Isolation and Structural Characterization of New Indium(III) Aqua Complexes: *trans*-$[InCl_2(H_2O)_4]^+$ and *trans*-$[InCl_4(H_2O)_2]^-$ as Supramolecular Adducts with Cucurbituril and Related Studies

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Keywords: Indium / Aluminum / Solid-state structures / Supramolecular chemistry / Aqua complexes / Cucurbituril

Aqua and aqua-chloride complexes of Al^{III} and In^{III} have been isolated from aqueous solutions and structurally characterized by X-ray analysis as supramolecular adducts with cucurbituril. Using this approach, *trans*-$[InCl_2(H_2O)_4]^+$ and *trans*-$[InCl_4(H_2O)_2]^-$ species were detected and isolated for the first time as parts of supramolecular assemblies of $[InCl_2(H_2O)_4]_3Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot4H_2O$ (**1**) and $(H_3O)_3[InCl_4(H_2O)_2]_3\cdot2(C_{36}H_{36}N_{24}O_{12})\cdot17H_2O$ (**2**). The hexaaqua indium(III) cation is present in $[In(H_2O)_6](NO_3)_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot9H_2O$ (**3**), and its geometry has been established by X-ray crystallography for the first time. The preparation and crystal structure of an Al^{III} hexaaqua ion – cucurbituril adduct $[Al(H_2O)_6]Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot18H_2O$ (**4**) is also reported. A comparison of In^{III} with its analogs in Group 13 shows closer similarity between In^{III} and Tl^{III} in the chloroaqua complexes than between In and its lighter congeners.

Introduction

Knowledge about coordination chemistry of Group 13 metals (Al − Tl) has rapidly expanded in the last decade.[1,2] This development involves both the introduction of new ligands and more careful examining of "old" and "simple" compounds. Still, detailed information of the nature of the species that are present even in simple systems is often lacking. Thus, from solutions of In^{III} in aqueous HCl, only $[InCl_6]^{3-}$ [2] and $[InCl_5(H_2O)]^{2-}$ [3] could be isolated so far. No other ionic species with higher H_2O/Cl ratios have been identified, except for a serendipitous preparation of a thiotrithiazyl salt, $[S_4N_3]^+$[*cis*-$InCl_4(H_2O)_2]^-$.[4] The *fac*-isomer of $[InCl_3(H_2O)_3]$ is also known. It is formed as a side-product from the reaction of $InCl_3$ with *n*-butyl acetate in hexane.[5a] The same *fac*-$[InCl_3(H_2O)_3]$ moieties also exist in $[InCl_3(H_2O)_3]\cdot$18-crown-6[5b] and in $[InCl_3(H_2O)_3]\cdot$3dioxane.[5c] Curiously enough, $InCl_3\cdot4H_2O$ contains five-coordinate $[InCl_3(H_2O)_2]$ units enmeshed in a network of hydrogen bonding with solvated water molecules.[6]

Recently we became interested in the isolation and structural characterization of often elusive aqua-complexes and mixed-ligand species containing coordinated aqua ligands by employing a supramolecular approach − crystallization with cucurbituril (*Cuc*).[7] Cucurbituril is a macrocyclic cavitand with two identical carbonyl-fringed portals.[8] It can coordinate alkali metal ions such as Na^+, K^+, Rb^+, Cs^+, Ca^{2+} directly, acting as a ligand.[9] It also forms strong hydrogen bonds of the N−H···O type with aliphatic and aromatic amines [10] and we expected even stronger hydrogen bonding with coordinated water molecules of aqua complexes which would enable their crystallization. This expectation has been validated and we wish to report the structures of $[InCl_2(H_2O)_4]_3Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot4H_2O$ (**1**), $(H_3O)_3[InCl_4(H_2O)_2]_3\cdot2(C_{36}H_{36}N_{24}O_{12})\cdot17H_2O$ (**2**), and $[In(H_2O)_6](NO_3)_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot9H_2O$ (**3**) as well as of an Al complex, $[Al(H_2O)_6]Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot18H_2O$ (**4**).

Results and Discussion

The synthesis of the supramolecular adducts **1**−**4** is straightforward. Cucurbituril is not soluble in water, but moderately soluble in 3 M HCl, in neutral KNO_3 solution as well as in solutions of other alkaline metals (due to the metal coordination to the C=O groups of *Cuc*). We also found that *Cuc* is soluble in aqueous solutions of In^{III} and Al^{III} salts, and in this case that the hydrogen bonding between the coordinated waters and the carbonyls of *Cuc* is operative, instead of the expected direct coordination as X-ray analyses show. The products are separated as colorless single crystals suitable for X-ray studies. They lose their water of crystallization very easily, so that **3** and **4** become opaque and lose their crystallinity in air within a few minutes. This fact explains the unsatisfactory agreement between the analytically deduced formula of **3** as the heptahydrate and the stoichiometry found by X-ray analysis (nonahydrate).

The structure of the *trans*-$[InCl_2(H_2O)_4]^+$ cation and the crystal packing in **1** are shown in Figure 1 and Figure 2. This is the first crystal structure in which *Cuc* molecules occupy a crystallographic position with the highest possible symmetry, D_{6h} (6/*mmm*). They form one-layered hexagonal packing with channels running along the *c* axis. There are outer-sphere Cl^- anions [Cl(3)] disordered over 12 positions around the centers of *Cuc* molecules, the Cl···Cl distances being 0.83 − 2.21 Å. The cation lies in the positions with

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D_{2h} (*mmm*) site symmetry and is also disordered over two orientations around the Cl−In−Cl (*c*) axis. Solvent water molecules [O(1w)] and another counterion Cl^- [Cl(2)] form columns along the $\bar{6}$ axis, Cl···O distances being 3.19 Å. Our attempts to resolve the disorder by assuming a space group with lower symmetry were unsuccessful. Selected bond lengths and angles are given in Table 1.

In the crystal structure of **2**, there are two different isomers, *cis* and *trans*, of the $[InCl_4(H_2O)_2]^-$ anion (Figure 3). The In−Cl and In−OH_2 bond lengths are similar in both isomers. The *cis* anion forms a hydrogen bond with and O···O distance of 2.64 Å between the coordinated water and an oxygen atom of the *Cuc* molecule. All *Cuc* molecules also contain disordered water in the center of the "barrel".

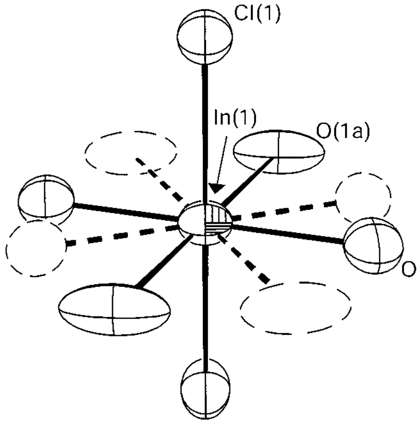

Figure 1. *trans*-$[In(H_2O)_4Cl_2]^+$ cation in **1** (50% probability ellipsoids). The second orientation is shown by dashed lines

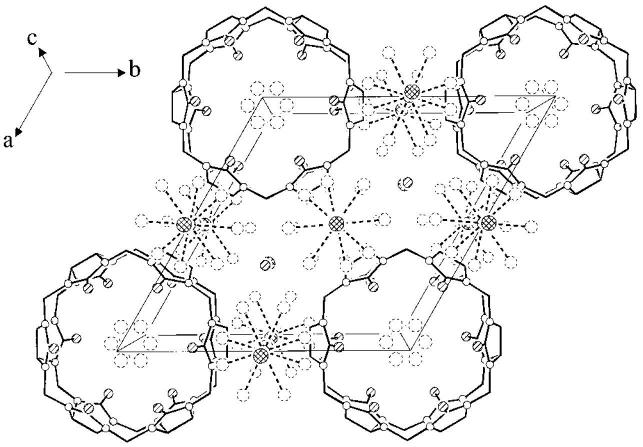

Figure 2. Crystal packing in **1**. Disordered atoms are shown by dashed lines

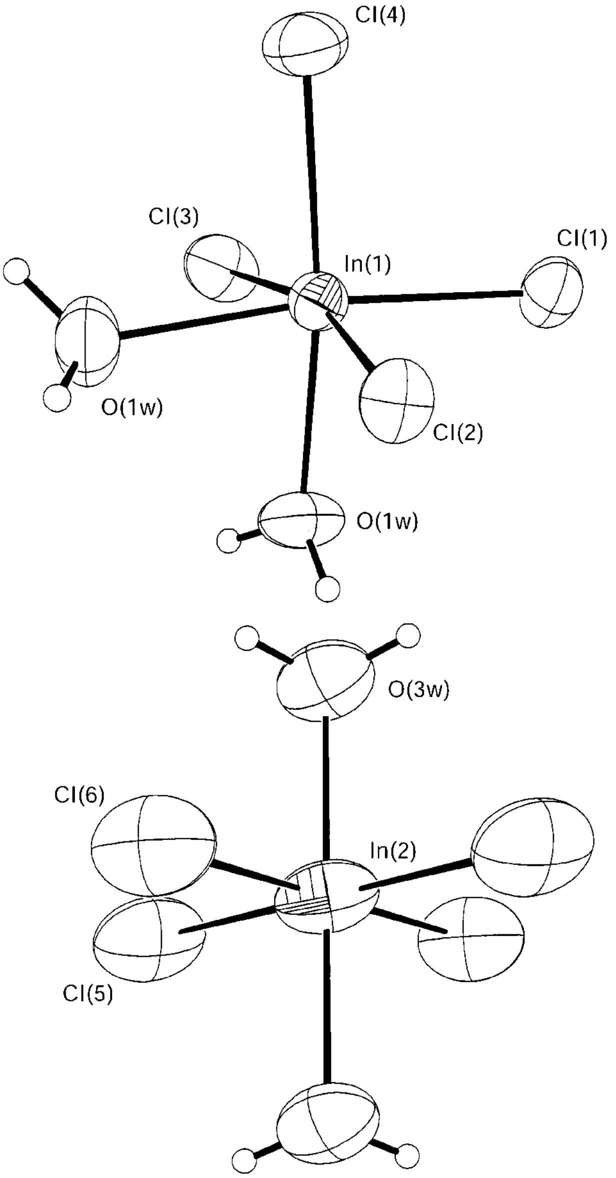

Figure 3. *cis*- (top) and *trans*-$[In(H_2O)_2Cl_4]^-$ (bottom) anion in **2** (50% probability ellipsoids)

Table 1. Main bond lengths [Å] and valence angles [°] in **1** (symmetry transformations used to generate equivalent atoms: #1 − *x*,−*y* + 1,−*z*; #2 − *x*,−*x* + *y*, *z*; #3 − *x*,−*x* + *y*,−*z* − 1; #4 − *x* + *y*, *y*, *z*)

In(1)−Cl(1)	2.423(5)	C(11)−N(11)	1.353(8)
In(1)−O(1a)	2.363(16)	N(11)−C(111)	1.454(7)
In(1)−O(2a)	2.118(18)	N(11)−C(11b)	1.448(9)
C(11)−O(11)	1.234(12)		
Cl(1)−In(1)−Cl(1)#1	180	O(11)−C(11)−N(11)	124.9(4)
O(1a)−In(1)−Cl(1)	90	N(11)#2−C(11)−N(11)	110.2(8)
O(1a)−In(1)−Cl(1)#1	90	C(11)−N(11)−C(111)	111.1(7)
O(1a)#1−In(1)−O(1a)	180	C(11)−N(11)−C(11b)	124.4(6)
O(2a)−In(1)−O(1a)#1	97.4(7)	C(11b)−N(11)−C(111)	123.4(7)
O(2a)−In(1)−O(1a)	82.6(7)	N(11)−C(111)−C(111)#3	103.7(5)
O(2a)−In(1)−O(2a)#1	180	N(11)−C(11b)−N(11)#4	112.2(7)

In the crystal, the *Cuc* molecules form parquet-like packing with anions between them (Figure 4). There are a lot of intermolecular hydrogen bonds between coordinated, solvent water, and the *Cuc* molecules. Our attempts to locate H_3O^+ cations were unsuccessful. Selected bond lengths and angles are given in Table 2.

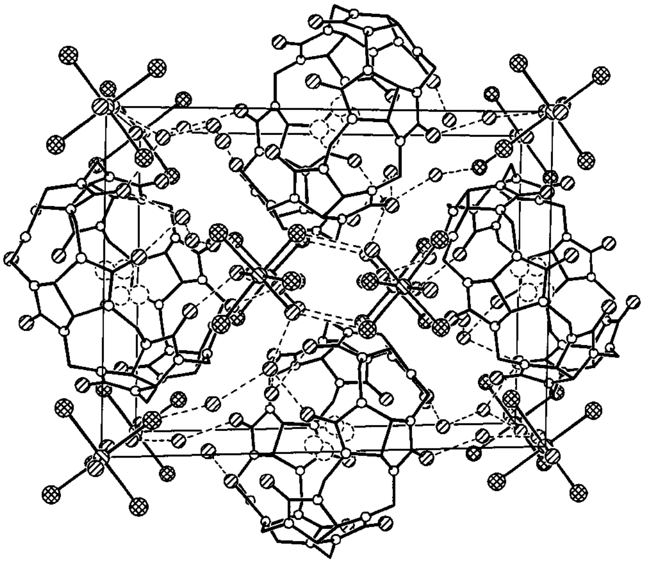

Figure 4. Crystal packing in **2**, view along the *a* axes. Hydrogen bonds are shown as dashed lines

Table 2. Main bond lengths [Å] and valence angles [°] in **2** (symmetry transformations used to generate equivalent atoms: #1 $-x,-y,-z+2$)

In(1)−Cl(1)	2.4637(13)	In(1)−O(2w)	2.252(4)
In(1)−Cl(2)	2.4626(13)	In(2)−O(3w)	2.237(5)
In(1)−Cl(3)	2.4778(14)	In(2)−Cl(5)	2.455(2)
In(1)−Cl(4)	2.4472(14)	In(2)−Cl(6)	2.470(2)
In(1)−O(1w)	2.222(4)		
Cl(1)−In(1)−Cl(3)	93.38(5)	O(1w)−In(1)−O(2w)	82.21(19)
Cl(2)−In(1)−Cl(1)	94.50(4)	O(2w)−In(1)−Cl(1)	172.19(14)
Cl(2)−In(1)−Cl(3)	165.90(5)	O(2w)−In(1)−Cl(2)	85.66(13)
Cl(4)−In(1)−Cl(1)	96.35(5)	O(2w)−In(1)−Cl(3)	84.95(14)
Cl(4)−In(1)−Cl(2)	96.00(5)	O(2w)−In(1)−Cl(4)	91.39(14)
Cl(4)−In(1)−Cl(3)	94.73(6)	O(3w)#1−In(2)−O(3w)	180
O(1w)−In(1)−Cl(1)	90.00(13)	O(3w)−In(2)−Cl(5)	91.68(17)
O(1w)−In(1)−Cl(2)	86.49(11)	O(3w)−In(2)−Cl(5)#1	88.32(17)
O(1w)−In(1)−Cl(3)	81.83(11)	O(3w)−In(2)−Cl(6)	89.16(16)
O(1w)−In(1)−Cl(4)	172.96(13)	O(3w)−In(2)−Cl(6)#1	90.84(16)

The crystal structure of **3** gives the first example of a structurally characterized $[In(H_2O)_6]^{3+}$ cation (Figure 5). The In−OH_2 distances are shorter than those found in the $[InCl_4(H_2O)_2]^-$ anion in **2**. Cucurbituril molecules are associated with indium aqua-cations by hydrogen bonds between portal oxygen atoms and water molecules, the O···O distances being 2.637 − 2.835 Å. In the crystal packing, these aggregates form parquet-like layers (Figure 6) connected by hydrogen bonds to solvent water molecules. Selected bond lengths and angles are given in Table 3.

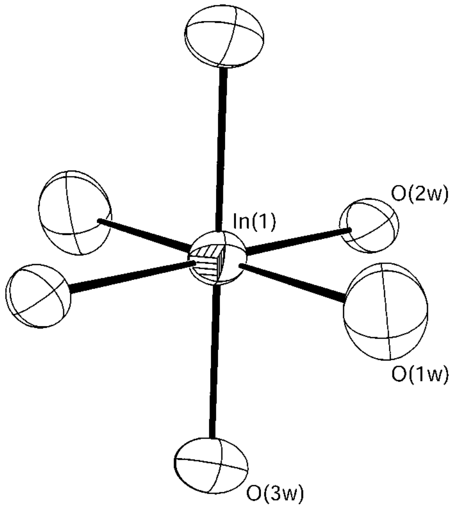

Figure 5. Crystallographically independent $[In(H_2O)_6]^{3+}$ cation in **3** (50% probability ellipsoids)

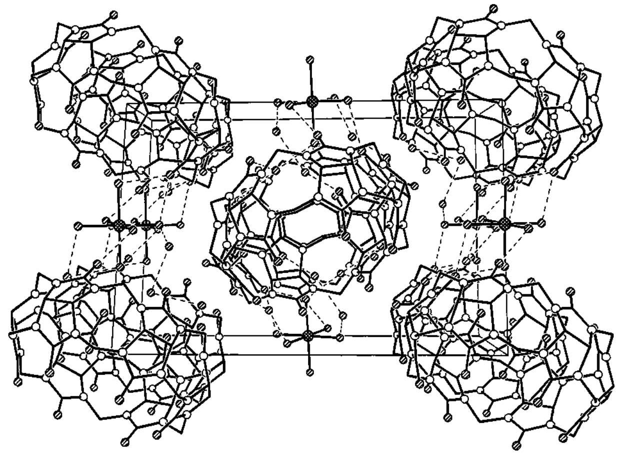

Figure 6. Crystal packing in **3**, view along the *a* axis. Hydrogen bonds are shown as dashed lines.

Table 3. Main bond lengths [Å] and valence angles [°] in **3** (symmetry transformations used to generate equivalent atoms: #1 $-x-2,-y+2,-z+3$; #2 $-x,-y+1,-z+2$)

In(1)−O(1w)	2.152(8)	In(2)−O(4w)	2.149(7)
In(1)−O(2w)	2.139(6)	In(2)−O(5w)	2.141(6)
In(1)−O(3w)	2.142(7)	In(2)−O(6w)	2.136(8)
O(1w)−In(1)−O(1w)#1	180	O(4w)−In(2)−O(4w)#2	180
O(2w)−In(1)−O(1w)	88.4(3)	O(5w)−In(2)−O(4w)	87.9(3)
O(2w)−In(1)−O(1w)#1	91.6(3)	O(5w)−In(2)−O(4w)#2	92.1(3)
O(2w)#1−In(1)−O(2w)	180	O(5w)−In(2)−O(5w)#2	180
O(2w)−In(1)−O(3w)	89.7(3)	O(6w)−In(2)−O(4w)	89.5(3)
O(2w)−In(1)−O(3w)#1	90.3(3)	O(6w)−In(2)−O(4w)#2	90.5(3)
O(3w)−In(1)−O(1w)	89.3(3)	O(6w)−In(2)−O(5w)	88.2(3)
O(3w)−In(1)−O(1w)#1	90.7(3)	O(6w)−In(2)−O(5w)#2	91.8(3)
O(3w)−In(1)−O(3w)#1	180	O(6w)−In(2)−O(6w)#2	180

The crystal of compound **4** contains $[Al(H_2O)_6]^{3+}$ cations, Cl^- anions, water and *Cuc* molecules associated by hydrogen bonds. One of the cations is disordered over two orientations with relative weights 0.793(6)/0.207(6) (Figure 7). Crystal packing (Figure 8) is based on the *pseudo*-body-centered motif of *Cuc* molecules with aluminum aqua-cations between them. Each *Cuc* molecule contains water molecule disordered over six positions around its center. Selected bond lengths and angles are given in Table 4.

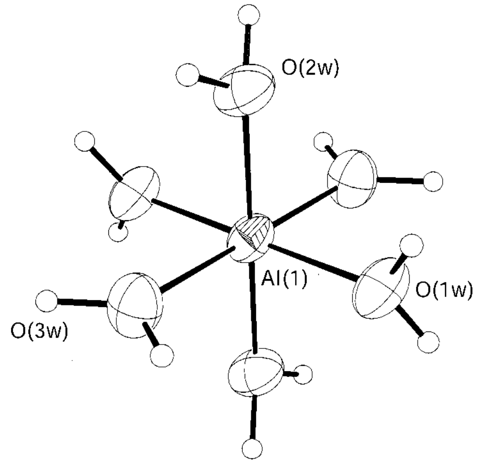

Figure 7. Crystallographically independent $[Al(H_2O)_6]^{3+}$ cations in **4** (50% probability ellipsoids)

The observed In−O distances in the hexaaqua indium cation of **3** are in good agreement with the value obtained from the X-ray study of aqueous solutions of In^{III} perchlorate, 2.16 Å.[11a] The same cation is present in the crystals of In alums, $M^{I}In(SO_4)_2·12H_2O$, though here quantitative structural data are lacking.[11b] In^{III} nitrate forms hydrates with 3, 4 or 5 water molecules, but to the best of our knowledge there is no direct structural information for any of these hydrates. Both the stoichiometry and the spectroscopic evidence of NO_3^- coordination exclude the presence of $[In(H_2O)_6]^{3+}$ in these compounds.[11c] In^{III} also coordinates nitrate in solutions,[11c] where the species $[In(H_2O)_5(\eta^1\text{-}NO_3)]^{2+}$ has been postulated, but in our case all three nitrates are in the outer sphere. The *trans*-$[InCl_2(H_2O)_4]^+$ cation found in **1** has its counterpart in Tl chemistry − *trans*-$[TlX_2(H_2O)_4]^+$ (X = Cl, Br, CN).[12] The analogy with Tl extends further still, because for both metals, crystals of the tetrahydrates $MCl_3·4H_2O$ contain trigonal bipyramidal $MCl_3(H_2O)_2$ molecules.[6,13] But for the tetrahalo complexes this analogy does not hold, with Tl^{III} giving only tetrahedral species $TlCl_4^-$,[12] whereas for In^{III} both *cis*- and *trans*-$[InCl_4(H_2O)_2]^-$ have been isolated, although $InCl_4^-$ [14] is also known. Of the lighter Group 13 metals, no evidence exists for Al of any mixed $[AlX_{6-n}(H_2O)_n]^{n-3}$ (X = Cl, Br, I) species both in the solid state and in solution, whereas for Ga there is ample evidence for them.[15] However, only $[GaX_4]^-$ salts with large organic cations could be isolated from aqueous solutions of Ga^{III} halides.[1] Thus, the $[InCl_4(H_2O)_2]^-$ species so far have no analogs among the other Group 13 metals.

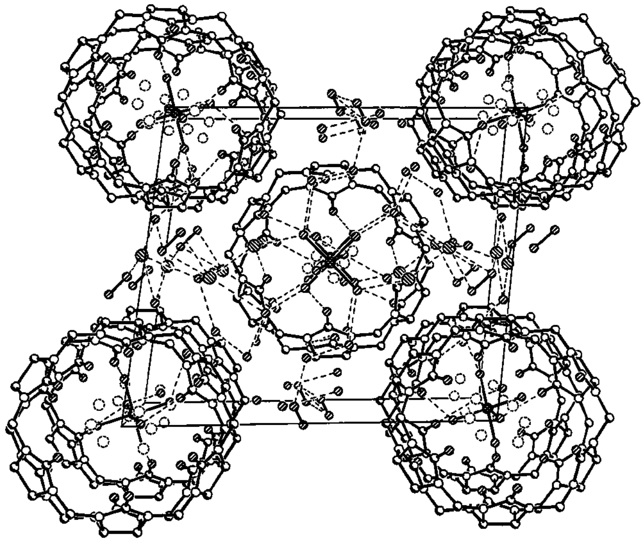

Figure 8. Crystal packing in **4**, view along the *a* axis. Hydrogen bonds are shown as dashed lines

Experimental Section

General: The salts, $AlCl_3·6H_2O$ and "$In(NO_3)_3·4.5H_2O$" were of commercial quality and used without further purification. Cucur-

Table 4. Main bond lengths [Å] and valence angles [°] in **4**.

Al(1)−O(1w)	1.869(3)	Al(2)−O(6w)	1.868(4)
Al(1)−O(2w)	1.880(3)	Al(2)−O(41w)	1.864(14)
Al(1)−O(3w)	1.876(3)	Al(2)−O(51w)	1.870(13)
Al(2)−O(4w)	1.877(4)	Al(2)−O(61w)	1.855(13)
Al(2)−O(5w)	1.880(4)		
O(1w)−Al(1)−O(1w)#1[a]	180	O(6w)−Al(2)−O(4w)#2	90.45(19)
O(1w)−Al(1)−O(2w)#1	90.69(13)	O(6w)−Al(2)−O(4w)	89.55(19)
O(1w)−Al(1)−O(2w)	89.31(13)	O(6w)−Al(2)−O(5w)	90.7(2)
O(1w)#1−Al(1)−O(2w)	90.69(13)	O(6w)−Al(2)−O(5w)#2	89.3(2)
O(1w)−Al(1)−O(3w)	89.12(13)	O(6w)−Al(2)−O(6w)#2	180
O(1w)#1−Al(1)−O(3w)	90.88(13)	O(41w)−Al(2)−O(41w)#2	180
O(2w)#1−Al(1)−O(2w)	180	O(51w)−Al(2)−O(41w)	90.4(7)
O(3w)−Al(1)−O(2w)#1	90.82(13)	O(51w)−Al(2)−O(41w)#2	89.6(7)
O(3w)−Al(1)−O(2w)	89.18(13)	O(51w)−Al(2)−O(51w)#2	180
O(3w)−Al(1)−O(3w)#1	180	O(61w)−Al(2)−O(41w)	89.8(6)
O(4w)#2−Al(2)−O(4w)	180	O(61w)−Al(2)−O(41w)#2	90.2(6)
O(4w)#2−Al(2)−O(5w)	89.0(2)	O(61w)−Al(2)−O(51w)	90.5(6)
O(4w)−Al(2)−O(5w)	91.0(2)	O(61w)#2−Al(2)−O(61w)	180
O(5w)−Al(2)−O(5w)#2	180		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z+1$; #2 $-x-1,-y,-z+2$.

Table 5. Crystal data and structure refinement for **1−4**

Compound	**1**	**2**	**3**	**4**
Formula	$C_{36}H_{68}Cl_9In_3N_{24}O_{28}$	$C_{72}H_{127}Cl_{12}In_3N_{48}O_{50}$	$C_{36}H_{66}InN_{27}O_{36}$	$C_{36}H_{84}AlCl_3N_{24}O_{36}$
Crystal system	hexagonal	triclinic	triclinic	triclinic
Space group	*P6/mmm*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions [Å, °]	a = 14.407(1) c = 10.331(1)	a = 12.7408(6) b = 13.7375(7) c = 18.216(1) α = 90.627(5) β = 101.568(4) γ = 92.194(4)	a = 13.036(2) b = 13.525(2) c = 19.520(3) α = 89.58(1) β = 84.93(1) γ = 70.89(1)	a = 12.843(1) b = 15.730(1) c = 17.745(1) α = 81.801(5) β = 83.575(6) γ = 74.255(6)
Volume [Å^3]	1857.0(3)	3120.7(3)	3238.4(9)	3405.0(4)
Z	1	1	2	2
D (calcd.) [Mg/m^3]	1.742	1.721	1.608	1.524
Crystal size [mm]	0.40 × 0.36 × 0.28	0.68 × 0.28 × 0.24	0.40 × 0.35 × 0.14	0.35 × 0.30 × 0.24
μ(Mo-K_α) [mm^{-1}]	1.337	0.913	0.481	0.257
Absorption correction	Integration	Integration	2 ψ-scans	5 ψ-scans
Reflns. collected	2320	11430	10036	12432
Unique reflns.	689	11049	9592	11863
R[int]	0.0215	0.0134	0.0302	0.0169
Observed reflns.	675	9551	6561	8643
Final *R* indices [$F \geq 4\sigma(F)$] [a]	$R1$ = 0.0750,	$R1$ = 0.0595,	$R1$ = 0.0833,	$R1$ = 0.0810,
$wR2$ = 0.3212	$wR2$ = 0.1773	$wR2$ = 0.2522	$wR2$ = 0.2355	
R indices (all data)	$R1$ = 0.0755,	$R1$ = 0.0672,	$R1$ = 0.1044,	$R1$ = 0.1050,
wR2 = 0.3217	$wR2$ = 0.1867	$wR2$ = 0.2650	$wR2$ = 0.2631	
GooF on F^2	3.155	1.079	1.022	1.023

[a] Definitions: $R1 = \Sigma\# \mid |F_o| - |F_c| \mid / \Sigma\# |F_o|$, $wR2 = \{\Sigma\# [w(F_o{}^2 - F_c{}^2)^2] / \Sigma\# [w(F_o{}^2)^2]\}^{1/2}$, GoF = $\{\Sigma\# [w(F_o{}^2 - F_c{}^2)^2] / (n-p)\}^{1/2}$.

bituril hydrate (water content corresponds approximately to that of the hexahydrate) was from Merck. *p*-Toluenesulfonic acid was purchases from Aldrich Chemical Company, Inc. Elemental analysis was performed by the analytical service of the Institute of Organic Chemistry SB RAS (Novosibirsk). The nitrate in **3** was determined by ion-exchange chromatography.

X-ray Structure Determination: The diffraction measurements for compounds **1−4** were performed at room temperature (293 K) with Bruker P4 (**1**, **4**) and Enraf−Nonius CAD4 (**2**, **3**) four-cycle diffractometers using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals of **3** and **4** were sealed onto quartz capillaries with traces of mother liquor to avoid decomposition by dehydration. The unit cell was determined from setting angles of 24 reflections in the $9 \leq \theta \leq 15°$ range. Data were collected using standard techniques ($\theta/2\theta$ scans with variable speed) up to $2\theta_{max} = 50°$. Structures were solved by direct methods using SHELXS97[16] (**1**, **4**) and SIR97[17] (**2**, **3**) programs. The hydrogen atoms of cucurbituril molecules were refined in rigid-body approximation. Some hydrogen atoms of water molecules were found in difference electron-density maps and refined by applying geometrical constraints. In the structure **3**, one of the NO_3^- ions appears to be disordered over several positions and therefore our attempts to locate it were unsuccessful. Nevertheless, the chemical analysis data for **3** are in good agreement with the proposed formula.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-144322 (**1**), -144323 (**2**), -144324 (**3**), -144325 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

$[InCl_2(H_2O)_4]_3Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot4H_2O$ (1): $In(NO_3)_3\cdot4.5H_2O$ (0.70 g, 1.8 mmol) was dissolved in a solution of cucurbituril (5 mL, 20 mM) in HCl (3 M) and kept at room temperature in an open beaker. Colorless hexagonal prisms of **1** separated after one week. Yield − 0.025 g (13%). − $C_{36}H_{68}N_{24}O_{28}Cl_9In_3$: calcd. C 22.19, H 3.52, N 17.25, Cl 16.37; found C 20.18, H 3.80, N 16.16, Cl 16.32.

$(H_3O)_3[InCl_4(H_2O)_2]_3\cdot2(C_{36}H_{36}N_{24}O_{12})\cdot17H_2O$ (2): In an aqueous solution of KNO_3 (1 M) and Hpts (0.01 M) was dissolved cucurbituril to a concentration 6.7 mM of cucurbituril. The white lamellar crystals were separated after standing for one day and a fraction of them (0.22 g) were dissolved in HCl (16 mL, 3 M). $In(NO_3)_3\cdot4.5H_2O$ (60 mg, 0.15 mmol) was dissolved in the solution (5 mL). Colorless prismatic crystals of **2** separated after one week. Yield − 0.015 g (7%). − $C_{72}H_{127}Cl_{12}In_3N_{48}O_{50}$: calcd. C 26.73, H 3.96, N 20.78, Cl 13.15; found C 26.18, H 3.67, N 20.41, Cl 12.15.

$[In(H_2O)_6](NO_3)_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot9H_2O$ (3): In a solution of $In(NO_3)_3\cdot4.5H_2O$ (3.94 g, 10.13 mmol) in water (10 mL), cucurbituril (0.10 g, 0.085 mmol) was dissolved after heating for 15 min on a hot plate. The solution was filtered and left in an open beaker for 1 day. Large colorless crystals of **3** separated, which, however, lost two water molecules. Yield − 0.081 g (19%). − $C_{36}H_{62}N_{27}O_{34}In$: calcd. C 28.23, H 4.08, N 24.69, NO_3^- 11.86, In 7.50; found C 28.00, H 4.07, N 24.85, NO_3^- 12.88, In 8.09.

$[Al(H_2O)_6]Cl_3\cdot(C_{36}H_{36}N_{24}O_{12})\cdot18H_2O$ (4): In a solution of $AlCl_3\cdot6H_2O$ (0.12 g, 0.5 mmol) in water (10 mL), cucurbituril (30 mg, 0.026 mmol) was dissolved after heating for 15 min on a hot plate. The solution was filtered and left in an open beaker for 4 days. Large colorless crystals of **4** separated, which, however, rapidly lost their water (1−2 minutes) and disintegrated when they were taken out of the mother liquor.

Acknowledgments

We are grateful to the Russian Foundation for Basic Research for supporting this work. We thank Dr. B. S. Smolyakov and Mrs. S. N. Filimonova for nitrate determination.

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Received May 16, 2000
[I00202]