SUPPLEMENTARY MATERIAL

1,2,4-Triazole functionalized adamantanes: A new library of polydentate tectons for the designing structures of coordination polymers†

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Contents:

1. Synthesis of the ligands

Selective bromination of adamantane

Bromination is a first convenient step for the multi-stage synthesis of functionalized adamantanes. The bromination could be carrient out in almost quantitative yield and highly selectively, yielding pure 1-mono-; 1,3-di-; 1,3,5-tri- and 1,3,5,7-tetrabrominated products:

1) Bromination of adamantane in net bromine at 40-50^{o}C for 2 h yields 100% of 1-bromoadamantane.

2) Bromination of adamantane in net bromine in the presence of Fe powder (r.t., 1-2 h) gives 1,3-dibromoadamantane in over 90% yield.

3) Bromination in net bromine in the presence of Fe powder at the reflux for 24 h provides pure 1,3,5-tribromoadamantane with more then 90% isolable yield.

4) Bromination in net bromine in the presence $AlCl_3$ at the reflux for 24 h gives pure 1,3,5,7-tetrabromoadamantane in almost 80% yield.

We have optimized preparation of most valuable partially brominated products. The following methods provide convenient large-scale preparations of 1,3-di- and 1,3,5-tribromoadamantanes.

1.1. Preparative synthesis of 1,3-dibromoadamantane

The procedure was developed as a large-scale adaptation of the literature method, which was given without any isolation details [I.R. Likhotvorik, N.L. Dovgan and G.I. Danilenko, *Zhurn. Organ. Khimii* (*Russ. J. Org. Chem.*), 1977, 13 (4), 897].

7.00 g of Fe powder was added at once to 280 mL bromine, the mixture was stirred for 30 min at r.t. and then cooled in an ice-bath. After this, 96.0 g adamantane was added in 5-6 g portions over period of 1 h under efficient stirring, which was accompanied with extensive evolution of HBr gas. The mixture was stirred for additional 1 h at r.t. and poured into 1 kg of crushed ice mixed with solid Na_2SO_3 (550 g). The deposit was carefully triturated and stirred until disappearance of the brown coloration. The product was filtered and washed with 100 mL 5% HCl and with 0.5 L water and dried in air. Repeated recrystallization from 2-propanol with charcoal gives pure 1,3-dibromoadamantane as colorless crystals with m.p. = 111-112^{o}C. The yield was 160.6 g (77%).

Evaporation of the 2-propanol filtrates and recrystallization of the combined residues provides additional 31.3 g of the pure product. The total yield: 191.9 g (92%).

1.2. Preparative synthesis of 1,3,5-tribromoadamantane.

The procedure was developed as a large-scale adaptation of the literature method [R.E. Delimarskii, V.N. Rodionov and A.G. Yurchenko, *Ukr. Khim. Zhurnal* (*Ukrainian J. Chem.*), 1988, 54, 437]. Synthesis of nearly 0.5 kg 1,3,5-tribromoadamantane was conducted in three separate equal bathces in order to minimize amount of bromine.

250 mL of bromine (without special purification) was placed into 1 L two-necked flask equipped with a large magnetic stirring bar and powerful double-Dimroth reflux condenser. 22.0 g of Fe powder was added at once and the mixture was stirred for 30 min at r.t. Then the mixure was cooled in an ice-bath, and 68.0 g adamantane was added in 4-5 g portions over period of 1 h. This was accompanied by immediate and extensive evolution of HBr. After the addition was completed, then mixtrure was extensively refluxed with stirring for 24 h. The excess of bromine was distilled off (bath temperature to 95^{o}C; 120 mL bromine recovered, which was used for the next identical batch) and the black residue, while hot, was poured into 0.3 kg of crushed ice mixed with excess of Na_2SO_3. The brown-black semi-solid product was combined after three identical batches (in total, 204.0 g adamantane brominated), it was extracted with 3 × 500 mL $CHCl_3$ and the aqueous layer was additionaly extracted with 3 × 150 mL $CHCl_3$. The combined extracts were subsequently washed with 500 mL of 7% Na_2SO_3 solution, 500 mL of 5% HCl solution and then with 500 mL water. The extract was dried with Na_2SO_4 and the solvent was distilled off to bath temperature 95-100^{o}C. The residue was cooled, the brownish crystalline product was filtered and washed with some cold $CHCl_3$. It was twice recrystallized from 2-propanol with charcoal giving pure colorless 1,3,5-tribromoadamantane with m.p.= 126-127^{o}C. The yield was 458.4 g (82%). Evaporation of the 2-propanol filtrates and single recrystallization of the combined residues provides additional 50.3 g (9%) of the colorless product with m.p.=126^{o}C. Total yield: 508.7 g (91%).

1.3. Synthesis of 1,3,5-Trihydroxyadamantane

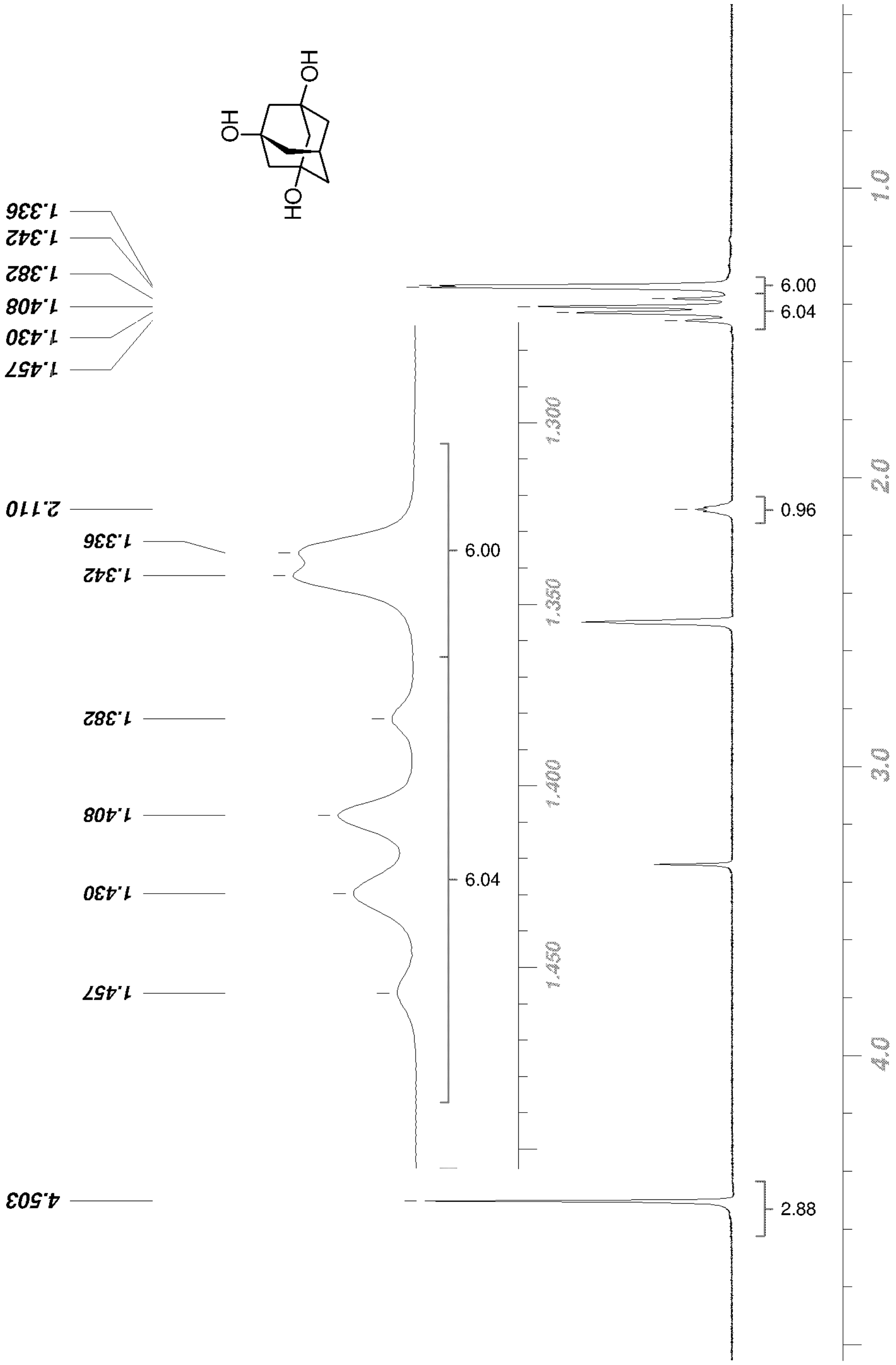
The synthesis was carried out according to the modified method of Stetter [Stetter, H.; Wulff, C., Uber Verbindungen Mit Urotropin-Struktur .18. Uber Die Bromierung Des Adamantans. *Chemische Berichte-Recueil* **1960,** 93, (6), 1366-1371].

The method of Stetter was satisfactorily reproduced on the same scale as originally reported. Though, the purity of the product was not high. Some coloration could not be removed by treatment with charcoal and subsequent recrystallization. The product also darkened with time as it contained traces of silver. Even more significant is that on larger scales the purity of the product was dramatically worse and the yields were not stable and consistent. The continuous extraction by alcohol was also not well-compatible with large scale synthesis and the use of multiple washings were not high-yielding because of lumping of inorganic salts and, probably, because of occlusion.

The modified method, appropriate for large-scale syntheses is described below:

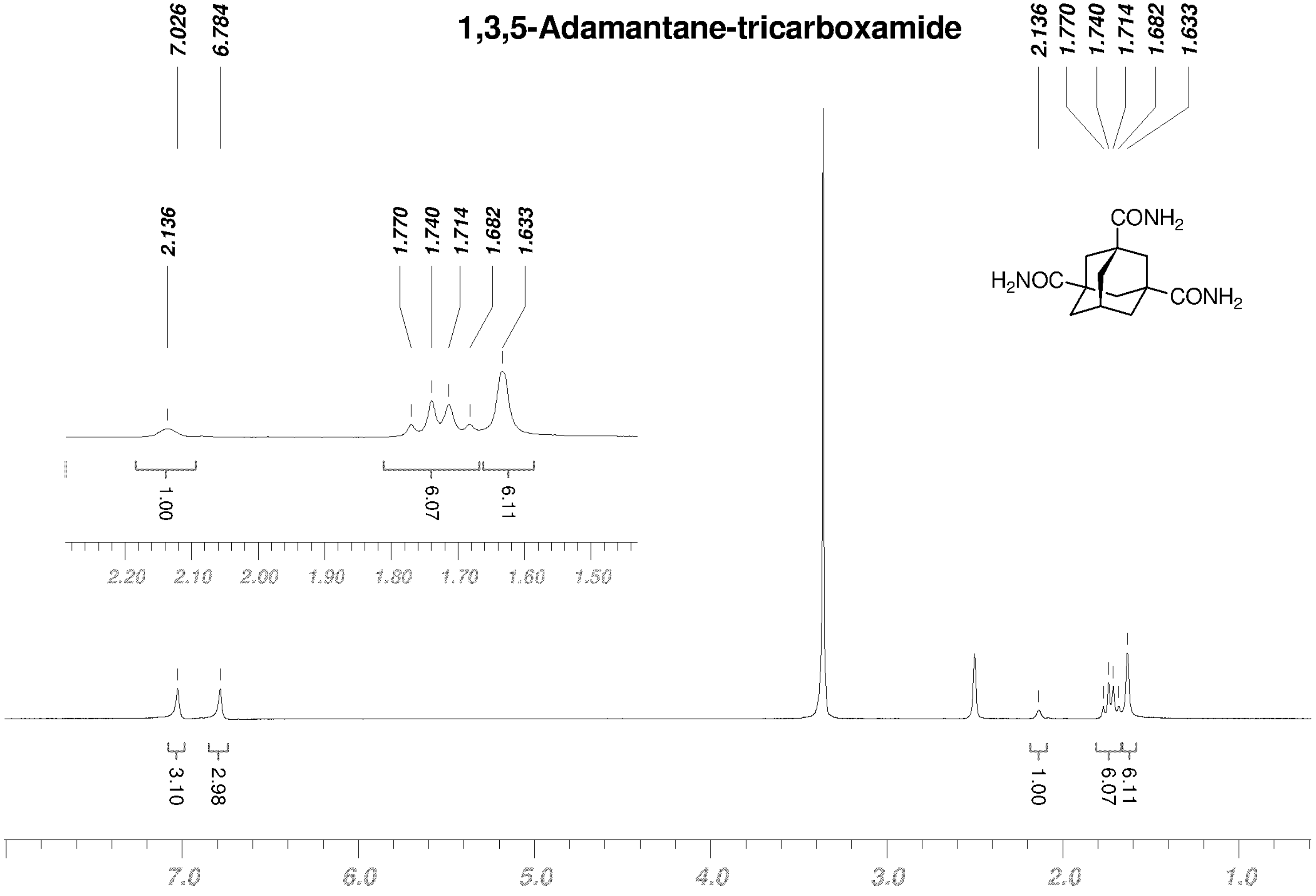
In a 1 L flask equipped with a large magnetic stirring bar, 100 mL of water was placed, to which 300 mL of conc. H_2SO_4 was added accurately to prevent overheating. The formed solution was cooled below 60°C and 90.0 g of Ag_2SO_4 was added at once and 54.0 g (14.5 mmol) of 1,3,5-tribromoadamantane was followed. The temperature was raised to 80°C and the reaction mixture was heated at that temperature exactly for 3 h.

In a short time after the beginning, the solid phase turned light yellowish-green and darkened as the reaction proceeded further, turning yellowish-brown with brown supernatant. After the reaction finished, the contents of the flask was cooled in an ice/water bath and poured on 400 g ice in a 2 L beaker. The resultant slurry was cooled down again and was carefully neutralized (pH~7) by slow addition of 25% aqueous ammonia (at the beginning, the reaction is quite violent, but addition of crushed ice to the reaction medium made the process tolerable; at the end, the total volume of the mixture was in the range of 1.5-2 L). 50 mL of conc. HCl was added then for precipitating the silver, remaining in the solution. The precipitate was filtered off and carefully washed by multiple portions of hot water (5x150 ml). The combined aqueous filtrates were neutralized (pH~7) again by conc. ammonia solution and concentrated down to ~700 ml. The formed solution with partially precipitated ammonium sulfate was diluted with water exactly to the point when most of the precipitate dissolved. The saturated saline solution containing some precipitate of the product was thoroughly extracted by 6x150 ml of iPrOH. The combined organic extracts were evaporated to dryness and the residue, consisted mainly of the product with some inorganic salts was recrystallized from 400 ml of wet dioxane (~3-5% water) by recycling the mother solution after cooling and the removal of the recrystallized product, which crystallizes out in a form of a hydrate. The hydrated product was dried on the air at 120°C until constant weight to give 19.63 g of 1,3,5-trihydroxyadamantane as a slightly yellow powder. The concentration of the mother liquour yields additional 2.75 g of crude product. The combined yield is 22.3 g (84%, lit. : 65%).

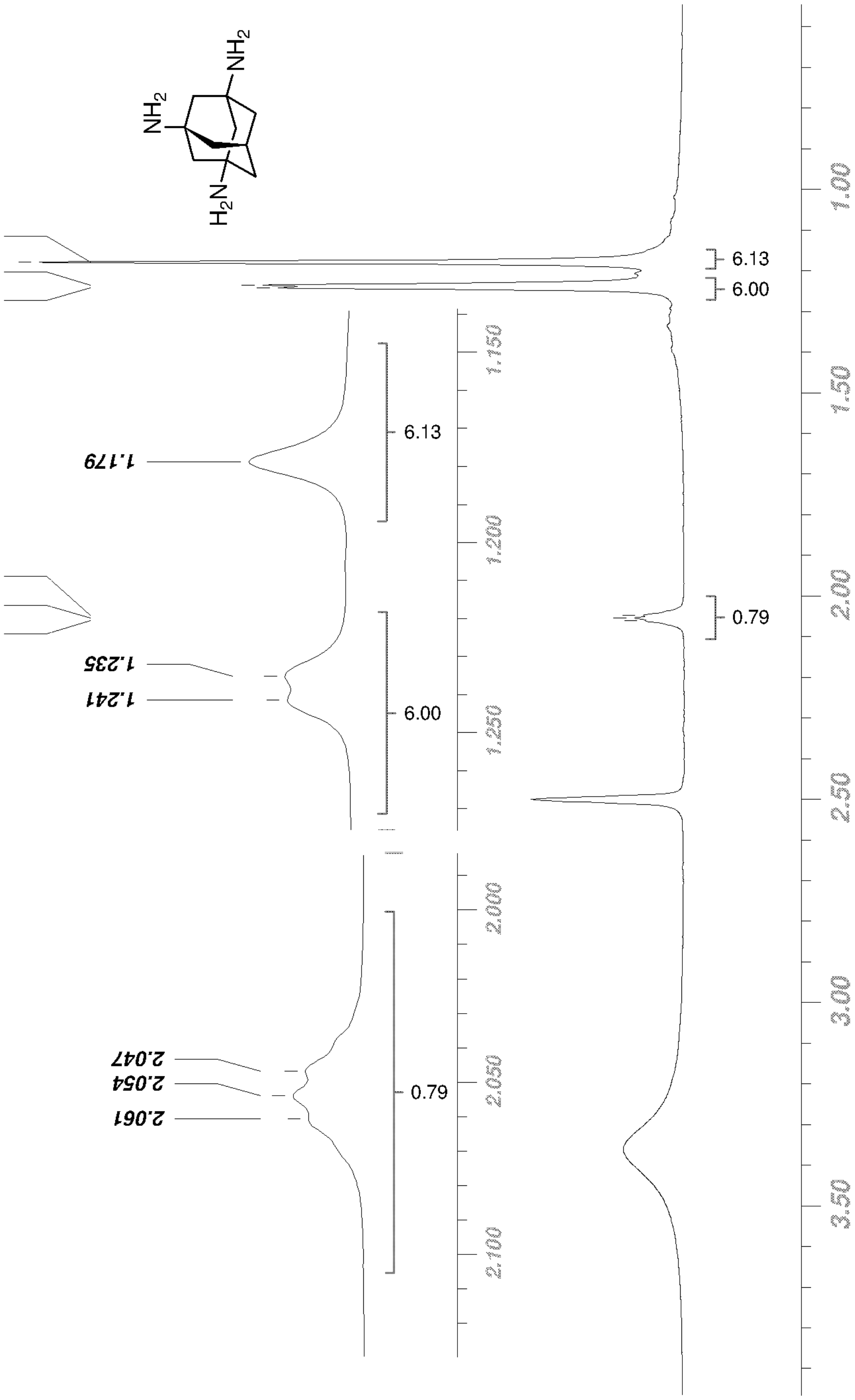


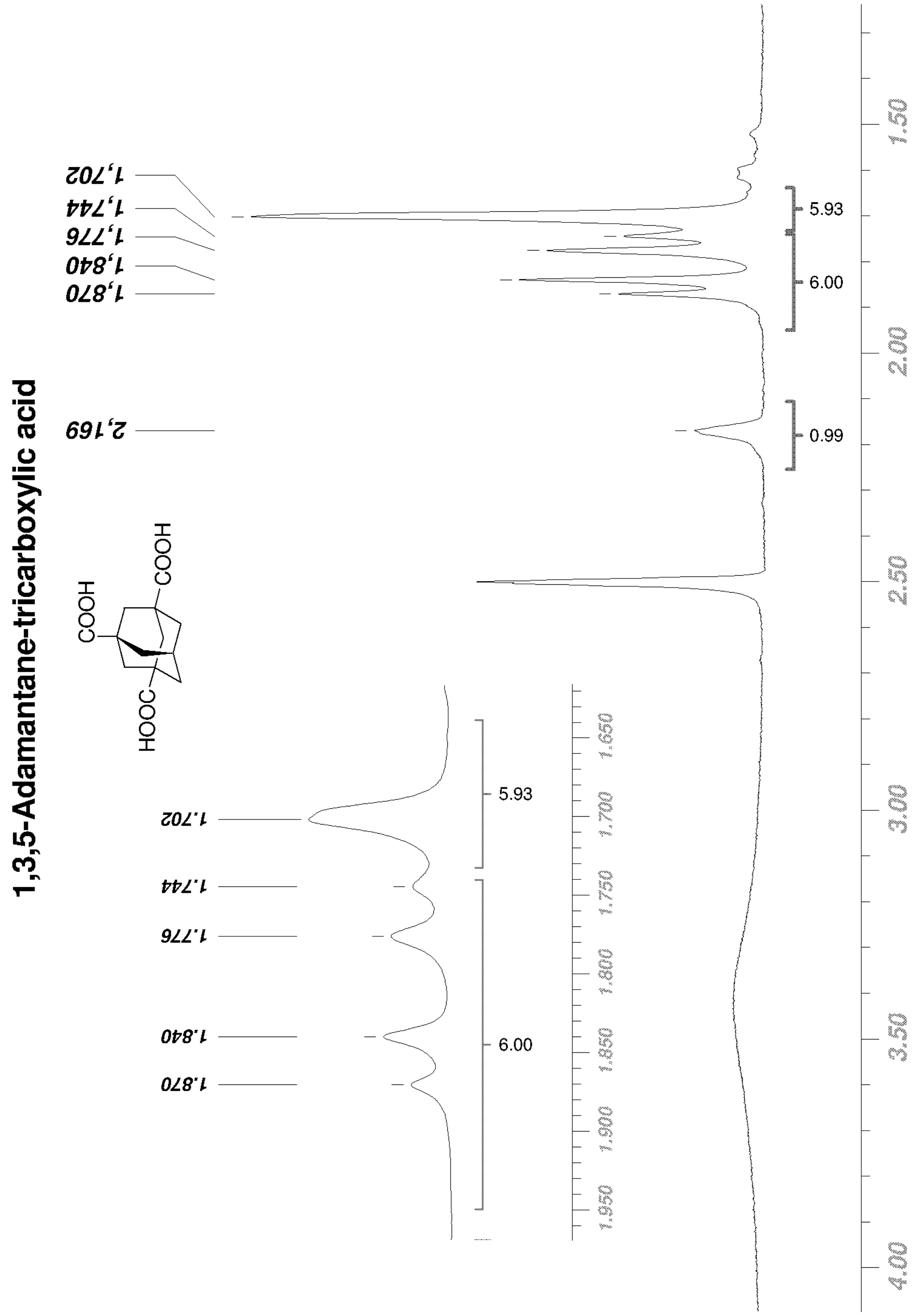
1,3,5-Trihydroxyadamantane

1,3,5-Adamantane-tricarboxamide



1,3,5-Triaminoadamantane




1,3,5-Adamantane-tricarboxylic acid
COOH
COOH
HOOC
1,702
1,744
1,776
1,840
1,870
2,169
5.93
6.00
0.99
1.50
2.00
2.50
3.00
3.50
4.00
1.702
1.744
1.776
1.840
1.870
5.93
6.00
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1.850
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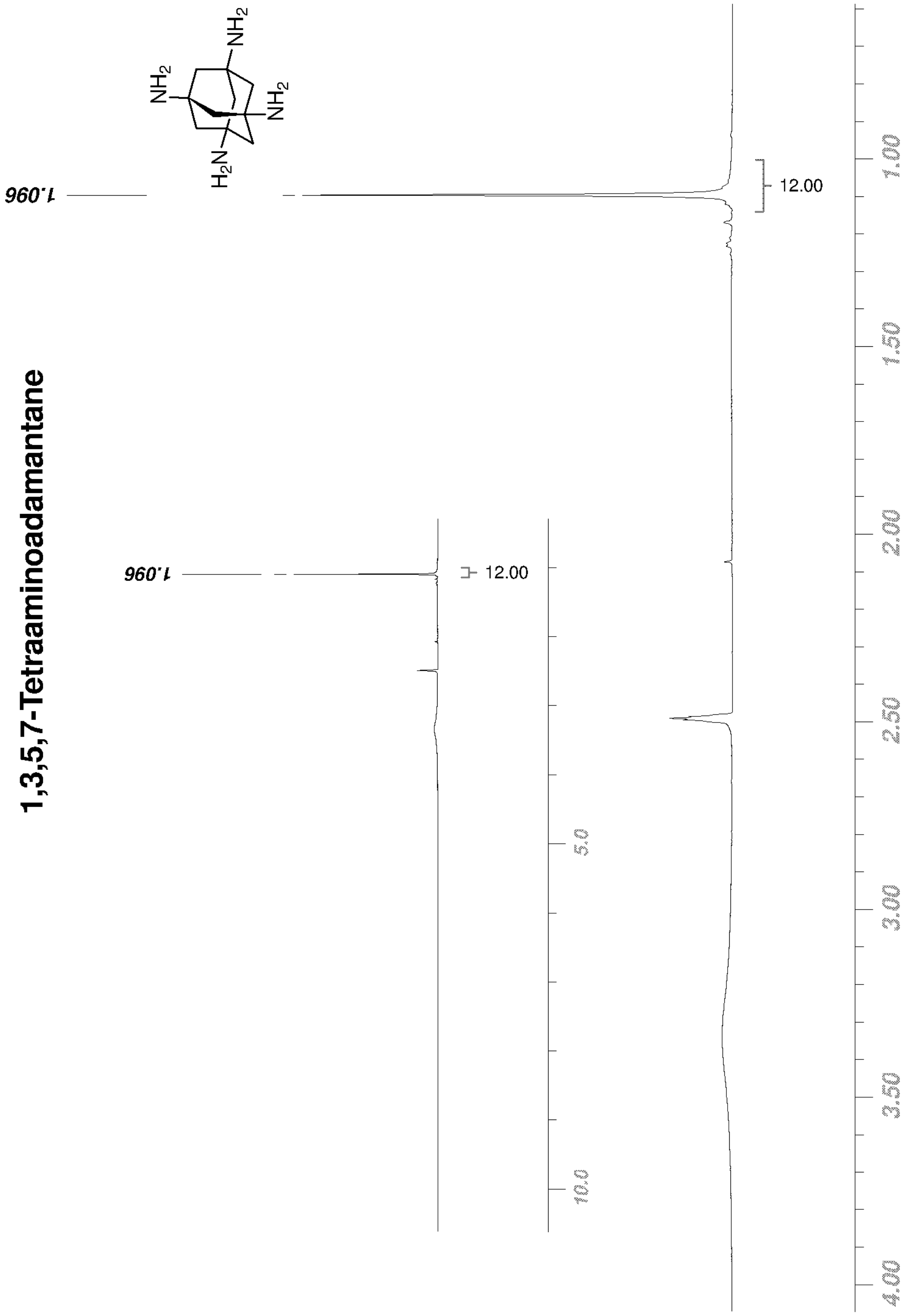

1,3,5,7-Tetraaminoadamantane

2. Details for the crystal structure refinements

2.1. Refinement of $[Cd_2\{tr_2ad\}_4(H_2O)_4](CdBr_4)_2\cdot 2H_2O$ (1)

Monoclinic crystals of **1**, with $\beta \approx 90^o$, exhibit common type of pseudomerohedral twinning emulating orthorhombic *P* lattice. In the latter case $R_{int} = 0.105$, however no solution was possible in any of the reasonable orthorhombic space groups (for example, *Pmmn*, $Pmn2_1$, $P2_12_12_1$, *etc*). The structure was successfully solved in the monoclinic space group $P2_1/n$ and refined as twin (the twin law $1\ 0\ 0\ 0\ \bar{1}\ 0\ 0\ 0\ \bar{1}$) with actually equal contributions of the twin components (the refined BASF parameter was 0.565).

All non-hydrogen atoms were refined anisotropically. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.95 Å (triazole), 0.99 Å (CH_2 adamantane) and 1.00 (CH adamantane). The OH-hydrogen atoms were located and then constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S1. Hydrogen bonding scheme for the structure $[Cd_2\{tr_2ad\}_4(H_2O)_4](CdBr_4)_2\cdot 2H_2O$ (**1**)

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	Br1	0.85	2.60	3.402(8)	157.3
O1	H2W	Br2	0.85	2.74	3.543(8)	157.8
O2	H3W	Br8	0.85	2.65	3.494(11)	173.7
O2	H4W	O1W	0.85	1.96	2.803(12)	171.4
O3	H5W	Br5	0.85	2.52	3.335(7)	161.0
O3	H6W	Br6	0.85	2.55	3.366(7)	161.0
O4	H7W	O2W	0.85	1.96	2.805(10)	175.7
O4	H8W	Br3 (-1+x, y, z)	0.85	2.47	3.324(7)	176.3
O1W	H9W	Br1	0.85	2.57	3.422(11)	174.1
O1W	H10W	N14	0.85	2.07	2.921(12)	173.3
O2W	H11W	Br6	0.85	2.55	3.397(7)	179.2
O2W	H12W	N17 (0.5-*x*, -0.5+*y*, 1.5-z)	0.85	2.05	2.901(11)	179.0

2.2. Refinement of $[Cd\{tr_2ad\}_4\{CdI_3\}_2]\cdot 4H_2O$ (2)

The refinement was standard. All non-hydrogen atoms were refined anisotropically. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.93 Å (triazole), 0.97 Å (CH_2 adamantane) and 0.98 (CH adamantane). The OH-hydrogen atoms were located and then constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S2. Hydrogen bonding scheme for the structure [Cd{*tr*$_2$*ad*}$_4${CdI$_3$}$_2$]·4H$_2$O (**2**)

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1C	N8	0.85	2.02	2.844(3)	161.7
O1	H1D	I1 (2-*x*, -*y*, -*z*)	0.85	2.75	3.531(2)	152.6
O2	H1C	N5 (2-*x*, 2-*y*, 1-*z*)	0.85	2.06	2.904(3)	170.9
O2	H1D	I3 (2-*x*, 1-*y*, -*z*)	0.85	3.18	3.898(3)	143.8

2.3. Refinement of [Ag$_2${*tr*$_2$*ad*}$_2$](NO$_3$)$_2$·2H$_2$O (3)

Crystals of the compound are non-merohedral twins exhibiting typical set of problems with the structure refinement. In spite of the reasonable R_{int} value (Table S3), the overall convergence was very poor, with very heavy residual electron density peaks in the region of silver-triazole chain and with systematically $F_o^2 \rangle\rangle F_c^2$. Then the data frames were indexed and integrated (with a soft tolerance for the reflection overlap at 5 pixels) as a two-domain system using RECIPE/TWIN facilities implemented in a Stoe IPDS software. The data were scaled and merged yielding a single dataset of about 84% completeness (coverage to $\theta = 26.0^{\circ}$) due to a partial overlap of the reflections, which correspond to the different domains of the crystal.

Table S3. Main features for the refinement of **3**, using either standard hkl file or scaled and merged hkl obtained for two-domain system.

	Standard integration	Two-domain integration
Meas/ Unique reflns	11271/ 8023	9057/ 6234
Dataset completeness, %	97.6	74.9
R_{int}	0.0537	0.0616
Parameters refined	496	496
$R1$ [I > 2σ(I)]	0.1253	0.0429
$wR2$ [all data]	0.3514	0.0909
Goof on F^2	1.151	0.864
Three largest peaks/ e Å^{-3}	3.54; 3.18; 3.15	0.57; 0.55; 0.50

For one of two unique non-coordinated NO$_3^-$ ions, the O-atoms are equally disordered over two positions. All non-hydrogen atoms were refined anisotropically, including the disordered O-atoms. In order to improve the refinement stabilty, the disordered nitrate was refined with soft restraints in geometry (±0.01 Å) and with SIMU refinement of the anisotropic thermal parameters for O-atoms. The CH-hydrogen atoms were constrained with $U_{\mathrm{iso}} = 1.2U_{\mathrm{eq}}$ of the parent C-atom and with C-H distances 0.94 Å (triazole), 0.98 Å (CH_2 adamantane) and 0.99 (CH adamantane). The OH-hydrogen atoms were located and then constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S4. Hydrogen bonding scheme for the structure $[Ag_2\{tr_2ad\}_2](NO_3)_2\cdot 2H_2O$ **(3)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1W	H1W	O1 (-1+x, y, z)	0.85	2.10	2.941(11)	172.3
O1W	H2W	O2	0.85	2.17	3.009(11)	172.0
O2W	H3W	O5 (2-x, 1-y, 1-z) [a)]	0.85	2.18	3.009(14)	163.7
		O5A (2-x, 1-y, 1-z)	0.85	2.23	3.042(17)	160.6
O2W	H4W	O6 (1-x, 1-y, 1-z)	0.85	2.33	3.137(14)	159.4
		O6A (1-x, 1-y, 1-z)	0.85	2.16	2.974(12)	161.2

a) O5 and O5A, O6 and O6A correspond to different orientations of the disordered NO_3^- anion.

2.4. Refinement of $[Cd\{tr_3ad\}_2](NO_3)_2\cdot 6H_2O$ (4)

Refinement of Cd-organic framework atoms was standard. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.93 Å (triazole), 0.97 Å (CH_2 adamantane) and 0.98 Å (CH adamantane).

Some minor problems were associated with the disorder in the region of non-coordinated anions and water molecules. One water molecule is equally disordered by symmetry over three positions (1/3O···1/3O 1.11 Å), related by a 3-fold axis. These positions overlap with the additional water molecule, which adopt two closely separated positions (O···O 1.29 Å) disordered over the 3-fold axis.

The nitrate anions are also disordered by symmetry and overlap with water molecules (third equivalent). Two anions adopt three positions, related by 3-fold axis thus the occuppancy factors for the entire NO_3^- sites were 0.66. In addition, NO_3^- group possesses two orientations, thus the partial occupancies for the atoms were 0.33.

It was possible to resolve this disorder with the restrained molecular geometry for NO_3^- (N-O 1.222±0.005; O···O 2.105±0.005 Å) and restraints in the thermal motion (EADP) for the entire NO_3^- moiety. All the disordered atoms were refined anisotropically, but the H-atoms were not added for water molecules.

2.5. Refinement of $[Cd\{tr_3ad\}_2]CdCl_4\cdot 3H_2O$ (5)

Refinement of Cd-organic framework atoms was standard. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.95 Å (triazole), 0.99 Å (CH_2 adamantane) and 1.00 Å (CH adamantane). The OH-hydrogen atoms were located and then fixed with $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

There is disorder in the region of guest anion/water, which is similar to that in the structure of (**7**). The $CdCl_4^{2-}$ anion is equally disordered by symmetry (the same was observed for the refinement in the acentric space group *R*3*c*) in such a way that three Cl-atoms are ordered and are common for two orientations, while Cd-Cl fragment is equally disordered from two axial sides of the Cl-Cl-Cl triangle. Positions of this disordered fragment are overlapped with the solvate water molecule (O1), which thus was also refined with a partial occupancy factor 0.50. The disorder was trated without any restraints in geometry and thermal parameters and all corresponding atoms were refined anisotropically.

Table S5. Hydrogen bonding scheme for the structure $[Cd\{tr_3ad\}_2]CdCl_4\cdot 3H_2O$ **(5)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	N2	0.86	2.08	2.899(10)	159.2
O1	H2W	Cl1	0.87	2.72	3.549(12)	160.3

2.6. Refinement of $[\{Cu_3(OH)\}_2(SO_4)_5(H_2O)_2\{tr_3ad\}_3]\cdot 26H_2O$ (6)

The refinement was somewhat complicated by the problems arising from the disorder of part of the solvate water molecules, SO_4^{2-} anions and triazole rings:

1) In the anionic cluster, $[Cu_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)(\mu_2\text{-}tr)_3(SO_4)_3(H_2O)]^{3-}$, at least two out of three present monodentate equatorial sulfate ligands show “rotational” disorder of three non-coordinated O-atoms. This disorder was resolved with restrained tetrahedral geometry of the SO_4^{2-} groups (S-O 1.480±0.005 Å) and with equal anisotropic thermal parameters for the disordered O-atoms (EADP). Partial occupancies of the disorder components were refined as additional free variable parameters giving almost equal contributions at 0.57/0.43 and 0.54/0.46. Relatively high parameters for the thermal motion of O-atoms corresponding to the third monodentate sulfate, and also for $\mu_3\text{-}SO_4$-cap of the cationic cluster were also indicative of the disorder. However, it was not possible to resolve it. The corresponding atoms were refined anisotropically for the sake of overall convergence.

2) Very high anisotropy for the thermal motion of one of the singly coordinated triazole groups (N27-C37-N25-N26-C38; N26 is coordinated to Cu) suggests the disorder as “rotation” around N27···N26 axis. The disorder was resolved with equal 0.50 partial contributions for C37, N25 and C38 atoms, restraints in the triazole bond lengths, FLAT ±0.01 restraints for the coplanarity of the ring atoms and SIMU restraints for the anisotropic thermal values.

3) It was possible to locate 3 coordinated water molecules (long axial Cu-O bonds at 2.29-2.57 Å) and 16 solvate water molecules, one of which is 0.65/0.35 disordered over two closely separated positions. The coordinated water molecules and 7 solvate water molecules were refined anisotropically, while other 9 solvate water were left isotropic in view of the relatively large thermal parameters (U_{iso} = 0.137-0.174 $Å^2$, for two components of the disordered water molecule U_{iso} = 0.102 and 0.111 $Å^2$).

4) The remaining solvate water molecules are badly disordered and it was impossible to found a stable refinement model. This electron density was modelled using SQUEEZE routine, as it implemented in PLATON: 822 e / unit cell are found, which were attributed to 80 additional water molecules, 10 per the formula unit. This gives total density of 1.569 g cm^{-3}.

5) With the exception of 9 isotropic solvate water molecules, all non-hydrogen atoms were refined anisotropically. The CH-hydrogen atoms were constrained with U_{iso} = 1.2U_{eq} of the parent C-atom and with C-H distances 0.95 Å (triazole), 0.99 Å (CH_2 adamantane) and 1.00 (CH adamantane).

The OH-hydrogen atoms were located for μ_3-OH groups and for two coordinated water molecules. These H-atoms were then constrained with O-H distances set to 0.85 Å (H_2O) and 1.00 Å (μ_3-OH) and U_{iso} = 1.5U_{eq} of the parent O-atom. For the remaining water molecules, the H-atoms were not added considering disorder in the solvent region. Corresponding H-bond parameters are presented below:

Table S6. Hydrogen bonding scheme for $[\{Cu_3(OH)\}_2(SO_4)_5(H_2O)_2\{tr_3ad\}_3]\cdot 26H_2O$ **(6)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O2	H2W	O6 (1-*x*, *y*, 0.5-*z*)	1.00	1.69	2.584(6)	147.2
O24	H3W	O5 (1-*x*, *y*, 0.5-*z*)	0.85	1.97	2.818(7)	175.8
O24	H4W	O6W (-0.5+*x*, 0.5+*y*, *z*)	0.85	1.84	2.690(8)	175.5
O25	H5W	O3W	0.85	1.86	2.712(9)	179.4
O25	H5W	O9W	0.85	2.00	2.845(10)	179.4

2.7. Refinement of [Cd{*tr*$_3$*ada*}$_2$]$CdI_4 \cdot 3H_2O$ (7)

The CdI_4^{2-} anion is equally disordered by symmetry in such a way that three iodine atoms are ordered and are common for two orientations, while Cd-I fragment is equally disordered from two axial sides of the I-I-I triangle. Positions of this disordered fragment are overlapped with the solvate water molecule (O1W), which thus was also refined with a partial occupancy factor 0.50. The disorder was trated without any restraints in geometry and thermal parameters and all corresponding atoms were refined anisotropically.

Refinement of Cd-organic framework atoms was standard. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.94 Å (triazole), 0.98 Å (CH_2 azaadamantane). The OH-hydrogen atoms were constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S7. Hydrogen bonding scheme for the structure [Cd{*tr*$_3$*ada*}$_2$]$CdI_4 \cdot 3H_2O$ **(7)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1W	H1W	I1 (1-*y*, *x*-*y*, *z*)	0.85	3.03	3.835(18)	157.6
O1W	H2W	N2	0.85	2.18	2.975(17)	156.0

2.8. Refinement of [$Cu_3(OH)_2${*tr*$_3$*ada*}$_2(H_2O)_4$]$(ClO_4)_4$ (8)

One of two unique ClO_4^- anions displays disorder by two overlapping positions, with the refined partial occupancy factors 0.80/0.20. The major contribution of the disorder was freely refined anisotropically. For the minor component, the Cl atom was anisotropic, while O-atoms were left isotropic. This minor component was refined with restrained geometry (Cl-O 1.42±0.01 Å; O···O 2.30±0.01 Å) and with SIMU restraint for the isotropic thermal parameters of O-atoms.

Table S8. Hydrogen bonding scheme for the structure [$Cu_3(OH)_2${*tr*$_3$*ada*}$_2(H_2O)_4$]$(ClO_4)_4$ **(8)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	N7 (*x*, 0.5-*y*, 0.5+*z*)	0.86	2.06	2.710(4)	132.2
O2	H2W	O5	0.86	2.13	2.945(9)	158.4
O2	H3W	O11 (0.5+*x*, 0.5-*y*, 1-*z*)	0.85	1.83	2.681(5)	171.6
O11	H4W	O7 (-0.5+*x*, *y*, 0.5-*z*)	0.86	2.20	3.056(5)	170.3
O11	H5W	O6 (1-*x*, -*y*, 1-*z*)	0.86	2.01	2.858(6)	170.2

This minor 0.2 component of the ClO_4^- generates short contact with distal aqua-ligand O11 indicating that the latter possibly adopts a partial occupancy. However, site of O11 was refined with the occupancy factor 1.00. All the H-atoms were located and then constrained. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances allowed to refine giving C-H 0.94-1.00 Å (triazole) and 0.88-0.97 Å (CH_2 azaadamantane). The same approach was used for the OH-hydrogen atoms constrained with $U_{iso} = 1.5U_{eq}$ of the parent O-atom (O-H distances 0.85-0.86 Å).

2.9. Refinement of $[Cu_2\{tr_3ada\}_2(H_2O)_3](SO_4)_2{\cdot}7H_2O$ (9)

The refinement was standard. All non-hydrogen atoms were refined anisotropically. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.94 Å (triazole), 0.97 Å (CH_2 azaadamantane). All the OH-hydrogen atoms were located and then constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-

Table S9. Hydrogen bonding scheme for the structure $[Cu_2\{tr_3ada\}_2(H_2O)_3](SO_4)_2{\cdot}7H_2O$ (**9**)

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	O2W (*x*, -1+*y*, *z*)	0.85	1.88	2.729(3)	175.4
O1	H2W	O7	0.85	1.84	2.692(3)	175.5
O2	H3W	O9	0.85	1.87	2.699(3)	166.0
O2	H4W	O6W (2-*x*, 1-*y*, 1-*z*)	0.85	2.05	2.884(4)	166.0
O3	H5W	O7 (*x*, 0.5-*y*, 0.5+*z*)	0.85	2.03	2.876(3)	173.1
O3	H6W	O9 (*x*, 0.5-*y*, 0.5+*z*)	0.85	1.90	2.748(4)	173.2
O1W	H7W	O4 (1-*x*, 0.5+*y*, 0.5-*z*)	0.85	2.05	2.894(4)	172.8
O1W	H8W	O5 (*x*, 1+*y*, *z*)	0.85	2.01	2.856(4)	171.9
O2W	H9W	O1W	0.85	1.99	2.797(5)	158.7
O2W	H10W	O3W	0.85	2.01	2.797(5)	152.8
O3W	H11W	O4 (1-*x*, 0.5+*y*, 0.5-*z*)	0.85	2.05	2.870(5)	161.4
O3W	H12W	N20 (1-*x*, 1-*y*, 1-*z*)	0.85	2.10	2.924(4)	162.5
O4W	H13W	O10	0.85	1.89	2.736(4)	174.5
O4W	H14W	O7W	0.85	2.18	2.971(6)	155.6
O5W	H15W	N15	0.85	2.09	2.926(4)	168.7
O5W	H16W	O6	0.85	1.92	2.759(4)	170.1
O6W	H17W	N8 (*x*, 1.5-*y*, -0.5+*z*)	0.85	2.18	2.973(4)	155.0
O6W	H18W	O11	0.85	1.92	2.759(5)	167.5
O7W	H19W	O8	0.85	2.20	3.014(6)	159.5
O7W	H20W	N10	0.85	2.42	3.198(5)	151.6

atom. The O-atoms for one of the SO_4^{2-} anions and one of 7 solvate water molecules have slightly higher thermal parameters (up to U_{iso} = 0.123 Å^2), however there are no any signs of the disorder.

2.10. Refinement of [Cd_2{*tr*$_3$*ada*}$_3$]Cl_4·28H_2O (10)

The problems were associated with a relatively weak diffraction from the crystals (nearly 10 of which were tested in order to select a more satisfactory one) and with disorder in the region of large crystal channels.

Refinement of Cd-organic framework atoms was standard. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.95 Å (triazole), 0.99 Å (CH_2 azaadamantane).

One chloride anion (0.5 equivalents per Cd) appears to be entrapped into the pocket of the structure, with 6 symmetry related directional CH(tr)···Cl hydrogen bonds. This chloride was refined anisotropically giving good thermal parameters. One water molecule, which lie in the proximity to the Cd-organic framework and forms H-bond to triazole N-atom (N···O *ca*. 2.80 Å) was also located. This molecule is equally disordered over two closely separated positions (1/2O···1/2O 0.97 Å), which were refined anisotropically, but without H-atoms.

Other anions are badly disordered in the channels of the structure, also overlapping with the solvate water molecules, most of which are totally disordered. This electron density was modelled using Squeeze routine implemented in PLATON – 634 e / unit cell, corresponding to electron density of 3Cl and 25H_2O per formula unit (Cd_2).

2.11. Refinement of [Ag{*tr*$_4$*ad*}]NO_3·3.5H_2O (11)

Non-coordinated NO_3^- anion is unequally disordered over two closely separated positions (situated almost parallel at *ca*. 0.8-1.3 Å). The refined contributios were 0.60/0.40. The disorder was resolved with the restrained geometry (N-O 1.25±0.01 Å; O···O 2.17±0.01 Å) and FLAT (±0.01 Å) restraint for the planarity of NO_3^- atoms. Only the N-atoms of both components were refined anisotropically, while O-atoms were left isotropic.

In all other aspects, the refinement was standard. All non-hydrogen atoms of the Ag-organic linkage were refined anisotropically. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.93 Å (triazole) and 0.97 Å (CH_2 adamantane). The OH-hydrogen atoms were located and then constrained with O-H distances set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S10. Hydrogen bonding scheme for the structure [Ag{*tr₄ad*}]NO_3·3.5H_2O **(11)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O4	H1W	N2	0.85	2.00	2.847(7)	173.4
O4	H2W	N11 (1-x, 1-y, 1-z)	0.85	2.04	2.890(6)	177.1
O5	H3W	N4	0.85	2.21	3.002(7)	154.3
O6	H4W	N4	0.85	2.46	3.093(8)	131.6
O6	H5W	O7	0.85	2.07	2.721(10)	133.0
O7	H6W	O6 (2-x, -y, 1-z)	0.85	2.20	2.872(10)	135.6
O7	H7W	O2A (1.5-x, -0.5+y, z) [a)]	0.85	1.86	2.66(2)	157.0
		O2 (1.5-x, -0.5+y, z)	0.85	2.25	2.988(15)	144.7

[a)] O2 and O2A are components of the disordered NO_3^- anion.

2.12. Refinement of [Cu{*tr₄ad*}(H_2O)](ClO_4)$_2$·3H_2O (12)

The non-coordinated ClO_4^- anion is unequally disordered by two overlapping positions (one O-atom is common for both contributions). The partial occupancy factors were set 0.70/0.30, as was suggested by refinement of the isotropic thermal parameters. Soft restraints in the ClO_4^- geometry (Cl-O 1.42±0.01 Å; O···O 2.30±0.01 Å) were applied and the disordered atoms were refined anisotropically with SIMU restraints for two pairs of very closely separated O-atoms. Two present solvate water molecules are also disordered over two close positions (0.99 and 1.29 Å). They were refined anisotropically with partial occupancies 0.50/0.50 and 0.55/0.45, and the corresponding H-atoms were not added.

The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.94 Å (triazole), 0.98 Å (CH_2 adamantane). The OH-hydrogen atom for the coordinated water molecule O1 (mirror plane) was located and then constrained with O-H distance set to 0.85 Å and $U_{iso} = 1.5U_{eq}$ of the parent O-atom.

Table S11. Hydrogen bonding scheme for the structure [Cu{*tr₄ad*}(H_2O)](ClO_4)$_2$·3H_2O **(12)**

Donor (D)	Hydrogen	Acceptor (A)	D-H/Å	H···A/Å	D···A/Å	∠DH···A/°
O1	H1W	O3W	0.85	1.96	2.80(2)	169.4

2.13. Refinement of [Cd_3Cl_6\{*tr_4ad*\}$_2$]·$9H_2O$ (13)

Refinement of Cd-organic framework atoms was standard. The CH-hydrogen atoms were constrained with $U_{iso} = 1.2U_{eq}$ of the parent C-atom and with C-H distances 0.95 Å (triazole), 0.99 Å (CH_2 adamantane). Very high anisotropy for thermal motion of the coordinated Cl-ligands led us to refinement of two-component disordering model, with equal 0.5 contributions of two closely separated chlorine atoms (Cl1···Cl1 0.715 Å; Cl2···Cl2 0.707 Å). Actually the same problem was connected with ring atoms of the non-coordinated triazole group (N8-C5-N7-N7a-C5a). In this case we were not able to resolve the possible disordering scheme. Corresponding atoms were refined anisotropically without restraints in the geometry. The solvate water molecules are also disordered (some of them are in special positions); they were refined with partial occupancy factors 0.5 and left isotropic. No H-atoms were added to these solvate water molecules.