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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Z. Naturforsch. 2010, 65b, 304 – 310; received November 23, 2009
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, \([\text{Cu}(\text{trans-tachH})_2](\text{ClO}_4)_4 \cdot (\text{H}_2\text{O})\) (1), \([\text{Cu}(\text{trans-tachH})_2](\text{ClO}_4)_4 \cdot 2\text{MeOH}\) (2), \([\text{Cu}(\text{trans-tachH})_2(\text{ClO}_4)](\text{ClO}_4)_3\) (3) and \([\text{Cu}(\text{trans-tach})(\text{trans-tachH})(\text{ClO}_4)_2](\text{ClO}_4)_3\cdot \text{H}_2\text{O}\) (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...
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 \{Cu3Cl\} [15] clusters. In the case of the \{Cu3Cl\} 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 \{M12\} 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 \{Ni12\} to \{Co12\} 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/crystallisation conditions but with different coordination modes and degree of protonation: [Cu(trans-tachH)2](ClO4)4·H2O (1), [Cu(trans-tachH)2](ClO4)4·2MeOH (2), [Cu(trans-tachH)2](ClO4)2·(ClO4)3 (3) and [Cu(trans-tach)(trans-tachH)(ClO4)2](ClO4)·H2O (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.

**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](ClO4)4·H2O (1)**

The first compound to crystallise from the solution is invariably the species [Cu(trans-tachH)2](ClO4)4·(H2O), 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
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 CuII ions arranged around three perchlorate anions to form a triangular motif, and the other a highly distorted trimer of octahedral CuII 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 CuII 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 CuII 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
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(CIO4)2]·2MeOH (2)

In this complex, [Cu(trans-tachH)2(CIO4)2]·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 CuII 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)(trans-tachH)-(ClO4)2](ClO4)·H2O (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 CuII 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...
Table 1. Assignment of CSI-MS data collected for the mother liquor that gives rise to compounds 1–4.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>522.06</td>
<td>[Cu(C6H5N3)(ClO4)2H]3-</td>
</tr>
<tr>
<td>622.02</td>
<td>[Cu(C6H5N3)(ClO4)2H2]2+</td>
</tr>
<tr>
<td>682.94</td>
<td>[Cu2(C6H5N3)2(ClO4)3]2+</td>
</tr>
</tbody>
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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 mononuclear diligand complex, and also with the addition of a second CuII 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](ClO4)4·(H2O). Compound 2 differs from 1 only by the associated solvent molecules, [Cu(trans-tachH)2](ClO4)4·2MeOH, in that two methanol molecules have replaced one water molecule. The result in terms of packing, however, is more diomatic, 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 ClO4− 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](ClO4)4·(H2O) (1)

Cu(ClO4)2·6H2O (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 C12H34Cl4CuN6O17 (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](ClO4)4·2MeOH (2), [Cu(trans-tachH)2](ClO4)4·(H2O) (1), [Cu(trans-tachH)2](ClO4)4·(H2O) (1), and [Cu(trans-tachH)2](ClO4)4·(H2O) (1)·H2O (4)

Compounds 2, 3, and 4 were obtained as described for 1 after a period of 3 d as reddish (2), violet (3), and pink (4)
crystals 2: Yield: ca. 5.3 %, 8.62 mg (stable in solution for less than 24 h). – Elemental analysis for C\textsubscript{14}H\textsubscript{20}Cl\textsubscript{4}Cu\textsubscript{6}N\textsubscript{6}O\textsubscript{18} (785.85) (%): calcd. C 21.39, H 4.36, N 12.14, found C 21.23, H 4.35, N 12.13. – FT-IR (KBr): \(\nu\) = 3221 (m), 1517 (m), 1049 (s), 2920 cm\(^{-1}\) (w).

3: Yield: ca. 2.1 %, 3.14 mg (stable in solution for less than 24 h). – Elemental analysis for C\textsubscript{14}H\textsubscript{20}Cl\textsubscript{4}Cu\textsubscript{6}N\textsubscript{6}O\textsubscript{16} (721.77) (%): calcd. C 21.97, H 4.47, N 11.64, found C 21.93, H 4.48, N 11.69. – FT-IR (KBr): \(\nu\) = 3229 (w), 2922 (w), 2956 (w), 2859 (w), 2850 (w), 1519 (m), 1517 (m), 1088 (m), 1038 (s), 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\textsubscript{14}H\textsubscript{20}Cl\textsubscript{4}Cu\textsubscript{6}N\textsubscript{6}O\textsubscript{13} (639.33) (%): calcd. C 22.54, H 5.20, N 13.15, found C 21.65, H 4.22, N 10.98. – FT-IR (KBr): \(\nu\) = 3296 (s), 3251 (s), 3156 (s), 1600 (s), 1519 (m), 912 (s), 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 [\(\lambda\) (Mo\textsubscript{Kaa}) = 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 P1\(^\text{1}\), compound 1 in P6\(_3\)2\(_2\) 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 and B are constants adjusted by the program; b GoF = \(\sum||F_o|-|F_{cal}||^2/\sum wF_o^2\) (all refl.) = 0.0936/0.2661, 0.0423/0.1105, 0.1145/0.2410, 0.0500/0.1377, where \(n_{obs}\) is the number of data and \(n_{param}\) the number of refined parameters.
Acknowledgement

We would like to thank the EPSRC, WestCHEM and the University of Glasgow for funding.