle, and the other can be seen angled towards the centre (Fig. 4 (top right)).

The second trimer is also stabilised by hydrogen-bonding interactions ($d(N\cdots O)$ range 2.838(8)–2.970(4) Å), however, whereas in the first triangular trimer the hydrogen bonds are arranged along the sides of a triangle, in the second trimer all the interactions pass through a centrally templating perchlorate anion (Fig. 4 (top left)). The coordinating perchlorate ions which make up the circumference of the ring are all disordered over two positions, where each position is an elongated axial coordination site at a Cu^{II} centre.

The packing of the molecules of **1** gives rise to a startling nanoporous architecture. The two trimeric subunits are arranged such that layers of 'triangle' and 'ring' units are observed and are arranged in an ABBABBA packing motif which can be clearly illustrated when viewed along the crystallographic *a* axis (Fig. 4 (middle)). Individual trimers and layers are linked together through hydrogen-bonding interactions with disordered perchlorate counterions between ligand amino groups. When these layers are viewed along the crystallographic *c* axis, a nanotube-like architecture can be observed, with a tube diameter of *ca.* 7 Å (Fig. 4 (bottom)). Despite the large and elegant architecture

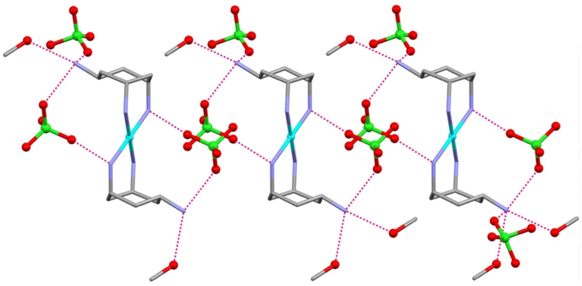

Fig. 5. The hydrogen-bonding pattern in the chain configuration of the monomers of **2** (shown in pink). All colour assignments are as shown previously, hydrogen atoms are removed for clarity (colour online).

assembled in **1**, the crystals are extremely unstable and only exist for a number of hours in solution. Upon redissolution, the same mother liquor yields three more *trans*-tach copper(II) perchlorate compounds (**2**–**4**).

*Structure analysis of [Cu(trans-tachH)$_2$](ClO$_4$)$_4$· 2MeOH (**2**)*

In this complex, [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$· 2MeOH, (**2**), all the pendant amino groups are protonated. The stoichiometry differs from that of **1** only in the inclusion of two methanol molecules within the lattice instead of a water molecule. The primary structure is a simple mononuclear unit, with a square planar Cu^{II} centre coordinated by two *trans*-tach ligands through the chelating head groups, arranged in an *anti* configuration. Four non-coordinated perchlorate counterions and two methanol molecules complete the crystal structure. The monomers are stabilised through hydrogen bonding between the protonated pendant *trans*-amino groups and the associated methanol and perchlorate molecules (d(N···O) range 2.839(4)–3.012(4) Å), resulting in a stepped chain configuration (Fig. 5). This chain packing motif is in contrast to the nanotube-type architecture seen in **1**.

*Structure analysis of [Cu(trans-tachH)$_2$(ClO$_4$)]-(ClO$_4$)$_3$ (**3**)*

In the second structure to come from the evaporation of the mother liquor, all the pendant amino groups are protonated, but in contrast to **1** and **2**, the copper(II) centre coordinates one perchlorate anion, and no solvent molecules are found in the crystal structure. Two *trans*-tach ligands are coordinated to a square-based pyramidal copper(II) centre in a *syn* configuration, and interact with each other through hydrogen bonding interactions with two perchlorate counterions between the ligands. The elongated axial coordination site of the copper atom is taken up by a perchlorate counterion with a Cu–O distance of 2.48(1) Å. Each ligand is involved in hydrogen bonding with one further perchlorate counterion linking the mononuclear complexes into an extended chain-like arrangement (d(N···O) range 2.869(2)–2.980(1) Å) (Fig. 6).

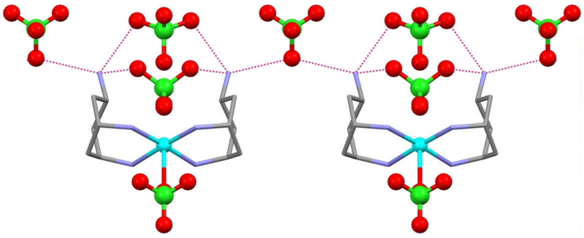

Fig. 6. The hydrogen-bonding pattern in the chain configuration of the monomers of **3** (shown in pink). All colour assignments are as shown previously, hydrogen atoms are removed for clarity (colour online).

*Structure analysis of [Cu(trans-tach)(trans-tachH)-(ClO$_4$)$_2$](ClO$_4$)·H$_2$O (**4**)*

The final structure to crystallise is again a monomeric complex, but in this case only one of the two non-coordinated amino groups of the ligand is protonated. The two *trans*-tach ligands are coordinated in an *anti* configuration to a pseudo Jahn-Teller-distorted octahedral Cu^{II} centre, with the two axial coordination sites occupied by perchlorate anions with Cu–O distances of 2.75(1) and 2.80(1) Å. The monomers are connected through hydrogen bonding into chains, which are then further hydrogen-bonded to form a 3D network (d(N···O) range 2.60(5)–3.052(5) Å) (Fig. 7). The network formed is very

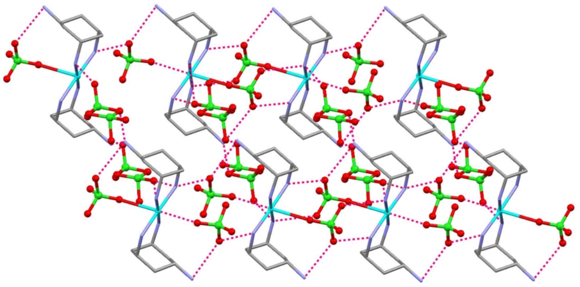

Fig. 7. The hydrogen-bonding pattern in the chain configuration of the monomers of **4**. Pink lines represent *intra*-chain and *inter*-chain hydrogen bonds. All colour assignments are as shown previously, hydrogen atoms are removed for clarity (colour online).

Table 1. Assignment of CSI-MS data collected for the mother liquor that gives rise to compounds **1**–**4**.

m/z	Assignment
522.06	$[Cu(C_6H_{15}N_3)_2(ClO_4)_2H]^+$
622.02	$[Cu(C_6H_{15}N_3)_2(ClO_4)_3H_2]^+$
682.94	$[Cu_2(C_6H_{15}N_3)_2(ClO_4)_3]^+$

different from that observed in **1**, and no tube-like motif is observed.

To gain information regarding the building blocks present in solution, cryospray mass spectrometry was carried out on the mother liquor at 253 K, and the results of this study illustrate the variety of fragments present in solution which are transferred to the gas phase. Species corresponding to varying degrees of protonation and aggregation could be observed, providing an initial insight into the self-assembly and a glimpse of the various building blocks present in the mother liquor (Table 1). It would appear that the standard unit in the self assembly observed is the mononuclear diligand complex, which can be seen as the mono- and di-protonated species and also with the addition of a second Cu^{II} centre. This corresponds well to the building blocks seen in **1**–**4** and indicates that all four coordination complexes found are also present in the solution phase.

Conclusions

The reaction of copper(II) perchlorate with *trans*-tach in methanol gives rise to four different species, all of which can be precipitated from a common reaction mixture. The different species are all mononuclear complexes, but differ in their protonation, solvent content and counterion binding. Despite the stark differences in packing motifs displayed, the formulae for compounds **1**–**4** are remarkably similar. Compound **1** packs into a nanotube-like motif along the crystallographic *c* axis and can be formulated as [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·(H$_2$O). Compound **2** differs from **1** only by the associated solvent molecules, [Cu(*trans*-tachH)$_2$](ClO$_4$)$_4$·2MeOH, in that two methanol molecules have replaced one water molecule. The result in terms of packing, however, is more diamatic, with a less densely packed array formed. Compound **3** differs from **1** by having one perchlorate counterion coordinated to the copper(II) centre and no lattice solvent molecules, and compound **4** differs in so far as its ligands are only monoprotonated, and the copper(II) centre coordinates two perchlorate counterions. Therefore, we can tentatively postulate that compound **1** is a transient species, only being stable in solution for 1 h and isolatable in a < 1 % yield, whereas compounds **2** and **3** are metastable species (appearing after a few days, and crystals being stable for several weeks in solution), and compound **4** appears to be the overall most stable product that is formed in highest yield, since over long time periods compounds **1**–**3** dissolve and reprecipitate as compound **4**. In further work we will attempt to stabilise compound **1**, and to investigate the possible migration of ClO_4^- anions through the channel-like architecture as well as more accurately follow the transformation of the compounds.

Experimental Section

Reactions in water were carried out using deionised water prepared using an Elgastat B118/B deioniser. Other solvents were supplied by Fisher Chemicals while all other reagents were supplied by Aldrich Chemical Company Ltd., Fisher Chemicals, or VWR International, and were used without further purification unless otherwise stated. The ligand *trans*-tach was synthesised from 1,3,5-triaminobenzene following literature methods [19]. All other reagents and solvents were purchased as AR grade and used without further purification. Fourier transform infrared (FT-IR) spectra were run on a JASCO FTIR 410 spectrometer. Mass spectra were collected using a Bruker microTOFQ spectrometer with the Cryospray attachment.

*[Cu(trans-tachH)$_2$](ClO$_4$)$_4$·(H$_2$O) (**1**)*

Cu(ClO$_4$)$_2$·6H$_2$O (76.6 mg, 0.207 mmol) was added to a solution of *trans*-tach (50 mg, 0.388 mmol) in methanol (30 mL), which had been acidified to pH = 7.59 *via* the drop-wise addition of perchloric acid (11 %), and stirred for 30 min until completely dissolved, giving a purple colour. The solution was then set up to crystallise by diethyl ether diffusion or evaporation. After the period of approximately 50 min purple single crystals (hexagonal plates) had formed. Yield: *ca.* 0.36 %, 0.55 mg (crystals stable for less than 1 h in solution). – Elemental analysis for $C_{12}H_{34}Cl_4CuN_6O_{17}$ (739.79) (%): calcd. C 19.48, H 4.63, N 11.36; found C 19.57, H 4.25, N 10.96. – FT-IR (KBr): ν = 3296 (m), 3251 (m), 3147 (m), 3107 (m), 1597 (s), 1516 (s), 1176 (s), 1151 (s), 1089 (s), 1036 (b.v.s), 912 (s), 777 (m), 685 cm^{-1} (m).

*[Cu(trans-tachH)$_2$](ClO$_4$)$_4$·2MeOH (**2**),*
*[Cu(trans-tachH)$_2$(ClO$_4$)](ClO$_4$)$_3$(**3**), and*
*[Cu(trans-tach)(trans-tachH)(ClO$_4$)$_2$](ClO$_4$)·H$_2$O (**4**)*

Compounds **2**, **3**, and **4** were obtained as described for **1** after a period of 3 d as reddish (**2**), violett (**3**), and pink (**4**)

Table 2. Crystal structure data for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{12}H_{34}Cl_4CuN_6O_{17}$	$C_{14}H_{40}Cl_4CuN_6O_{18}$	$C_{12}H_{32}Cl_4CuN_6O_{16}$	$C_{12}H_{33}Cl_3CuN_6O_{13}$
M_r, g mol^{-1}	739.79	785.86	721.78	639.33
Crystal size, mm^3	0.40 × 0.20 × 0.05	0.40 × 0.26 × 0.06	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.05
Crystal system	hexagonal	triclinic	orthorhombic	triclinic
Space group	$P6_322$	$P\bar{1}$	*Pnma*	$P\bar{1}$
a, Å	14.188(2)	8.1205(2)	14.444(2)	9.6463(10)
b, Å	14.188(2)	8.5001(2)	11.2712(18)	10.1623(10)
c, Å	77.835(15)	11.6673(3)	16.382(3)	13.5771(11)
α, deg	90	86.515(1)	90	106.420(8)
β, deg	90	77.901(1)	90	97.402(8)
γ, deg	120	68.424(1)	90	104.559(9)
V, Å^3	13569(4)	732.15(3)	2667.0(7)	1206.7(2)
Z	18	1	4	2
D_{calcd}, g cm^{-3}	1.63	1.78	1.80	1.76
μ, mm^{-1}	5.0 (CuK_α)	1.2 (MoK_α)	5.6 (CuK_α)	1.3 (MoK_α)
F(000)	6858	407	1484	662
hkl range	$-13 \le h \le +15$	$-11 \le h \le +11$	$-16 \le h \le +16$	$-11 \le h \le +10$
	$-15 \le k \le +14$	$-11 \le k \le +11$	$-12 \le k \le +12$	$-12 \le k \le +12$
	$-84 \le l \le +70$	$0 \le l \le +16$	$-18 \le l \le +18$	$-16 \le l \le +16$
Refl. measured	53642	15419	12893	12610
Refl. unique	6519	4238	2085	4320
R_{int}	0.0723	0.0560	0.0790	0.0332
Param. refined	565	224	196	315
Flack parameter	0.39(3)	–	–	–
$R(F)$ / $wR(F^2)$[a] (all refl.)	0.0936 / 0.2661	0.0423 / 0.1105	0.1145 / 0.2410	0.0500 / 0.1377
GoF (F^2)[b]	1.091	1.041	1.168	0.978
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	2.54 / −0.74	0.77 / −0.68	1.03 / −1.25	1.07 / −0.82

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [b] GoF = $S = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

crystals **2**: Yield: *ca.* 5.3 %, 8.62 mg (stable in solution for less than 24 h). – Elemental analysis for $C_{14}H_{40}Cl_4CuN_6O_{18}$ (785.85) (%): calcd. C 21.40, H 5.13, N 10.69; found C 20.23, H 4.36, N 11.51. – FT-IR (KBr): ν = 3219 (mb), 3136 (mb), 1595 (mb), 1516 (wb), 1049 (sb), 920 cm^{-1} (w).

3: Yield: *ca.* 2.1 %, 3.14 mg (stable in solution for less than 24 h). – Elemental analysis for $C_{12}H_{32}Cl_4CuN_6O_{16}$ (721.77) (%): calcd. C 19.97, H 4.47, N 11.64; found C 20.03, H 4.49, N 11.69. – FT-IR (KBr): ν = 3294 (w), 3252 (w), 3117 (wb), 1597 (m), 1516 (m), 1150 (m), 1088 (m), 1038 (sb), 914 (m), 883 (m), 779 (w), 687 (m), 621 cm^{-1} (s).

4: Yield: *ca.* 16.7 %, 22.10 mg (stable in solution for more than 2 d). – Elemental analysis for $C_{12}H_{33}Cl_3CuN_6O_{13}$ (639.33) (%): calcd. C 22.54, H 5.20, N 13.15; found C 19.65, H 4.22, N 10.98. – FT-IR (KBr): ν = 3296 (s), 3251 (s), 3156 (s), 1600 (s), 1519 (m), 1092 (sb), 925 (m), 914 (m), 627 cm^{-1} (s).

X-Ray structure determination

Suitable single crystals of **1**–**4** were grown and mounted onto the end of a thin glass fiber using Fomblin oil. X-Ray diffraction intensity data were measured at 150 K on a Nonius Kappa-CCD diffractometer [λ(MoK_α) = 0.71073 Å], graphite monochromator. Structure solution and refinement for **1**–**4** was carried out with SHELXS-97 [20] and SHELXL-97 [21] *via* WINGX [22]. Corrections for incident and diffracted beam absorption effects were applied using empirical [23] or numerical methods [24]. Compounds **2** and **4** crystallised in the space group $P\bar{1}$, compound **1** in $P6_322$ and compound **3** in *Pnma*, as determined by systematic absences in intensity data, intensity statistics and the successful solution and refinement of the structures. Compound **1** was refined as a racemic twin, with the inversion matrix TWIN −1 0 0 0 −1 0 0 0 −1 2 (shown as TWIN-defaults), and the BASF coefficient 0.39(3) was refined (Table 2). All structures were solved by a combination of Direct Methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters and refinement statistics for **1**–**4** are listed in Table 2.

CCDC 755421–755424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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