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Supramolecular Intercluster Compounds Consisting of Gold Clusters and Keggin Anions

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Supramolecular intercluster compounds, that is, assemblies of different, well-defined inorganic building blocks with diameters of >1 nm, consisting of $[Au_9(PPh_3)_8]^{3+}$ clusters and Keggin anions $[PW_{12}O_{40}]^{3-}$ were synthesized as single-crystals by a diffusion method. Depending on the solvent combination, two modifications with different core geometries of the gold cluster and different overall packing type can be obtained as a single-phase in macroscopic amounts. This approach leads toward the study of nanostructured matter with high translational symmetry and the principles of nanoscopic self-assembly.

Introduction

Supramolecular chemistry aims to organize molecular building blocks by means of noncovalent interactions into complex arrangements.[1] Efforts to synthesize suitable building blocks, to develop methods for their assembly, and understand the underlying fundamental principles are currently driven over all magnitudes – ranging from molecules to nano-, *meso*-, and macroscopic compounds.[1,2] In particular, nanoscopic self-assembly is envisioned to be the alternative to lithographic techniques for future electronic or optic devices. By the assembly of different building blocks into superlattices, materials can be obtained that exhibit new properties that are due to cooperative effects. One step in this direction are binary nanoparticle superlattices.[3] Recently, progress has been made in the experimental realization of such compounds, which gives insight into the driving forces of nanoparticle crystallization.[4] Depending on the types of interaction (van der Waals, hard sphere, or ionic interaction) and the relative size of the ligand stabilized nanoparticles, a whole variety of packing types were observed.

Although the principles of self-assembly and the interparticle interactions vary over the different magnitudes, one rule holds for all: the quality of the arrangements depends on the uniformity of the building blocks. This prerequisite is commonly fulfilled very well for a molecular assembly but not for the assembly of nanoparticles (except protein crystallization), which exhibit an intrinsic size distribution. The resulting violations of translational symmetry on the atomic scale would undermine at least some of the enthusiastic expectations connected to the properties of nanostructured matter. Anyhow, such defects would thwart structure determinations with atomic resolution, which is an important prerequisite for a detailed understanding of structure-directing forces and the resulting physical properties. Our approach for overcoming these limitations is based on the generation of supramolecular intercluster compounds (SICC), that is, assemblies of different, well defined, inorganic building blocks with diameters of 1 nm or larger.

The variety of inorganic clusters that have been studied in manifold, and clusters of several nanometers in size have been uniformly synthesized and crystallized.[5,6] Only a few examples of compounds consisting of different inorganic clusters have been reported and all are constructed of different polyoxometalates as anionic building blocks.[7,8]

SICCs can be seen as a bridge between the molecular self-assembly and the self-assembly of nanoparticles. While the latter is dominated by nondirectional interactions of spherical particles leading to more or less densely-packed structures that can mostly be derived from simple ionic or intermetallic compounds, the arrangements in the former are strongly dependent on the shape of the molecules and directional interactions, which can lead to structures with either low symmetry or density. For SICCs, a tendency for structures with a dense packing of the clusters can be expected. However, because of deviations from a perfect spherical shape, local directional, or steric interactions, a wide range of arrangements might be realized. Because of the size of the building blocks, voids filled with solvent molecules are likely to occur in such arrangements. Unlike binary nanoparticle superlattices, it is possible to grow SICCs as single-crystals with high translational order, such that details of the supramolecular arrangements can be elucidated by X-ray diffraction.

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Results and Discussion

In this communication, we report the crystallization and structural characterization of the first supramolecular intercluster compounds consisting of different types of building units, the gold cluster $[Au_9(PPh_3)_8]^{3+}$ and the Keggin anion α-$[PW_{12}O_{40}]^{3-}$. It is noteworthy that the $[Au_9(PPh_3)_8]^{3+}$ cluster although being one of the first gold clusters to be discovered,[9,10] accessible in gram-scale quantities, and widely investigated, has never been characterized by single-crystal X-ray diffraction because of heavy disorder. Structural characterization of Au_9^{3+} clusters was successful only by the employment of *para*-substituted ligands.[10–12] In the solid state, two skeletal isomers of $[Au_9(PR_3)]^{3+}$ clusters were found; in solution the clusters undergo fast rearrangements.

The mixing of solutions of $[Au_9(PPh_3)_8](NO_3)_3$ and $(NBu_4)_3[PW_{12}O_{40}]$ in acetonitrile leads to a microcrystalline, orange precipitate of the 1:1 compound $[Au_9(PPh_3)_8]$-$[PW_{12}O_{40}]$ (**1**). For growing single-crystals for X-ray diffraction, an interdiffusion method was employed. The building blocks were separately dissolved in solvents of different density and layered carefully on top of each other. Depending on the types of solvents and the concentration, two types of crystals were obtained, orange needles of compound **1** and greenish-black plates or prisms of a second compound **2**. Both compounds contain $[Au_9(PPh_3)_8]^{3+}$ and α-$[PW_{12}O_{40}]^{3-}$ in a 1:1 ratio, but exhibit different Au_9 skeletal isomers and packing types. Although in some solvent combinations simultaneous growth of both compounds was observed, **1** and **2** can be obtained selectively in DMF-acetonitrile and DMF-acetone, respectively.

Compound **1** crystallizes in the tetragonal space group *P*4/*n* with two formula units in the unit cell.[13] The skeletal geometry of the $[Au_9(PPh_3)_8]^{3+}$ cluster, which is located on a four-fold axis, resembles the shape of a centered crown with eight Au atoms surrounding the central Au1 atom (Figure 1a). The radial Au–Au bond lengths are 266.2(1) pm and 266.9(1) pm and the peripheral bond lengths are 277.7(1) pm and 280.6(1) pm. This centered crown geometry was first observed in the related $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8](BF_4)_3$.[12] The central P atom of the Keggin anion α-$[PW_{12}O_{40}]^{3-}$ resides on a position exhibiting $\bar{4}$ symmetry (Wyckhoff position 2a) and the whole anion is found to be ordered (Figure 1b). The W–O and P–O bond lengths of this well-known anion are in agreement with those previously found in other crystal structure determinations.[14] Figure 2 shows the overall packing of **1**, which can be derived from the CsCl structure type. Both the gold cluster and the Keggin anion are coordinated by each other in the form of distorted cubes. The distortion originates mainly from the nonspherical shape of the Au_9 cluster. Furthermore, the eight peripheral Au atoms can be divided into an upper and lower part of the crown. Four Au atoms, respectively, are bonded to PPh_3 ligands pointing directly towards the corners (4 × Au2) and the edges (4 × Au3) of the coordination cube (Figure 3). The distances between the central Au1 and the central P1 of the Keggin anions are 1339 pm and 1444 pm. This separation leads to the slight distortion of the Au_9 skeleton from the D_{4d} symmetry with the Au2–Au2 distances [344.8(1) pm] being shorter than the Au3–Au3 distances [350.2(1) pm]. The gold clusters exhibit close contacts not only to the eight Keggin anions (H···O distances 230–250 pm) but also to six neighboring gold clusters (H···H distances <270 pm), which is expected for the CsCl packing type. The Au1–Au1 distances are 1367 pm and 1723 pm and can be regarded as an approximation for the short and long van der Waals diameters of the gold cluster. The van der Waals diameters of $[PW_{12}O_{40}]^{3-}$, which is not perfectly spherical as well, can be estimated to range from 1050 pm to 1350 pm. As both building blocks are oriented with their short diameters parallel to the *c* axis, a relatively dense packing is achieved. The estimated radii ratios of 0.75–0.80 are close to the theoretical value of 0.73, which is calculated for touching spheres with cubic coordination. Although the estimation of the radii ratios for such building blocks with a rather irregular surface seems to be a rough approximation, it can be concluded that the CsCl structure-type is at least a very dense and therefore effective packing for this intercluster compound. A search for voids in the crystal structure (PLATON,[15] probe radius 1.2 Å) led to a value of 11.5% of the accessible volume. The largest voids (202 Å^3) can be found in between two adjacent Keggin anions that lie along [001].

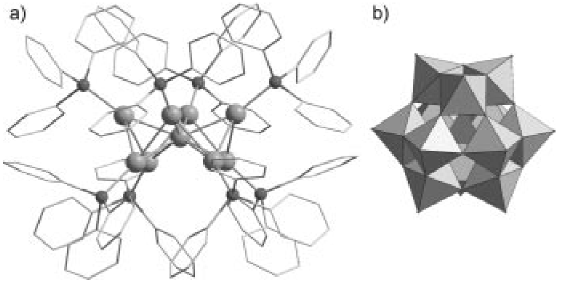

Figure 1. a) Structure of the crown isomer of the $[Au_9(PPh_3)_8]^{3+}$ cluster. Hydrogen atoms are omitted for clarity. b) Structure of the Keggin anion α-$[PW_{12}O_{40}]^{3-}$ in polyhedral representation.

Compound **2** crystallizes in the space group *C*2/*c* with four formula units in the unit cell.[13] Different from **1**, the $[Au_9(PPh_3)_8]^{3+}$ cluster is not in the crown skeletal geometry but in a "butterfly-shaped" geometry (Figure 4a), which was first observed in the compound $[Au_9\{P(p\text{-}C_6H_4Me)_3\}_8](PF_6)_3$.[12] The cluster resides on a crystallographic site of C_2 symmetry (4e). While the ligand shell exhibits only this C_2 symmetry, the symmetry of the Au skeleton is close to D_{2h}. The radial Au···Au bond lengths range from 266.1(1) pm to 273.8(1) pm and the corresponding peripheral bond lengths vary from 278.8(1) pm to 292.6(1) pm. Thus, the average Au···Au bond lengths and their variations are considerably larger than those of the crown isomer. The Keggin anion was found to be disordered over two orientations with the resulting superposition exhibiting inversion symmetry (Wyckhoff position 4d). This kind of disorder has been encountered several times before for Keggin anions and can be realized by 90° rotations

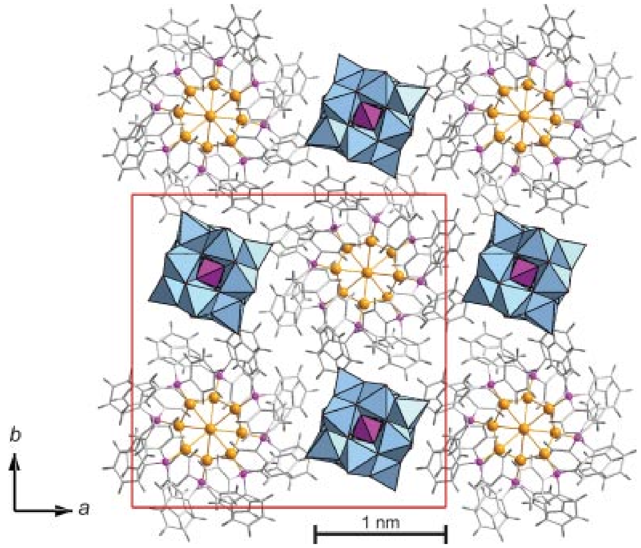

Figure 2. View of the crystal structure along [001]. The Keggin anions are located at $z = 0$ and the gold clusters at $z = 0.42$ and $z = 0.58$, respectively.

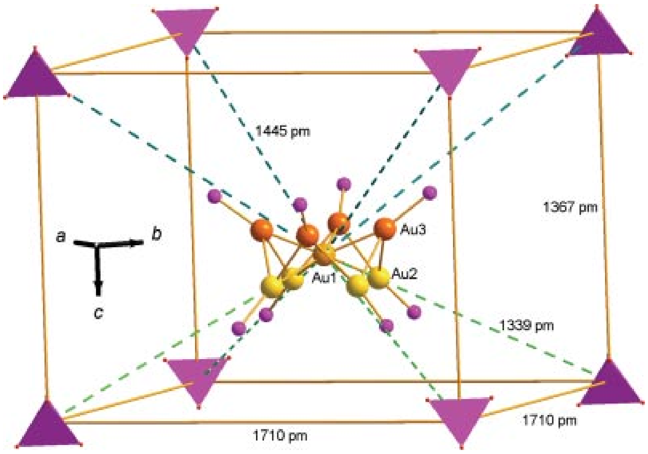

Figure 3. Coordination of the gold cluster by eight anions. The ligands of the peripheral Au atoms are pointing directly towards (Au2, yellow spheres) or in between (Au3, orange spheres) the anions.

along one of the $\bar{4}$ axes of the central tetrahedron.[16] In Figure 4b, it can be seen that the outer silhouette of the two orientations is almost equal, so that this crystallographic disorder is likely to occur. The packing scheme of **2** can be derived from the NaCl structure-type (Figure 5). The Keggin anions are coordinated by six $[Au_9(PPh_3)_8]^{3+}$ clusters (shortest O···H contacts <250 pm) in the form of a distorted octahedra with center-to-center distances of 1300, 1304, and 1391 pm. Vice versa, the gold clusters are coordinated by six Keggin anions octahedrally as well. The gold clusters are oriented in such a way that the eight PPh_3 ligands, which surround the Au skeleton in almost a cubic fashion, point towards the eight faces of the coordination octahedron.

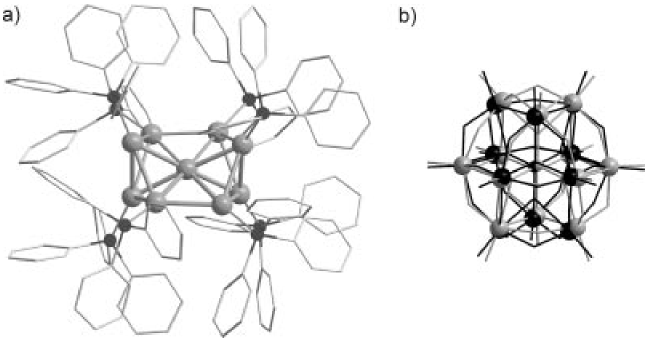

Figure 4. a) Structure of the "butterfly-shaped" isomer of the $[Au_9(PPh_3)_8]^{3+}$ cluster. Hydrogen atoms are omitted for clarity. b) Superposition of the two orientations of the α-$[PW_{12}O_{40}]^{3-}$ anion in **2**.

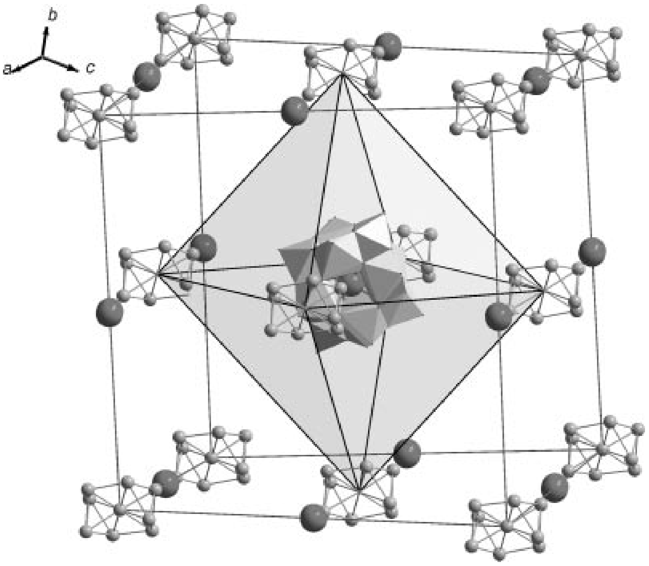

Figure 5. Similarity of the packing of **2** to the NaCl structure type: the gold clusters are packed face-centered cubic and the Keggin anions (dark grey spheres) occupy the octahedral voids.

The effective van der Waals diameter of the "butterfly-shaped" $[Au_9(PPh_3)_8]^{3+}$ isomer can be estimated to be about 1650 pm to 1750 pm. The silhouette of this isomer is more spherical than that of the crown isomer. In case of a regular closed packing of touching hard spheres with this diameter, the octahedral voids could occupy spheres with a diameter not greater than about 700 pm. The diameter of the Keggin anion (1050 pm to 1350 pm) is significantly larger than that, which has several consequences. First, not all of the twelve neighboring gold clusters are in close contact to the central gold cluster. The center-to-center distances in the distorted cuboctahedron vary from 1680 pm to 2108 pm. Furthermore, the misfit of the Keggin anions leads to substantial voids. The solvent accessible volume was calculated to be 19.6%. There appear to be four crystallographically equivalent solvent pockets per unit cell (average coordinates 0, 0.185, 0.25), but single solvent molecules could not be located during crystal structure refinement because of disorder. The crystals lose solvent molecules rapidly upon removal from the mother liquid. From geometric considerations about six molecules (DMF or acetone) per formula unit would fit into the voids.

Conclusions

In conclusion, we have synthesized two representatives of SICCs in macroscopic amounts and determined their crystal structures. We think that this may become a versatile and efficient approach to new, well-defined, nanostructured materials. Currently, we are modifying the building-blocks in order to study the underlying principles of such supramolecular structures and their formation.

Experimental Section

$Au_9(PPh_3)_8(NO_3)_3$ ("Au_9") and $Au_8(PPh_3)_8(NO_3)_2$ ("Au_8") were prepared by the reduction of $AuPPh_3NO_3$ with $NaBH_4$, and its subsequent reaction with excess triphenylphosphane according to the procedure given in ref.[17] α-$[n\mathrm{Bu}_4N]_3PW_{12}O_{40}$ ("PW_{12}") was prepared by precipitation of an aqueous solution of commercially available tungstophosphoric acid with $n\mathrm{Bu}_4NBr$ and subsequent recrystallization from acetone.[18] **1**: Upon mixing acetonitrilic solutions of Au_9 and PW_{12}, an orange, microcrystalline powder of **1** precipitates immediately. Larger crystals can be obtained by an interdiffusion method, which was optimized in glass tubes with a diameter of 8 mm at 20 °C. Single-crystals of **1** were obtained by the careful layering of Au_9 in DMF (0.3 mL, 1 µmol/mL) followed by DMF/acetonitrile (1:1, 1.0 mL), and PW_{12} in acetonitrile (0.3 mL, 1.5 µmol/mL). After several days, orange needles that tend to dendritic intergrowth form. If the diffusion is carried out with Au_8 as starting material, the Au_8 cluster rearranges back to the Au_9 cluster and **1** crystallizes as the only compound, which was checked by X-ray diffractometry. Interestingly, the obtained crystals are larger and less intergrown than those obtained with Au_9 as the starting material. Single-crystals suitable for X-ray diffraction were washed with acetonitrile, dried in air, and mounted on glass capillaries. Larger scale synthesis of **1** was carried out in glass tubes with a diameter of 2 cm. $[(n\mathrm{Bu}_4N)]_3PW_{12}O_{40}$ (133 mg, 36.9 µmol) in DMF (8 mL) was carefully layered with DMF/acetonitrile (1:1, 4 mL), followed by $Au_9(PPh_3)_8(NO_3)_3$ (100 mg, 24.6 µmol) in acetonitrile (8 mL). After 5 to 7 d, the orange needles were collected on a fine glass frit, washed with acetonitrile, and dried under vacuum. Yield: 142 mg (85%). ATR-IR (neat sample), $Au_9(PPh_3)_8^{3+}$: $\tilde{\nu}$ = 1586(w), 1571(w), 1479(m), 1436(m), 1384(w), 1331(w), 1310(w), 1185(w), 1161(w), 1097(m), 1028(w), 987(sh), 738(m), 707(m), 686(m); $PW_{12}O_{40}^{3-}$: $\tilde{\nu}$ = 1079(s), 977(s), 893(m), 808(s). The PXRD pattern corresponds to the calculated pattern from the single-crystal X-ray structure determination (see Supporting Information). Room-temperature unit cell parameters of a = 2433.2 pm and b = 1386.5 pm were determined by the Le Bail method.

The preparation of **2** as a single phase is more difficult, as the formation of **2** and **1** is dependent on the concentrations in the crystallization zone. In 8 mm tubes Au_9 in DMF (0.3 mL, 2.5 µmol/mL) followed by DMF/acetone (1:1, 0.8 mL) and PW_{12} in acetone (0.3 mL, 3.0 µmol/mL) are carefully layered. After several days, greenish-black crystals appear, and the solution is still slightly yellow. The crystals lose solvent rapidly upon removal from the mother liquid and, as a consequence, turn opaque and diffract poorly. Thus, single-crystals for X-ray diffraction were directly transferred into inert oil, picked with a loop and cooled with liquid nitrogen. Up-scaling of the crystallization in larger tubes was not successful, as substantial amounts of **1** formed simultaneously. Instead, larger amounts of **2** were prepared by simply filling 12 to 16 of the small tubes at once. Yield: ca. 3.3 mg per tube (ca. 60%). ATR-IR (neat sample), $Au_9(PPh_3)_8^{3+}$: $\tilde{\nu}$ = 1584(w), 1569(w), 1478(m), 1434(m), 1383(w), 1308(w), 1182(w), 1161(w), 1096(m), 1027(w), 986(sh), 740(m), 706(m), 687(m); $PW_{12}O_{40}^{3-}$: $\tilde{\nu}$ = 1077(s), 974(s), 892(s), 806(s). The solvent loss is at least partially reversible. If the dried crystals are put into solvent, they turn transparent again. For powder X-ray diffraction the crystals were washed with DMF/acetone and acetone, dried in air, ground, and filled into a 0.7 mm capillary with additional solvent. The PXRD pattern corresponds to the calculated pattern from the single-crystal X-ray structure determination (see Supporting Information).

Supporting Information (see footnote on the first page of this article): Experimental and calculated PXRD patterns of **1** and **2**.

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[13] Crystal data and structure refinement for **1**: $C_{144}H_{120}Au_9P_9W_{12}O_{40}$, needle ($0.3\times0.1\times0.03$ mm^3), tetragonal, space group $P4/n$, a = 2417.8(2), c = 1367.1(2) pm, V = 7991.8(14)·10^6 pm^3, $\rho_{\text{calcd.}}$ = 2.804 g cm^{-3}, Z = 2, μ(Mo-K_α) = 16.98 mm^{-1}, F(000) = 6076, λ = 71.073 pm, Bruker-AXS-Smart-APEX-diffractometer, graphite monochromator, T = 100 K, ω-Scan, 72914 measured reflections, 6282 symmetry independent reflections ($2\theta_{\max}$ = 48.00°), 483 refined parameters; semiempirical absorption correction (SADABS[19]); structure solution and refinement with SHELXTL:[20] R_1 = 0.0545, wR_2 = 0.1376 [4967 $F_o > 2\sigma(F_o)$], R_1 = 0.0746, wR_2 = 0.1523 (all data). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated with the use of HFIX. No residual electron density for solvent molecules was detected. **2**: $C_{144}H_{120}Au_9P_9W_{12}O_{40}$, rhombic ($0.15\times0.12\times0.10$ mm^3), monoclinic, space group $C2/c$, a = 2932.1(2), b = 2107.8(2), c = 3243.8(2) pm, V = 18246(2)·10^6 pm^3, $\rho_{\text{calcd.}}$ = 2.457 g cm^{-3}, Z = 4, μ(Mo-K_α) = 14.87 mm^{-1}, F(000)= 12152, λ = 71.073 pm, Bruker-AXS-Smart-APEX-diffractometer, graphite monochromator, T = 100 K, ω-Scan, 76985 measured reflections, 19919 symmetry independent reflections ($2\theta_{\max}$ = 54.12°), 646 refined parameters; semiempirical absorption correction (SADABS[19]); structure solution and refinement with SHELXTL:[20] R_1 = 0.0499, wR_2 = 0.1193 [16370 $F_o > 2\sigma(F_o)$], R_1 = 0.0616, wR_2 = 0.1238 (all data). The $[PW_{12}O_{40}]^{3-}$ anion is disorderd over an inversion center, with the positions of the W and outer O atoms being very close to each other (see Figure 4b). Thus, chemically equivalent W–O bonds were restraint to common values. All C and O atoms were refined with isotropic displacement parameters and hydrogen atoms were calculated with the use of HFIX. Diffuse solvent molecules could not be found properly in the difference fourier map. Their contribution was eliminated by the SQUEEZE subprogram.[21] CCDC-615444 and -615445 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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