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Structure-Directing Effects in the Supramolecular Intercluster Compound $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$: Long-Range versus Short-Range Bonding Interactions

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Although being composed of trivalent ions, the crystal structure of the supramolecular intercluster compound $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$ is dominated by short-range intermolecular interactions, i.e., hydrogen bonds, and C–H/π interactions, avoiding a simple AB-type packing.

The assembly of nanoscopic particles into defined structures is particularly interesting because this is envisioned to be an alternative to lithographic techniques for future electronic or optical devices. Furthermore, nanostructured matter is expected to exhibit new physical properties because of cooperative effects in connection with the quantum confinement. Generally, the quality of the arrangements depends on the uniformity of the building blocks, which is a prerequisite for a low defect density and a large domain size. Violations of translational symmetry on the atomic scale would at least hamper structure determination with atomic precision, which is crucial for a detailed understanding of structure-directing forces and the resulting physical properties of nanostructured materials. Commonly, structure determination with atomic resolution is not possible for superlattices constituted of nanoparticles exhibiting an intrinsic size distribution.[1]

Our approach for overcoming these limitations is to study the possibility of employing different, well-defined, large inorganic clusters as building blocks for new nanostructured materials. Numerous large, inorganic molecules have been intensively studied during the past decades; examples include metal clusters,[2] polyoxometalates,[3] metal chalcogenide,[4] hydroxide and carboxylate clusters,[5] or even fullerenes. Growing single crystals of such clusters has been achieved in many cases; however, the synthesis of intercluster compounds, i.e., solids constituted of at least two different types of clusters, has remained virtually unexplored. Thus, the first task one has to tackle is the exploration of suitable building blocks and methods for their crystallization.

We have chosen cationic gold clusters and polyoxometalate polyanions as building blocks because of their stability and their ionic charge. The introduced Coulombic interactions will contribute substantially to the lattice energy, which will benefit from long-range order and thus provide a high crystal quality. This has been successfully demonstrated for Au_9^{3+} clusters and $PW_{12}O_{40}^{3-}$ Keggin anions.[6]

From a structural chemistry point of view as well, the intercluster compounds can be considered to form an interesting class of materials distinct from nanoparticle superlattices, molecular assemblies, or coordination polymers. While nanoparticle superlattices are mostly dominated by nondirectional interactions of close-to-spherical particles, leading to more or less densely packed structures that can be related to simple ionic or intermetallic compounds,[7] the structures of molecular crystals are strongly dependent on the shape of the molecules and directional interactions present, which can lead to structures with either low symmetry or low density.[8] Rohl and Mingos investigated the packing principles of several heterocubane salts.[9] Our intercluster compounds constitute building blocks that are even larger in size and carry relatively high Coulombic charges. Thus, the contributions of the different structure-

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directing forces and the role of the solvent molecules, which are comparatively small but abundant, are not clear beforehand. However, a tendency toward structures with a dense packing of the clusters can be expected. However, because of deviations from a perfectly spherical shape as well as local directional or sterical interactions, a wide range of arrangements might be realized. Because of the large size of the building blocks, voids or channels filled with solvent molecules are likely to occur in such compounds.

In this Communication, we present the formation of the intercluster compound $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$ (**1**), which can be grown as single crystals in macroscopic amounts by a solvent diffusion method, and study the influence of different, intermolecular forces on its crystal structure.[10]

1 consists of $[Au_9(PPh_3)_8]^{3+}$ clusters and decavanadate anions $[V_{10}O_{28}H_3]^{3-}$. Because the polyoxometalate anions form hydrogen-bonded dimers and the gold clusters occupy two different sites, the description as $[Au_9(PPh_3)_8]_2[V_{10}O_{28}H_3]_2$ with four formula units in the unit cell seems to be appropriate. Au_9^{3+} clusters are known to form two skeletal isomers;[11] out of these, the "butterfly-shaped" skeletal geometry with a core symmetry of almost D_{2h} is realized in **1** (Figure 1a). Au···Au bond lengths are in accordance to those of the respective clusters in the monoclinic phase of $[Au_9(PPh_3)_8][PW_{12}O_{40}]$.[6] The decavanadates form dimers through hydrogen bonding. The O···O distances for the six hydrogen bonds range from 270 to 273 pm. In order to identify the OH groups, bond valence sums of all oxygen atoms were calculated.[12] In each decavanadate moiety, they range from 1.7 to 2.0, with the exception of three oxygen atoms that have significantly lower bond valence sums of 1.2−1.3. These can be expected to be directly bonded to a proton and give rise to the hydrogen-bonding pattern as depicted in Figure 1b and as observed in other decavanadate compounds.[13]

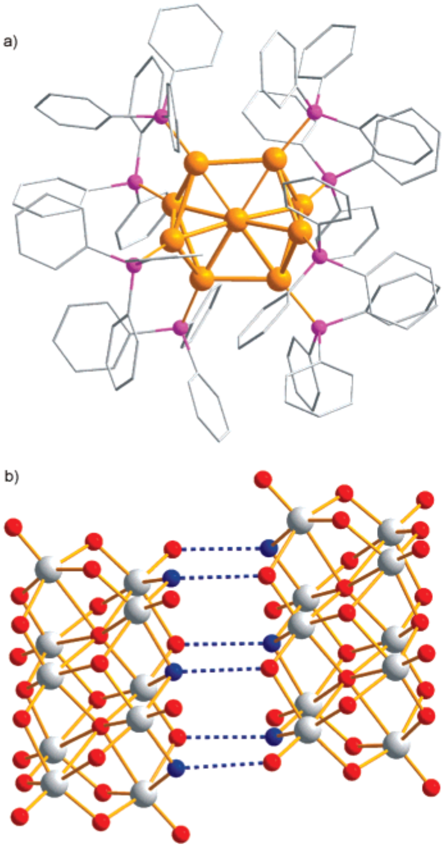

Figure 1. (a) Structure of the $[Au_9(PPh_3)_8]^{3+}$ cluster in **1**. Hydrogen atoms are omitted for clarity. (b) Structure of the decavanadate dimer in a ball-and-stick representation. Oxygen atoms marked with blue carry a proton, giving rise to six hydrogen bonds within the dimer.

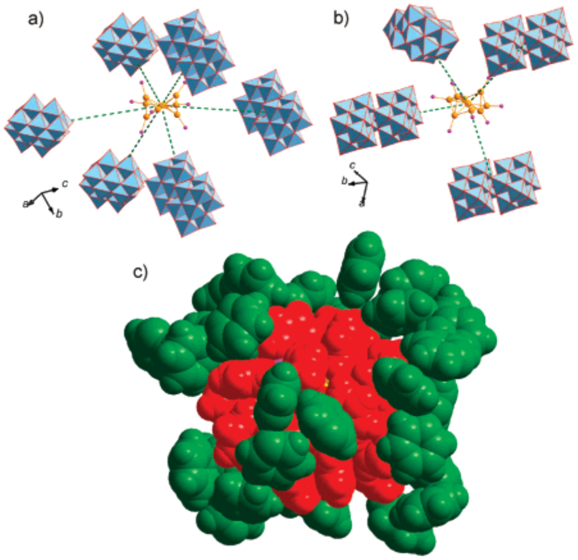

Figure 2. (a) Distorted octahedral coordination of Au_9−II and (b) distorted tetrahedral coordination of Au_9−I by the decavanadate dimers. (c) Visualization of the C−H/π contacts: The Au_9−I cluster (red) is in close contact with 32 phenyl rings of neighboring Au_9 clusters (green).

The crystal structure of **1** can best be rationalized by distinguishing three main building blocks: the $(V_{10})_2$ dimer and the two crystallographically independent gold clusters Au_9−I and Au_9−II. The $(V_{10})_2$ dimers are arranged as in a distorted hexagonal close packing with the stacking direction along [010]. The shortest O···O distances between different $(V_{10})_2$ dimers are larger than 1.0 nm and, consequently, the $(V_{10})_2$ dimers are in direct contact with gold clusters, exclusively. Inspection of the gold clusters reveals that Au_9−I is coordinated by four $(V_{10})_2$ dimers in the form of a distorted tetrahedron and Au_9−II by six $(V_{10})_2$ dimers in a distorted octahedral arrangement (Figure 2). Furthermore, both gold clusters are in close contact with eight surrounding gold

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(10) Crystallographic data for $C_{296}H_{253}N_3O_{56}P_{16}Cl_4V_{20}Au_{18}$: $M = 9949.5$, monoclinic, space group $P2_1/n$, $a = 22.510(2)$ Å, $b = 33.749(3)$ Å, $c = 46.872(5)$ Å, $\beta = 90.654(2)°$, $V = 35606(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.856$ g cm^{-1}, μ(Mo Kα) = 8.04 mm^{-1}, $T = 100(2)$ K, 309 758 reflections measured, 81 832 unique ($R_{int} = 0.059$), 59 781 have $I > 2\sigma$, 3634 refinement parameters, and R1(obs) = 0.044, R1(all) = 0.065, wR2(obs) = 0.106, and wR2(all) = 0.1138. Non-hydrogen atoms were refined individually with anisotropic displacement parameters. Hydrogen atoms were calculated using the HFIX command. The difference Fourier maps contain substantial amounts of diffuse electron density attributed to (partially disordered) solvent molecules. Three acetonitrile and two dichloromethane solvent molecules could be refined with isotropic displacement parameters. The remaining electron density was treated by the SQUEEZE procedure of the PLATON program package.[14]

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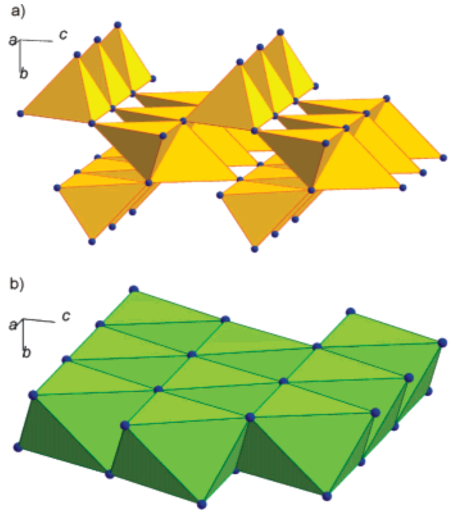

Figure 3. Packing features of **1**: The blue balls correspond to the centroids of the vanadate dimers, which form a hexagonal close packing. (a) Only those tetrahedral voids that are occupied by the Au_9−I clusters are marked, as described in the text. (b) Additionally, the Au_9−II clusters occupy all octahedral voids.

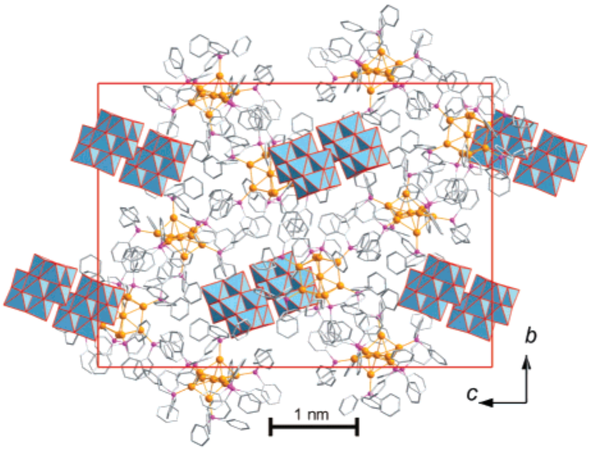

Figure 4. View of the crystal structure of **1** along [001], with the decavanadate dimers being in a polyhedral representation.

clusters via several C−H/π interactions between the phenyl rings of the ligands (Figure 2c). The overall packing type of **1** can be directly derived from a distorted Cs_2S structure.[14] The $(V_{10})_2$ dimers are positioned as in the hexagonal close packing along [010]. The Au_9−I clusters occupy half of the tetrahedral voids. These tetrahedra are connected by corner and edge sharing, as depicted in Figure 3a. The Au_9−II clusters occupy all of the octahedral voids (Figure 3b). A projection of the crystal structure of **1** is shown in Figure 4.

A detailed analysis of the crystal structure of **1** reveals that a "simple" AB-type ionic packing is not realized, although the long-range Coulombic interaction can be expected to be high with trivalent ions. There are several short-range interactions that can be regarded as structure-directing forces, which are the six hydrogen bonds per decavanadate dimer and numerous intermolecular C−H/π interactions between the slightly polarized aromatic protons and the π-electron density of the PPh_3 ligands. The latter interactions arise from neighboring phenyl groups being in edge-to-face orientation, a common, structure-directing motif in inorganic supramolecular chemistry, and which have shown to contribute substantially to the overall lattice energy.[15] This tendency of the gold clusters to be in close contact with each other might as well be the reason why the monoclinic form of $[Au_9(PPh_3)_8][PW_{12}O_{40}]$ crystallizes in the NaCl structure type, although the CsCl structure type seems to be more effective from space-filling considerations.[6]

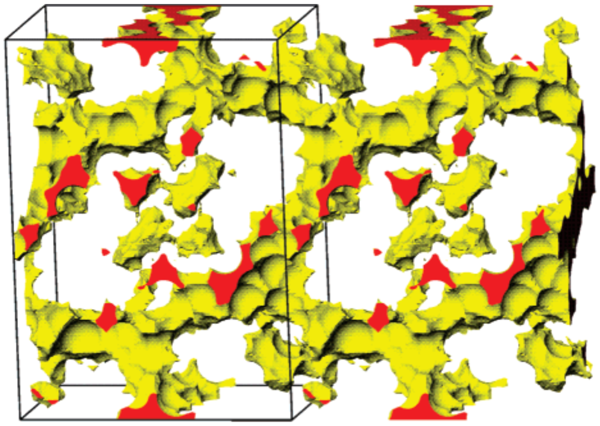

Figure 5. Visualization of the solvent-accessible volume of **1**, which forms three-dimensionally interconnected channels.

Features that are very likely to occur in intercluster compounds are voids or channels filled with small solvent molecules because of the size of the building blocks. The solvent-accessible volume of **1** is calculated to be 25.6% (PLATON;[16] probe radius 1.2 Å). The solvent molecules occupy three-dimensionally interconnected channels (Figure 5), which in this case facilitates their rapid loss upon removal of the crystals from the mother liquid. This is downgrading crystallinity because there are no covalent bonds between the clusters that would constitute a rigid network.

In summary, it has been shown that intermolecular interactions such as hydrogen-bonding, π, or van der Waals interactions have a decisive influence on the crystal structures of intercluster compounds, although the Coulombic energy can be expected to provide the highest contribution to the lattice energy. We have introduced the term supramolecular intercluster compounds for these kinds of materials and believe that this route of utilizing charged building units may become a versatile approach to new, well-defined, and well-characterized nanostructured materials. Selective introduction of intermolecular interactions, e.g., by modifying the ligand periphery, will offer access to a variety of different arrangements, which could give rise to different material properties.

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Supporting Information Available: Experimental details, characterization, bond valence sum calculations, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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