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$[Mo_{12}O_{40}P][C_{44}H_{38}P_2][CoC_{10}H_{10}]$ * $3(C_3H_7NO)$: A quasi-ternary intercluster compound

Fabienne Gschwind [*], Martin Jansen

Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

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ABSTRACT

Binary intercluster compounds (IC) can be reduced to basic structure types of ionic solids. We examined the validity of this concept for ternary compounds, on the example of a quasi-ternary intercluster compound made from a Keggin anion ($[PMo_{12}O_{40}]^{3-}$), an organic cation (*o*-xylylenebis(triphenylphosphonium)), and a complex (cobaltocenium). The new compound and its two related quasi-binary IC were investigated by X-ray diffractometry, examined for intermolecular interactions such as hydrogen-bonding, π–, or van der Waals-interactions, and evaluated for possible reductions to basic structure types.

RÉSUMÉ

Les composés binaires d'inter-cluster peuvent – de part leur structure – être réduits à des solides ioniques à structure basique. Nous avons examiné si ce concept pouvait aussi être appliqué à un système de composé inter-cluster ternaire. On s'est proposé d'étudier l'exemple d'un inter-cluster quasi ternaire composé d'un anion Keggin ($[PMo_{12}O_{40}]^{3-}$), d'un cation organique (*o*-xylylenebis(triphenylphosphonium)) et d'un complexe cationique de cobalt (cobaltocenium). Le nouveau composé ternaire ainsi que ses deux composés inter-clusters quasi binaires respectifs ont été caractérisés par la diffraction aux rayons X et leurs structures cristallines ont été analysées quant aux liaisons hydrogène, aux interactions π et aux interactions van der Waals.

1. Introduction

Nanoparticles have attracted great attention in modern science [1]. While bulk materials or atomic structures show specific physical properties, the physical responses of nanoparticles are size-dependent [2]. These are manifestations of quantum size effects, [3–5] which can be observed, for instance, in electronic [6,7] and optical properties [8], or in superparamagnetism [9].

Despite some recent progress related to the self-assembly of nanoparticles, problems still remain. Conventional nanoparticles generally have an intrinsic size distribution, which leads to imperfect lattices and can causes severe disorder on the atomic level. In contrast to molecular crystals, lattices of nanoparticles have little to no translation order on an atomic scale. Furthermore, compositional homogeneity, i.e., homogeneous size distribution of nanoparticles, can be difficult to achieve and the interpretation of physical properties can therefore be hindered. Of course, such materials escape X-ray structure determination within atomic resolution, which is a fundamental requirement for a detailed understanding of the chemical and physical properties of nanoparticles.

Recently, we developed an approach to overcome this problem, wherein we combine well-defined building blocks via self-assembly to new binary compounds, which

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[*] Corresponding author.
E-mail address: f.gschwind@fkf.mpg.de (F. Gschwind).

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are called intercluster compounds (IC) [10]. ICs exist in combination with fullerides and cationic complexes [11], polyoxometalates (POM) with clusters [12–15]. These ICs were analyzed via single-crystal diffraction, which showed that all the precursor building blocks mostly retained their original constituents [16,17].

Many ICs that configuration are composed from two different building blocks (binary ICs) can be reduced to basic structure types of ionic solids. As examples, the structures of $[Au_9(PPh_3)_8][PW_{12}O_{40}]$ [15] and $[Ag_8(2,20\text{-bipy})_6(C{\equiv}C^tBu)_4][BF_4]_4$ [14] exhibit NaCl type-packing. ICs can also be used to understand the fundamental principles of structure-directing effects, and long- and short-range bonding interactions [13,18].

We intended to extend this concept and to explore whether similar structural relationships are valid for quasi-ternary ICs and basic structure types of ternary compounds based on atomic constituents.

A few quasi-ternary compound systems consisting of a polyoxometalate and two different cationic components exist [19,20], but none of these structures were intentionally prepared, and the arrangements of their basic structure type were not investigated. These kinds of ternary systems could offer a completely new approach for the synthesis of ICs, and could also be used for the production of the multimetallic compounds used as single-source precursors for metal oxides [21].

For the study of a ternary IC, we have chosen three constituents: a triply charged anion, phosphomolybdic acid (the POM in this instance), a dicationic organic molecule, *o*-xylylenebis(triphenylphosphonium), and a singly charged cationic cobaltocenium complex.

We first investigated the quasi-binary systems, where the cobaltocenium complex and the organic ligand were each assembled separately with the POM. The packing behaviors of these binary systems were studied to determine the presence of basic structure types. Thereafter, the quasi-ternary IC was synthesized via self-assembly and we investigated its structural behavior.

The synthesis, characterization, and study of the structure-directing effects of the quasi-ternary IC and, as references, both related quasi-binary compounds, are presented here.

We chose to use the term *quasi-binary* and *quasi-ternary*, since we are disregarding the counter ions or solvent molecules.

2. Results and discussion

In order to have a better understanding of the quasi-ternary compound, we will first present both quasi-binary compounds, one comprising POM and cobaltocenium, and the other composed of POM and the organic molecule (*o*-xylylenebis(triphenylphosphonium)).

2.1. Crystal structures

2.1.1. $[PMo_{12}O_{40}][CoC_{10}H_{10}]_3 * 2(C_2H_6OS)$, 1

When phosphomolybdic acid and bis(cyclopentadienyl)cobalt(III) hexafluorophosphate (also known as cobaltocenium hexafluorophosphate) are mixed in DMSO, yellow crystals can be obtained after crystallization.

The asymmetric unit of **1** consists of one $[Mo_{12}O_{40}P]^{3-}$ polyanion, three cobaltocenium cations, and two DMSO solvent molecules. Compound **1** crystallizes in the triclinic space group *P*-1. The ratio of the Keggin ion to the cobaltocenium cations is 1:3 and is different from the observed ratio in the very similar ferrocenium system [22]. Fig. 1 shows the packing of **1** in the solid state along the *x*-direction, with each cobalt ion in a different color for enhanced visualization.

Each anion is surrounded by three cobaltocenium cations, with a distance between the framework oxygen atoms of the anion and the cyclopentadienyl rings of the cobaltocenium moieties of 3.074 to 3.213 Å. This indicates that the interactions between the cobaltocenium cations and the polyanions in **1** are much stronger than the previously observed interactions in ferrocenium compounds [22]. The closest Co···Co distance among the neighboring cobaltocenium cations is 7.191 Å. Interactions also exist between the polyanions along *b* (O24···O24: 3.296 Å) and along *a* (O6···O6: 3.392 Å), at the closest distance of the terminal oxygen atoms to the neighboring Keggin anions, which might be considered as 1D Keggin anion chains. The DMSO solvent molecules fill the voids formed by the POM and interact via hydrogen bonds between the methyl groups and the polyanions. Further H-bonding can also be observed between the hydrogen atoms of the cyclopentadienyl rings and the oxygen atoms of the polyoxometalate framework. These H-bonds range from about 2.37 Å to 2.60 Å. Table 1 shows a selection of the most relevant contacts.

The packing scheme can be derived from the Li_3Bi structure type, in which the POMs form a face-centered likes arrangement. Co2 and the POMs form a NaCl structure, and Co1/Co3 with POM form a CaF_2 lattice. In total, the Li_3Bi structure is obtained, where Co1 and Co3 are situated in the tetrahedral voids, while Co2 is located in the octahedral voids (Supporting informations).

2.1.2. $[PMo_{12}O_{40}][C_{44}H_{38}P_2]_2[Br] * 2(C_3H_7NO)$, 2

The crystal structure of **2** consists of the $[Mo_{12}O_{40}P]^{3-}$ anion, two *o*-xylylenebis(triphenylphosphonium) cations, one bromide anion, and two DMF solvent molecules. The quasi-binary compound **2** crystallizes in the monoclinic space group *C*2/c. The asymmetric unit is formed by half of the anion, one *o*-xylylenebis(triphenylphosphonium) cation, one half occupied bromide anion, and one DMF molecule. Four of the six phenyl "pods" of the *o*-xylylenebis(triphenylphosphonium) cation point toward the polyanion, giving the impression that the anion is capped with an organic moiety (Fig. 2). The two remaining phenyl pods, which are located on the same side as the xylylene moiety, and the xylylene moiety itself, point to the neighboring polyanion and also form short contacts to the free bromide ion and the solvent molecule. The relevant non-bonded C–H···O interactions [23] are listed in Table 2.

The shortest intermolecular distance involves a carbon atom of one of the phenyl rings of *o*-xylylenebis(triphenylphosphonium) and one oxygen atom of the polyoxomolybdate anion [C42···O16 3.107(17) Å]. The resulting packing arrangement shows rows in the *y*-direction