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Structure-Directing Forces in Intercluster Compounds of Cationic $[Ag_{14}(C{\equiv}Ct\mathrm{Bu})_{12}Cl]^{+}$ Building Blocks and Polyoxometalates: Long-Range versus Short-Range Bonding Interactions

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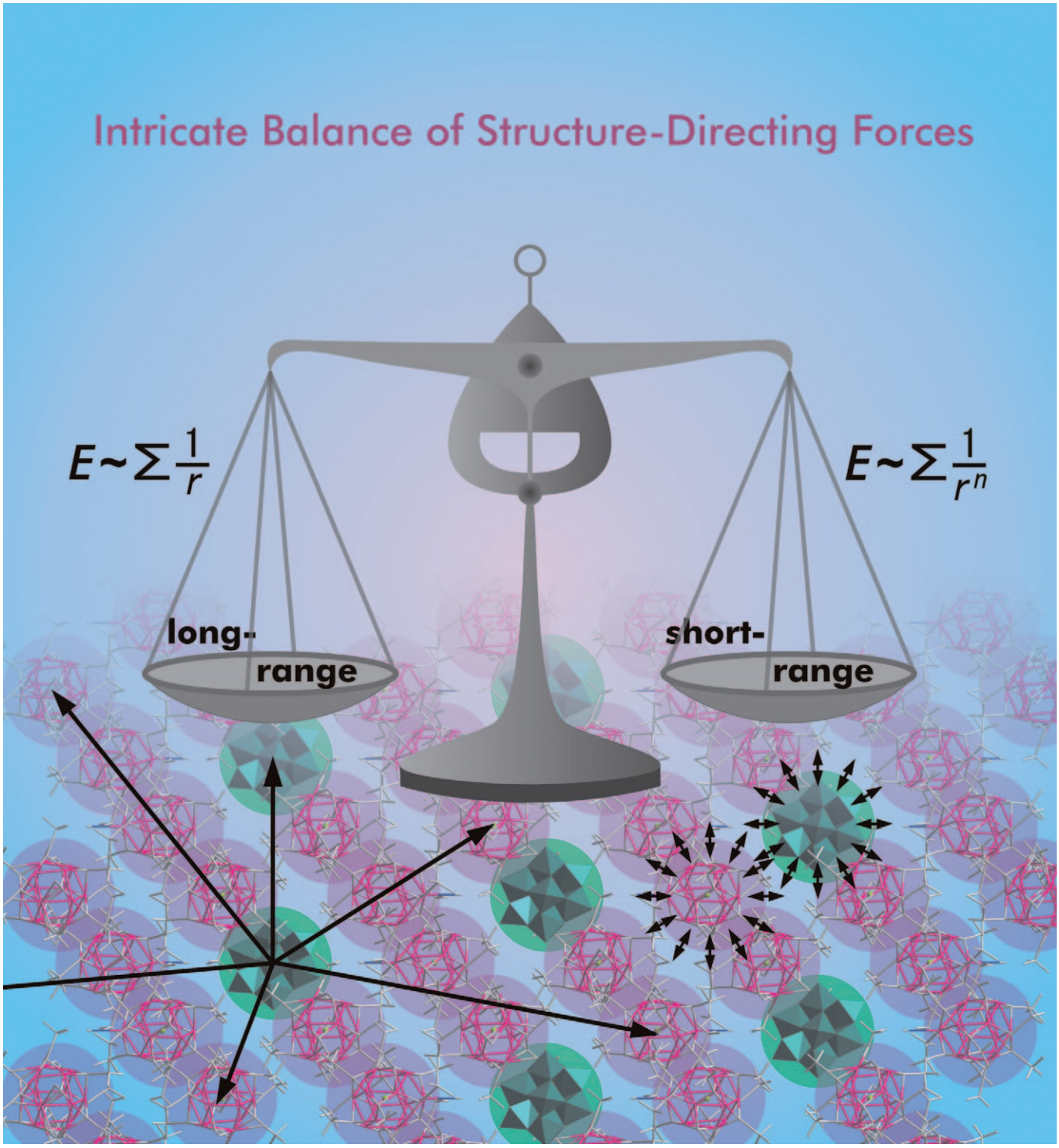

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Abstract: Crystallization of $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$ and different polyoxometalates in organic solvents yields a series of new intercluster compounds: $[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[W_6O_{19}]$ (**1**), $(nBu_4N)[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[PW_{12}O_{40}]$ (**2**), and $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]_2[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[SiMo_{12}O_{40}]$ (**3**). Applying the same technique to a system starting from polymeric $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$ and the polyoxometalate $(nBu_4N)_2[W_6O_{19}]$ results in the formation of $[Ag_{14}(C{\equiv}CtBu)_{12}(CH_3CN)_2][W_6O_{19}]$ (**4**). Here, the Ag_{14} cluster is generated from polymeric $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$ during crystallization. In a similar way, $[Ag_{15}(C{\equiv}CtBu)_{12}(CH_3CN)_5][PW_{12}O_{40}]$ (**5**) has been obtained from $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$ and $(nBu_4N)_3[PW_{12}O_{40}]$. The use of charged building blocks was intentional, because at these conditions the contribution of long-range Coulomb interactions would benefit most from full periodicity of the intercluster compound, thus favoring formation of well-crystalline materials. The latter has been achieved, indeed. However, as a most conspicuous feature, equally charged species aggregate, which demonstrates that the short-range interactions between the "surfaces" of the clusters represent the more powerful structure direction forces than the long-range Coulomb bonding. This observation is of significant importance for understanding the mechanisms underlying self-organization of monodisperse and structurally well-defined particles of nanometer size.

Keywords: cluster compounds · intercluster compounds · polyoxometalates · silver · supramolecular chemistry

Introduction

In general, each pure chemical compound displays a set of well-defined intrinsic chemical and physical properties. However, the specific properties of solid matter starts to depend on its particle size as soon as the latter falls below a critical threshold, which is typically in the range of 1–100 nm. This length scale demarcates the so-called field of nanoscience, the main objective of which is to tune the properties of materials by adjusting the particle sizes, and to subject them to assemble as nanoparticle superlattices.[1–4] Indeed, such lattices have become available over an extended range of particle sizes. However, due to the size distributions inherent to conventional populations of nanoparticles such lattices are rather imperfect. The respective severe violations of translational symmetry on the atomic scale thwart structure determinations with atomic resolution, which is a fundamental prerequisite for any detailed understanding of chemical and physical properties. We have shown that one possibility to overcome these limitations is to employ different, well-defined, large inorganic clusters as building blocks for new nanostructured superlattices, the intercluster compounds.[5–10] At selecting suitable building blocks with diameters exceeding 1 nm, we have given preference to charged species, which should obey in some general sense Pauling's crystal chemical rules for extended ionic solids. Such building blocks are actually multipoles. However, since the individual local charges will be small, one may consider the charged nanopaticles as volumes exhibiting a certain net excess charge, adding long-range Coulomb interactions to the overall lattice energy, thus favoring the formation of well-ordered crystalline arrangements.

We have shown this concept of growing supramolecular intercluster compounds to be feasible using the examples of gold clusters, polyoxometalates, and fullerides, disclosing a new facet of gold cluster chemistry[8] at the same time. The first compound obtained, consisted of the gold phosphine cluster $[Au_9(PPh_3)_8]^{3+}$ and the heteropolytungstate $[PW_{12}O_{40}]^{3-}$.[5] Depending on the solvent, two different modifications have been obtained. In the meantime, several intercluster compounds based on gold phosphine clusters and polyoxometalates have been synthesized.[6] Particularly interesting structural features have been discovered in the combination of Au_7 and Au_8 clusters with fullerides.[7]

Although it would be possible, in principle, to crystallize intercluster compounds from mixtures of diverse metal clusters and polyoxometalates as encountered in respective homogeneous equilibria, at the present stage of our studies we prefer to use solutions containing stable and unimodal metal clusters and polyoxometalates. The silver alkynyl compounds, known since the early 1960s,[11] appeared to fulfill the requirements mentioned. In particular, the recently synthesized cationic cluster $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][OH]$[12] has been shown to have a long lifetime in solution. The cage is composed of fourteen silver atoms and twelve *tert*-butylethynyl ligands, and has a chloride anion at its center. The silver atoms form a close to regular rhombic dodecahedron. The same cationic cluster was later synthesized free of halogen by O. M. Abu-Salah et al.[13] Both clusters are about 1.5 nm in diameter and have proven to be stable in solution.[14] The chloride-centered cluster bears an ionic charge of +1 and the empty one +2.

Another access to the Ag_{14} cluster is to use oligomeric smaller clusters like $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\ H_2O\}_n$ as a feed stock in solution. It has been shown previously by T. C. W. Mak et al. that $Ag_n{\subset}C{\equiv}C{-}R$ (R = aryl or alkyl; n = 1-5) can function as supramolecular synthons for the synthesis of

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discrete molecules as well as of 1D, 2D, and 3D networks.[15] Thus, the polymeric cluster $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\ H_2O\}_n$ fulfills our preconditions, moreover it is soluble in different solvents. Here, we report on the synthesis and characterization of a new family of intercluster compounds based on Ag_{14} clusters.

Results and Discussion

Starting from reactants containing the appropriate anionic and cationic cluster building blocks, the new intercluster compounds **1–5** have been obtained by metathesis reactions. While sufficiently crystalline materials of **1–3** have been obtained by slowly combining the solutions of the respective starting materials, growing crystals of **4** and **5** in a size and quality suitable for single-crystal x-ray diffraction required to run precipitation under diffusion control. All products are colorless, except for the yellow crystals of **3**. This color originates from the yellow polyoxometalate $[SiMo_{12}O_{40}]^{4-}$ used in its synthesis. At ambient conditions all compounds are stable in air, but due to loss of solvent the crystals get pulverulent if stored in absence of excess solvent.

The anionic cluster building blocks are the polyoxometalates $[W_6O_{19}]^{2-}$, $[PW_{12}O_{40}]^{3-}$ and $[SiMo_{12}O_{40}]^{4-}$, see Figure 1 a–c. The compositions of the polyoxometalates are in

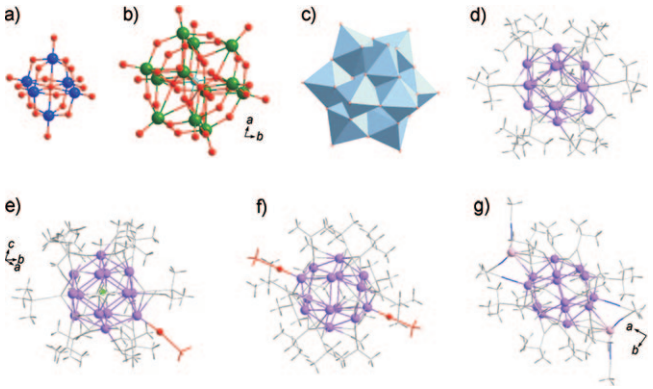

Figure 1. Structures of the silver clusters and the polyoxometalates used as building blocks a) $[W_6O_{19}]^{2-}$, b) $[PW_{12}O_{40}]^{3-}$, c) $[SiMo_{12}O_{40}]^{4-}$, d) $[Ag_{14}(C{\equiv}CtBu)_{12}]^{2+}$, e) $[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]^{+}$, f) $[Ag_{14}(C{\equiv}CtBu)_{12}(CH_3CN_2)]^{2+}$, and g) $[Ag_{15}(C{\equiv}CtBu)_{12}(CH_3CN)_5]^{3+}$.

accordance with the structures known from literature.[16–18] The cationic components in all representatives contain the same Ag_{14} core entity. The fourteen silver atoms form a near-regular rhombic dodecahedron. The Ag–Ag bond lengths are in the range of 2.88–3.11 Å and are comparable to those observed in the starting material $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$.[12] The Ag_{14} core is surrounded by twelve *tert*-butylethynyl ligands (see Figure 1 d) in all intercluster compounds **1–5**. In **1–3**, synthesized from $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$, the cationic clusters have a chloride anion at their centers and an additional acetonitrile molecule coordinated (see Figure 1 e). Using polymeric $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6H_2O\}_n$ as a feed stock providing larger silver clusters yielded the intercluster compounds **4** and **5**. The cationic building block of **4** is based on the same Ag_{14} core with twelve *tert*-butylethynyl ligands as in compounds **1–3**, but is not centered around a chloride anion; furthermore it is coordinated by two additional acetonitrile molecules in opposite positions (see Figure 1 f). The silver cluster contained in **5** differs most because there is an additional $\{Ag(CH_3CN)_3\}^{+}$ group bound to one of the silver ions (see Figure 1 g). With this additional group the cluster has to be formulated as $[Ag_{15}(C{\equiv}CtBu)_{12}(CH_3CN)_5]^{3+}$.

Since among all classes of chemical bonding long-range Coulomb interaction benefits most from perfect crystalline order, we have used charged building blocks in our attempts to create solids consisting of well-defined particles of sizes exceeding 1 nm, and at the same time showing fully developed translational symmetry down to atomic dimensions. Following such a concept would suggest that Coulomb interactions not only contribute significantly to the overall lattice energy, but should also be structure-directing . Surprisingly, none of the intercluster compounds presented here seems to follow the simple rules of ionic crystals, namely that oppositely charged units should attract, while equally charged species should repel each other.

In contrast to such expectations, equally charged clusters form local aggregates (see Figures 3 and 4 below), which indicates that the Coulomb part of the lattice energy does not seem to develop significant structure-directing potential. Instead, optimal space filling and the sum of short-range weakly attractive forces mediated by hydrogen bonding or by dispersion interactions in general seem to dominate.

Compound $[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[W_6O_{19}]$ (**1**) consists of the $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]^{+}$ cluster and the polyoxometalate $[W_6O_{19}]^{2-}$ in a ratio of 2:1. The $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]^{+}$ clusters form a highly distorted hexagonal close packing while the Lindquist anions $[W_6O_{19}]^{2-}$ fill all of the octahedral sites in alternate layers (see Figure 2). Thus, the resulting layered structure can be reduced to a CsCl-type packing with every second polyoxometalate layer being empty.

The two crystallographically independent silver clusters of $(nBu_4N)[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[PW_{12}O_{40}]$ (**2**) differ only in their surroundings but not in their constitution. In the structure, there are additional tetrabutylammonium cations included for the sake of charge neutrality. The compound can be described as a layered structure, shown in Figure 3 a. Each layer consists of two rows of Keggin anions followed by four rows of silver clusters. The tetrabutylammonium cations are located in between the two rows of Keggin anions stabilizing the close arrangement of the highly charged polyoxometalates. This motif is repeated periodically. Figure 3 b shows the stacking of the layers. The double rows of polyoxometalates are embedded in a matrix of silver clusters, indicating some kind of phase separation as it is commonly encountered in lyotropic phases.[20] The pack-

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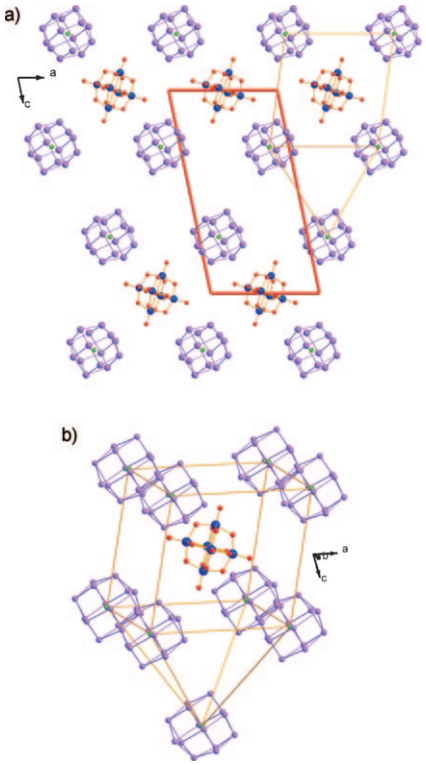

Figure 2. Crystal structure of **1** (the ligands are not shown for clarity). The unit cell is depicted in red. The section marked by yellow lines in a) is shown in b) perspectively.

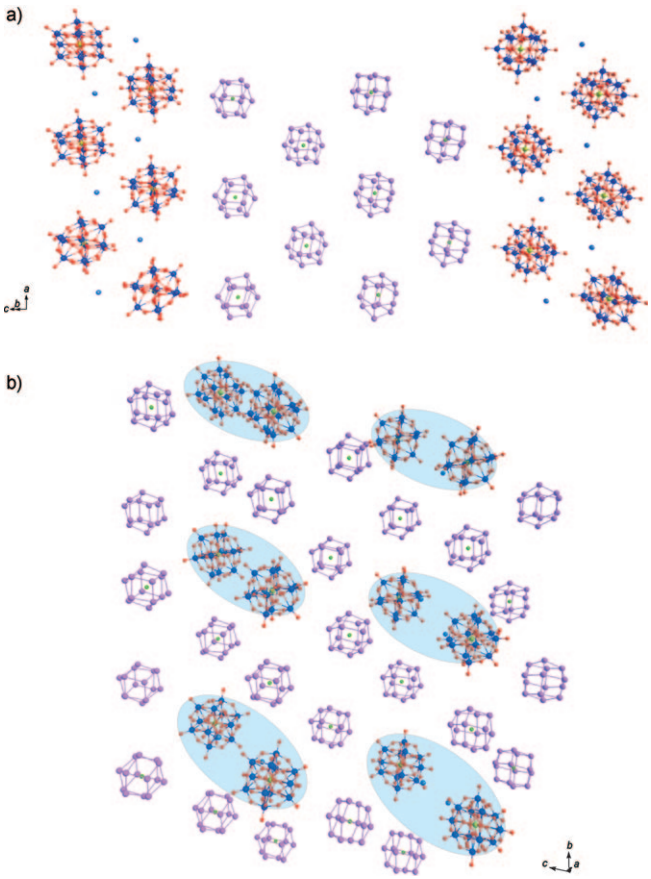

Figure 3. Layered structure of **2** (the ligands are not shown for clarity). Tetrabutylammonium cations are schematically shown as blue balls. a) Viewing direction perpendicular to one layer. b) Viewing direction parallel to the layers.

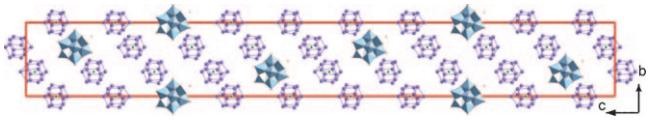

Figure 4. Projection of the unit cell of **3** along the [100] axis.

ing of the double rows is in between a hexagonal and tetragonal rod packing (see Figure 3b).

The crystal structure of $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]_2[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]_2[SiMo_{12}O_{40}]$ (**3**) shows an unusual structure in space group $R\bar{3}c$ with a remarkably long c axis of 151.4 Å (see Figure 4). It consists of two crystallographic different silver clusters $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]^+$ and $[Ag_{14}(C{\equiv}CtBu)_{12}Cl(CH_3CN)]^+$ and the Keggin anion $[SiMo_{12}O_{40}]^{4-}$. All nanometer-sized building blocks jointly arrange in the sense of a cubic, body-centered packing, which is including numerous direct contacts between equally charged cluster units (see Figure 5).

As in **1**, the crystal structure of $[Ag_{14}(C{\equiv}CtBu)_{12}(CH_3CN)_2][W_6O_{19}]$ (**4**) comprises the hexatungstate anion and an Ag_{14} cluster as building blocks. However, here the silver cluster is not centered around a chloride anion, but it is coordinated by two acetonitrile molecules in opposite positions (see Figure 1f). Therefore, it differs also in charge from the silver clusters discussed above and is formulated as $[Ag_{14}(C{\equiv}CtBu)_{12}(CH_3CN)_2]^{2+}$. Cluster **4** crystallizes in the rhombohedral space group $R\bar{3}$ with three formula units in the unit cell. The Ag_{14} clusters form a cubic close packing while the Lindquist anions $[W_6O_{19}]^{2-}$ fill all of the octahedral sites (see Figure 6a), thus generating the principal topology of the CsCl-type of structure.

$[Ag_{15}(C{\equiv}CtBu)_{12}(CH_3CN)_5][PW_{12}O_{40}]$ (**5**) crystallizes in the space group $P2_1/c$ with two formula units per unit cell. The silver cluster consists of the Ag_{14} cage surrounded by twelve *tert*-butylethynyl ligands and two acetonitrile molecules in opposite positions. There is an additional $\{Ag(CH_3CN)_3\}^+$ group bound to one of the silver ions. The extra silver ion is located alternating on one or the other side of the Ag_{14} cage and is found with half occupancy on both sides in the structure determination (see Figure 1g). The packing of the building blocks corresponds to the CsCl-type arrangement and is shown in Figure 6b.

Features that are generally likely to occur in intercluster compounds are voids or channels filled with small solvent molecules, just because of the size of the building blocks. This so-called solvent accessible volume can be calculated using the program Platon.[19] Structure **1** and **4** are rather closely packed, whereas the solvent accessible volume of **2** accounts to 13.2%, which separates into two voids of 638 $Å^3$ each. Cluster **3** displays an accessible volume of 17.2% di-

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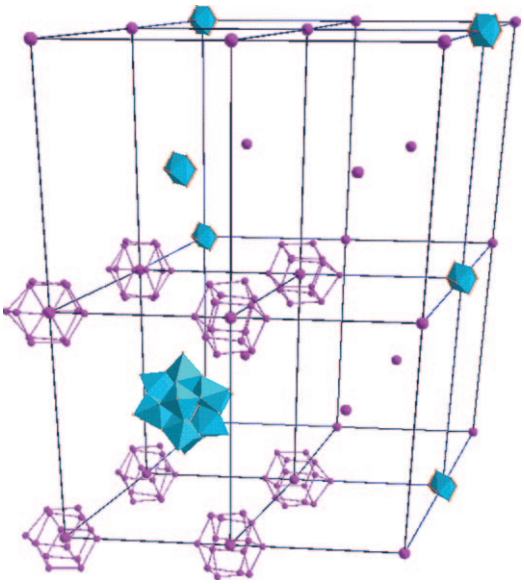

Figure 5. Structure of **3**, showing the joint body-centered cubic packing of the anionic and cationic building blocks.

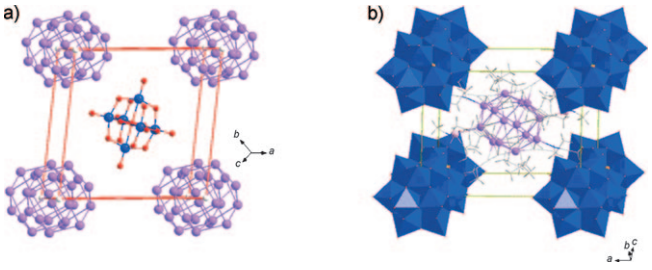

Figure 6. Crystal structure of a) **4** and b) **5**, emphasizing their relationship to the CsCl-type of structure. (The ligands are not shown for clarity.)

vided into 18 voids of 596 Å^3 per unit cell, while the solvent volume of **5** is found to be 21.7% resulting from four different voids of 931 Å^3 per unit cell.

Conclusion

It has been shown that it is possible to grow single crystals of intercluster compounds consisting of nanometer-sized silver clusters and polyoxometalate anions, in good quality. While **1** to **3** were synthesized by metathesis from solutions containing the pre-shaped building blocks, **4** and **5** are the first examples of supramolecular intercluster compounds where one of the building blocks was generated in situ during the crystallization. This opens the possibility to build intercluster compounds not only from building blocks synthesized separately in advance, but also by starting from smaller complexes, out of which larger ones form spontaneously while establishing the homogeneous equilibrium in solution. Such starting materials, as used here can then be regarded as synthons for supramolecular intercluster compounds. At the example of **5** it is demonstrated that via this in situ reaction, it is possible to obtain new clusters of unexpected structure.

Quite opposite to our expectation that the structures evolving for the purposefully approached intercluster compounds were primarily determined by the requirement to optimize the Coulomb part of the lattice energy, the structures observed indicate that in the first place packing efficiency is the structure-directing factor. High packing efficiency is implying at the same time optimal surface contact between adjacent clusters to result, thus optimizing short-range hydrogen bonding and diverse kinds of dispersion interactions. We conclude that the self-organization of charged nanosized building blocks is controlled by a sensitive competition between the long-range Coulomb forces and the diverse family of short-range bonding interactions. These insights are of relevance for understanding the structure-directing forces determining the topological features of extended solids consisting of nanometer-sized building blocks.

Experimental Section

Synthesis: All solvents were purchased from Fluka and used as received. $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$[12], $\{[Ag_3(C{\equiv}CtBu)_2][BF_4] \cdot 0.6\ H_2O\}_n$[14,21] and the polyoxometalates $(nBu_4N)_2[W_6O_{19}]$[16], $(nBu_4N)_3[PW_{12}O_{40}]$[17] and $(nBu_4N)_4[SiMo_{12}O_{40}]$[18] were prepared according to the procedure given in literature. All starting materials were checked for their purities using IR spectroscopy. The composition of the compounds **1**–**5** was analyzed with EDX in respect of the heavy elements.

*Clusters **1** and **2***: A solution of $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$ in acetonitrile (3 μmol ml^{-1}) was mixed for **1** with a solution of $(nBu_4N)_2[W_6O_{19}]$ in acetonitrile (1.5 μmol ml^{-1}), and for **2** with a solution of $(nBu_4N)_3[PW_{12}O_{40}]$ in acetonitrile (1.5 μmol ml^{-1}) respectively. After one day, small colorless plates of **1** or colorless prisms of **2** have formed. The crystals lose solvent molecules upon removal from the mother liquid.

*Cluster **3***: A solution of $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$ in acetonitrile (1.4 μmol ml^{-1}) was mixed 1:2 with a solution of $(nBu_4N)_4[SiMo_{12}O_{40}]$ in acetonitrile (0.9 μmol ml^{-1}). After one day, light the yellow, plate-like crystals of **3** have formed. The crystals lose solvent molecules upon removal from the mother liquid.

*Clusters **4** and **5***: These clusters were obtained by allowing solutions of the polymeric silver compound $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\ H_2O\}_n$ in acetonitrile (2 mg mL^{-1}) and $(nBu_4N)_2[W_6O_{19}]$ in dimethylformamide (4 mg mL^{-1}) in case of **4** and $(nBu_4N)_3[PW_{12}O_{40}]$ in acetone (4 mg mL^{-1}) in the case of **5**. For this purpose, 1 mL of the silver cluster solution was layered with 2 mL of a 1:1 mixture of acetonitrile/dimethylformamide and 1 mL of the polyoxometalate solution in glass tubes of 10 mm inner diameter. After a few days colorless crystals of **4** and **5** were grown at the interface of the two phases. The crystals lose solvent molecules upon removal from the mother liquid.

Single-crystal X-ray diffraction studies: All crystal structures were solved by direct methods (SHELX 97) and subsequent difference fourier maps and refined on F^2 (SHELXTL). The measurements were made on a AXS Bruker, Smart APEX diffractometer, with $Mo_{K\alpha}$ radiation ($\lambda = 0.7103$ Å) in the ω scan mode. Empirical absorption correction (SADABS) were applied. Further details of the measurements can be found in Table 1.

*Cluster **1***: All atoms but H atoms were refined with anisotropic displacement parameters. Three of the tert-butylethynyl ligands were found to be disordered and were refined with split positions and isotropic displacement parameters. Hydrogen positions were calculated using the HFIX command.

*Cluster **2***: Ag, W, P, and Cl atoms were refined with anisotropic displacement parameters, C and O atoms with isotropic displacement parameters.

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Table 1. Data collection and structure-determination parameters for **1**–**5**.

	1	**2**	**3**	**4**	**5**
crystal data					
formula	$C_{148}H_{222}Ag_{28}Cl_2N_2W_6O_{19}$	$C_{164}H_{250}Ag_{28}Cl_2N_3PW_{12}O_{40}$	$C_{292}H_{438}Ag_{56}Cl_4N_2SiMo_{12}O_{40}$	$C_{76}H_{114}Ag_{14}N_2W_6O_{19}$	$C_{82}H_{123}Ag_{15}N_5PW_{12}O_{40}$
M_r [g mol^{-1}]	6527.64	8240.16	11978.33	3972.97	5633.02
crystal system	triclinic	triclinic	rhombohedral	rhombohedral	monoclinic
space group, Z	$P\bar{1}$, 1	$P\bar{1}$, 2	$R\bar{3}c$, 6	$R\bar{3}$, 3	$P2_1/c$, 2
a [Å]	13.654(2)	15.7565(13)	21.8383(15)	17.9584(13)	17.5308(15)
b [Å]	13.723(2)	26.288(2)	21.8383(15)	17.9584(13)	19.1121(17)
c [Å]	26.145(4)	29.606(2)	151.390(12)	27.3933(40)	19.7921(17)
α [°]	79.391(3)	76.8430(10)	90	90	90
β [°]	76.693(3)	87.6320(10)	90	90	92.65(0)
γ [°]	79.121(3)	87.9590(10)	120	120	90
V [Å^3]	4630.8(18)	11926.4(17)	62527(8)	7650.9(14)	6624.23(104)
ρ_{calcd} [g cm^{-3}]	2.341	2.295	1.909	2.643	2.824
μ [g mm^{-1}]	6.667	8.077	2.98	9.405	12.602
data collection					
θ [°]	1.89–26.43	1.77–23.26	1.87–22.01	1.51–23.18	1.58–20.86
measured reflections	36211	74371	116317	16020	32658
unique reflections	18685	34225	8528	2414	6948
structure solution and refinement					
parameters	959	1311	365	184	532
$R1$ (all)/$R1$ $[F_o > 4\sigma(F_o)]$	0.0962/0.0765	0.1239/0.0864	0.1328/0.1104	0.0356/0.0305	0.0652/0.0502
$wR2$ (all)	0.2064/0.1926	0.2502/0.2190	0.3347/0.3079	0.0736/0.0691	0.1297/0.1213
GooF	1.072	1.008	1.036	1.077	1.043

Hydrogen positions were calculated using the HFIX command. The Keggin anion is disordered in two orientations. However, all atoms, except the four oxygen atoms in the central tetrahedron, were refined without split positions, as the latter are almost equal in the two orientations.

Cluster ***3***: Ag, Mo, Si, and Cl atoms were refined with anisotropic displacement parameters, C and O atoms with isotropic displacement parameters. Hydrogen positions were calculated using the HFIX command. The Keggin anion is located at a 32-position and disordered. However, all atoms, expect the four oxygen atoms in the central tetrahedral, were refined without split positions.

Cluster ***4***: All atoms were refined with anisotropic displacement parameters. Hydrogen positions were calculated using the HFIX command. Both clusters were ordered.

Cluster ***5***: Apart from C, N and H, all atoms were refined with anisotropic displacement parameters. Hydrogen positions were calculated using the HFIX command. The Keggin anion was disordered in two orientations and was refined similar to **2**.

CCDC-714953 (**1**), -714951 (**2**), -714952 (**3**), -714954 (**4**), and -714955 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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