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# [Mo<sub>12</sub>O<sub>40</sub>P][C<sub>44</sub>H<sub>38</sub>P<sub>2</sub>][CoC<sub>10</sub>H<sub>10</sub>]<sup>\*</sup> · 3(C<sub>3</sub>H<sub>7</sub>NO): A quasi-ternary intercluster compound

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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<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>), 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.

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## R É S U M É

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<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>), 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.

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## 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 cause 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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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  $[\text{Au}_9(\text{PPh}_3)_8][\text{PW}_{12}\text{O}_{40}]$  [15] and  $[\text{Ag}_8(2,20\text{-bipy})_6(\text{C}\equiv\text{C}^t\text{Bu})_4][\text{BF}_4]_4$  [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. $[\text{PMo}_{12}\text{O}_{40}][\text{CoC}_{10}\text{H}_{10}]_3 \cdot 2(\text{C}_2\text{H}_6\text{OS})$ , 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  $[\text{Mo}_{12}\text{O}_{40}\text{P}]^{3-}$  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  $\text{Li}_3\text{Bi}$  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  $\text{CaF}_2$  lattice. In total, the  $\text{Li}_3\text{Bi}$  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. $[\text{PMo}_{12}\text{O}_{40}][\text{C}_{44}\text{H}_{38}\text{P}_2]_2[\text{Br}] \cdot 2(\text{C}_3\text{H}_7\text{NO})$ , 2

The crystal structure of **2** consists of the  $[\text{Mo}_{12}\text{O}_{40}\text{P}]^{3-}$  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 *C2/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

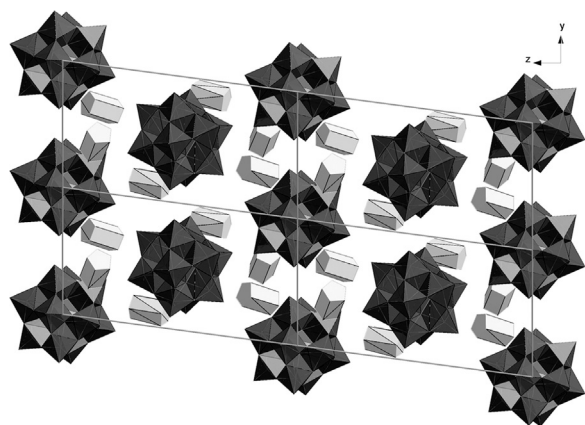


Fig. 1. Packing in the *x*-direction black polyhedra = POM, grey polyhedra = cobaltocenium (hydrogen atoms and DMSO solvent molecules are omitted for clarity).

consisting of alternating polyanions, organic moieties, and free bromine anions, which are aligned between the organic moieties (Fig. 3).

Four  $\pi$ – $\pi$  interactions [24] can be observed between the phenyl rings of the *o*-xylylenebis(triphenylphosphonium). One  $\pi$ – $\pi$ -stacking shows a T-shaped conformation with a distance of about 5.19 Å, measured between the centroids of the phenyl rings C1–C6 and C33–C39. The two other stacking interactions have typical parallel displacements, with a distance of 4.844 Å (measured between the centroids) between phenyl rings C1–C6 and C41–C46, and one further stacking between C7–C12 and C27–C32 (4.279 Å, measured between both centroids). An intermolecular C–H $\cdots$  $\pi$  bond can be found between phenyl ring C1–C6 and methyl group C100–H10D of the DMF solvent molecule in a distance of 2.81 Å measured between the H-atom and centroid.

In the reduced packing scheme, the polyanions are surrounded by organic moieties, which form strongly distorted octahedral layers, as observed in CdCl<sub>2</sub> and CdI<sub>2</sub>, respectively (Supporting informations). These layers are shifted against each other in such a way that a clear assignment is not possible. Bromine intercalation is observed between the layers of the polyoxomolybdate and organic molecules.

Table 1  
Hydrogen-bonding geometry of **1** (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C5–H5...O24 <sup>i</sup>	0.9300	2.5900	3.37 (2)	142.00
C6–H6...O42	0.9300	2.5200	3.415 (19)	162.00
C7–H7...O4	0.9300	2.4800	3.329 (16)	152.00
C100–H10A...O26	0.9600	2.6000	3.46 (3)	150.00
C102–H10...O28 <sup>ii</sup>	0.9600	2.5300	3.32 (4)	140.00
C13–H13...O29	0.9300	2.5300	3.13 (2)	123.00
C17–H17...O48 <sup>i</sup>	0.9300	2.5300	3.289 (18)	139.00
C23–H23...O5 <sup>iii</sup>	0.9300	2.4700	3.39 (3)	170.00
C30–H30...O8	0.9300	2.3700	3.22 (3)	151.00

Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $-x, 1-y, 1-z$ .

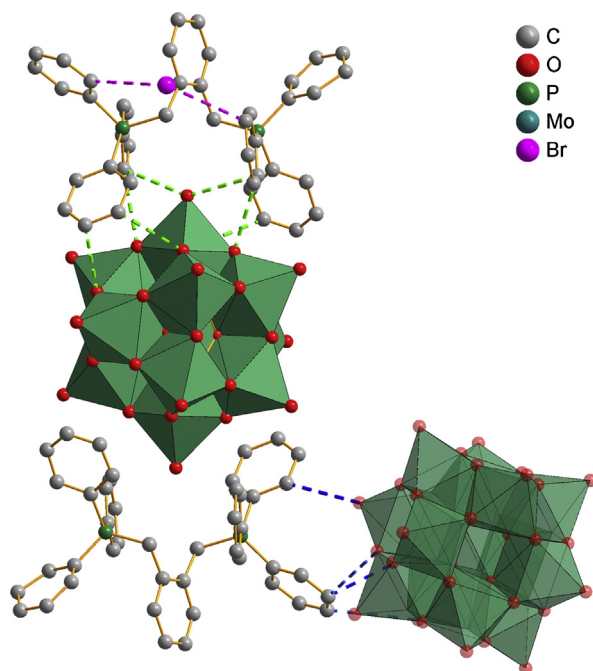


Fig. 2. Visualization of different H-bonds from the organic moiety to the polyanion (green, blue) and short contact to the bromide ion (pink).

### 2.1.3. [PMo<sub>12</sub>O<sub>40</sub>][C<sub>44</sub>H<sub>38</sub>P<sub>2</sub>][CoC<sub>10</sub>H<sub>10</sub>] \* 3(C<sub>3</sub>H<sub>7</sub>NO), **3**

In a one-pot reaction, phosphomolybdic acid, bis(cyclopentadienyl)cobalt(III) hexafluorophosphate, and *o*-xylylenebis(triphenylphosphonium) bromide were mixed in DMF. Compound **3** crystallizes in the triclinic space group *P*-1. Crystallization via gas diffusion affords green crystals of **3**. The asymmetric unit of this compound is built from one [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion, one dicationic *o*-xylylenebis(triphenylphosphonium), one monocationic cobaltocenium, and three DMF solvent molecules (Fig. 4).

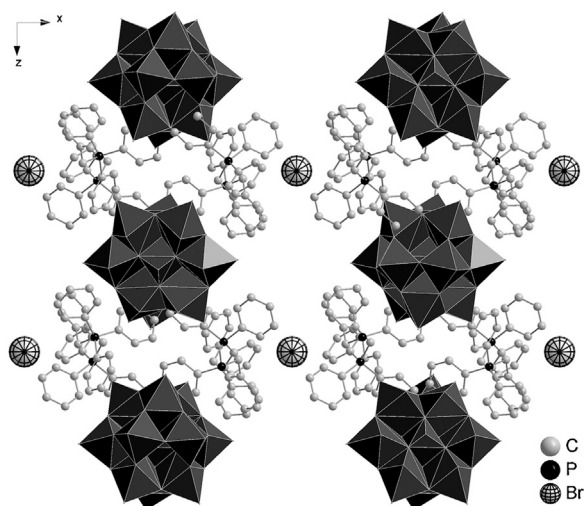


Fig. 3. Packing of **2** in the *y*-direction (hydrogen atoms are omitted for clarity).

**Table 2**  
Hydrogen-bonding and short contact geometry of **2** (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C3–H3...O31	0.9300	2.5200	3.35 (2)	148.00
C100–H10C...O20	0.9600	2.3800	3.05 (5)	126.00
C14–H14...O36 <sup>iv</sup>	0.9300	2.5600	3.327 (19)	140.00
C16–H16...O100 <sup>iv</sup>	0.9300	2.5900	3.32 (4)	136.00
C19–H19A...O6	0.9700	2.5500	3.465 (15)	158.00
C19–H19B...O15 <sup>vi</sup>	0.9700	2.5200	3.379 (13)	147.00
C23–H23...O100 <sup>iii</sup>	0.9300	2.5800	3.51 (3)	174.00
C26–H26A...Br1	0.9700	2.8500	3.818 (11)	172.00
C26–H26B...O15 <sup>vi</sup>	0.9700	2.5200	3.356 (12)	144.00
C32–H32...O3 <sup>vi</sup>	0.9300	2.4400	3.32 (2)	156.00
C35–H35...O10 <sup>viii</sup>	0.9300	2.5900	3.507 (17)	168.00
C40–H40...Br1	0.9300	2.8800	3.804 (13)	170.00
C42–H42...O16 <sup>i</sup>	0.9300	2.3200	3.107 (17)	143.00

Symmetry codes: (i)  $1/2-x, 3/2-y, -z$ ; (ii)  $-x, y, 1/2-z$ ; (iii)  $x, 1-y, 1/2+z$ ; (iv)  $1/2-x, 1/2+y, 1/2-z$ ; (v)  $1/2-x, -1/2+y, 1/2-z$ ; (vi)  $-x, y, 1/2-z$ ; (vii)  $x, -1+y, z$ ; (viii)  $x, 1+y, z$ ; (ix)  $1/2-x, 1/2+y, 1/2-z$ ; (x)  $-x, 1-y, -z$ ; (xi)  $1/2-x, 1/2-y, -z$ ; (xii)  $x, 1-y, -1/2+z$ .

The carbon atoms of the cyclopentadienyl ring of the cobaltocenium group are close to the oxygen atoms of the anion framework, from ca. 3.215 to 3.517 Å. This distance is approximately 0.2 Å longer than that in **1**, therefore showing a weaker interaction. The closest Co...Co distance between neighboring cobalt complexes is 6.916 Å, also 0.2 Å shorter than that in **1**.

The *o*-xylylenebis(triphenylphosphonium) cation has nearly the same arrangement around the POM as in **2**. Here also, the organic ligands cap the polyanions with four of the phenyl rings; the other phenyl pods hydrogen bond to the free DMF solvent molecule or to neighboring polyanions. Further H-bonding is summarized in Table 3. Different  $\pi$ – $\pi$  interactions [24] can be described between the phenyl rings: two T-shaped conformations, between phenyl ring C7–C12 to phenyl ring C27–C32 of a neighboring molecule (5.125 Å, measured between the centroids), and from phenyl ring C33–C38 to phenyl ring C1–C6 of a neighboring molecule (5.386 Å, measured between the centroids); and one parallel displaced  $\pi$ – $\pi$ -stacking between phenyl ring C33–C38 and phenyl ring C7–C12 (4.688 Å, measured between the centroids).

The packing of the building blocks shows a layer formation in *y*-direction, with a ABCBA system

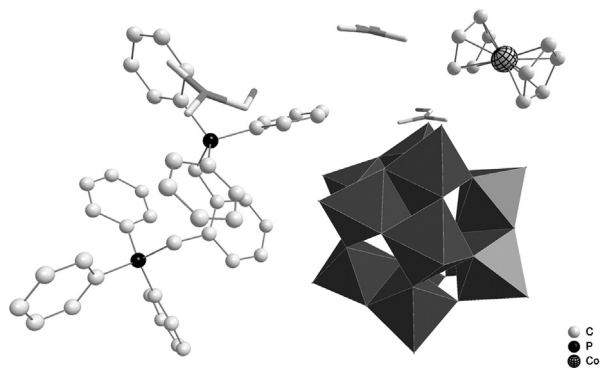


Fig. 4. Asymmetric unit of **3**; H-atoms are omitted for clarity.

**Table 3**  
Hydrogen-bonding geometry of **3** (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C2–H2...O200 <sup>i</sup>	0.9300	2.3800	3.305 (9)	177.00
C3–H3...O30 <sup>ii</sup>	0.9300	2.5500	3.262 (8)	134.00
C16–H16...O13 <sup>iii</sup>	0.9300	2.4800	3.260 (8)	141.00
C19–H19B...O200 <sup>i</sup>	0.9700	2.4400	3.371 (8)	162.00
C22–H22...O14	0.9300	2.4700	3.201 (6)	135.00
C26–H26B...O400 <sup>iv</sup>	0.9700	2.3000	3.251 (14)	168.00
C303–H30F...O33 <sup>v</sup>	0.9600	2.5800	3.419 (16)	145.00
C34–H34...O400 <sup>iv</sup>	0.9300	2.3700	3.297 (14)	172.00
C38–H38...O300 <sup>vi</sup>	0.9300	2.5200	3.340 (11)	147.00
C402–H40A...O11	0.9600	2.3800	3.293 (15)	159.00
C402–H40B...O14 <sup>v</sup>	0.9600	2.4800	3.303 (16)	144.00
C41–H41...O17 <sup>i</sup>	0.9300	2.4800	3.239 (7)	138.00
C53–H53...O10 <sup>v</sup>	0.9300	2.5900	3.289 (8)	132.00
C53–H53...O32 <sup>v</sup>	0.9300	2.5800	3.405 (8)	148.00
C53–H53...O35 <sup>v</sup>	0.9300	2.5000	3.198 (8)	132.00
C55–H55...O3	0.9300	2.6000	3.517 (9)	169.00
C58–H58...O10 <sup>vi</sup>	0.9300	2.5200	3.333 (8)	146.00

Symmetry codes: (i)  $-x, 1-y, 1-z$ ; (ii)  $-1+x, y, z$ ; (iii)  $-x, 1-y, -z$ ; (iv)  $1-x, 1-y, -z$ ; (v)  $1+x, y, z$ ; (vi)  $1-x, 1-y, 1-z$ .

(where A = *o*-xylylenebis(triphenylphosphonium), B = POM, C = cobaltocenium) can be observed (Fig. 5).

The thickness of the layer is of about 20 Å (almost the full length of the *c*-axes of the unit cell) and the layer-motive is repeated in *z*-direction.

The phenyl units C13–C18 points in the interface between two sandwich-layers, where also the three DMF solvent molecules are intercalated. The distance between these phenyl rings is about 3.52 Å (between C15 and C15 of the phenyl group in the neighbor row) and therefore at the upper limit of  $\pi$ – $\pi$  stacking range.

For the reduction of the structure we used atom P1 as marking point for the polyoxometalates, atom C25 for the ligand molecules and Co1 for the cobaltoceniums. The POMs are surrounded by four ligand molecules, while equally also the ligand molecules are surrounded by four POMs. This leads in a first view to a strongly distorted NaCl structure (Fig. 6a). Due to this strong distortion of the NaCl-cube it looks like each second cube is empty, but watching from a different direction it is visible that in each tetrahedral void one cobaltocenium is located (Fig. 6b), which leads to an overall strongly distorted anti-PbFCl structure type [25].

## 2.2. Vibrational spectroscopy and thermogravimetry

The vibrations of the polyoxometalate are visible in all spectra and correlate with known frequencies [26–28]. The IR frequency band observed at 1060  $\text{cm}^{-1}$  (signature IR1, for all three compounds in Fig. 7) corresponds to asymmetric stretching of the P–O and Mo–O<sub>t</sub> bonds of the polyoxometalate [26], while the broad band at about 960  $\text{cm}^{-1}$  (IR2) corresponds to the symmetric stretching of these bonds. The shoulder at about 880  $\text{cm}^{-1}$  (IR3) is assigned to asymmetric stretching of the Mo–O–Mo bonds. In the Raman spectrum, the bands at 986  $\text{cm}^{-1}$  and 964  $\text{cm}^{-1}$  (R1, for all three compounds) are attributed to the symmetric and asymmetric vibrations of Mo–O<sub>d</sub> [27,28]. A further band near 245  $\text{cm}^{-1}$  (R2, all three compounds) can be attributed to Mo–O<sub>a</sub>. The typical Cp–Co



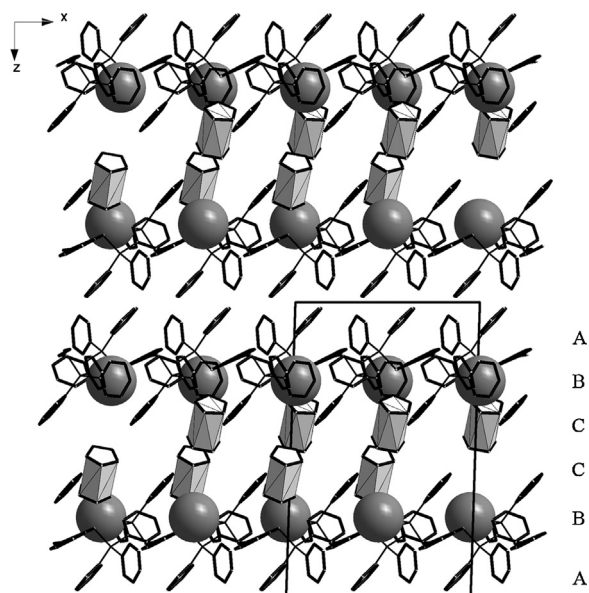


Fig. 5. Compound **3** in *y*-direction. With simplified scheme of the packing (white polyhedra = cobaltocenium, grey balls = P1 of POM, black sticks = organic moieties).

frequency at  $316\text{ cm}^{-1}$  is visible for compounds **1** and **3** (R3). Also observed in the spectra of both **1** and **3** are the different vibrations in the IR spectra for the cyclopentadienyl rings: C–H<sub>δ</sub> (ring) at about  $1414\text{ cm}^{-1}$  (IR4) and M–C<sub>ring</sub> at  $460\text{ cm}^{-1}$  (IR5). For **2**, the characteristic bands in the Raman

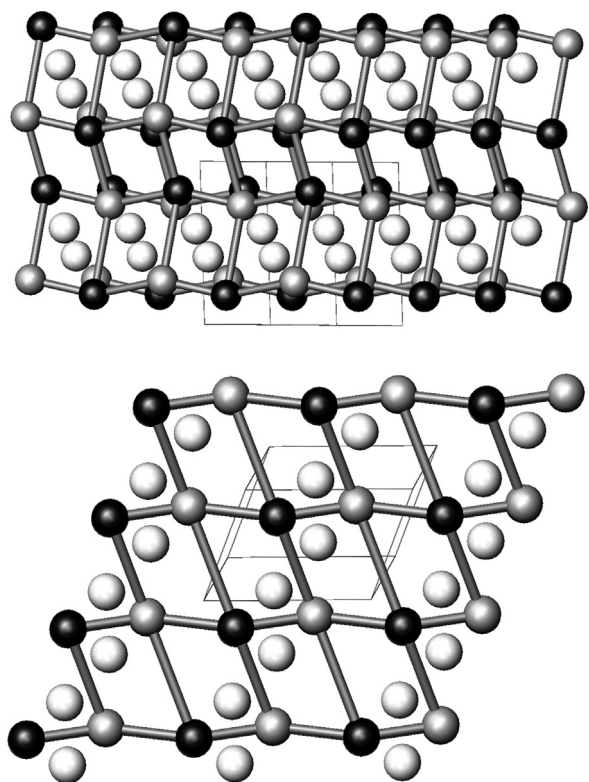


Fig. 6. a and b: two representations of the reduced structure of compound **3** (white = Co1, grey = P1 of POM, black = C25).

spectra are weak only: C–C (aliphatic chain) at about  $666\text{ cm}^{-1}$  (R4), C–H at  $1030\text{ cm}^{-1}$  (R5), and a very weak band at  $1582\text{ cm}^{-1}$  for C–P. In the IR, the typical bands are:  $1188\text{ cm}^{-1}$  for P=O (IR7), a C–C deformation vibration at  $1440\text{ cm}^{-1}$  (IR8), and the typical vibrations at  $2936\text{ cm}^{-1}$  and  $3115\text{ cm}^{-1}$  for C–C and C=C, respectively.

Thermogravimetric analysis was carried out in a flow of argon (Supporting informations). The polyanions start to decompose near  $450\text{ °C}$  for all three compounds. Compound **1** shows the highest stability, with decomposition of the cobalt complex first at about  $420\text{ °C}$ , while compounds **2** and **3** show the onset of decomposition for the organic ligand at  $300\text{ °C}$ . Decomposition of the solvents (DMF, DMSO) can be observed before  $150\text{ °C}$ .

### 3. Conclusion

In summary, it has been shown that building a multicomponent assembly using quasi-ternary ICs is an alternative route for creating well-defined and well-characterized nanostructured materials. The quasi-binary IC systems as well as the quasi-ternary IC itself were studied with regard to intermolecular interactions, such as hydrogen-bonding, and  $\pi$ –, and van der Waals-interactions. It was shown that the reduction to an ionic solid structure type was possible for the binary systems and for the ternary systems. Therefore, it is possible to extend the concepts of structural relationship also on quasi-ternary systems. Selective introduction of different building blocks (complexes, clusters, or organic compounds) will offer access to new compounds, which could show different materials properties.

### 4. Experimental

#### 4.1. General

All starting materials were purchased commercially and used without further purification. The syntheses of compounds **1–3** can be performed with basic laboratory equipment in air and at room temperature.

#### 4.2. $[\text{PMo}_{12}\text{O}_{40}][\text{CoC}_{10}\text{H}_{10}]_3 \cdot 2(\text{C}_2\text{H}_6\text{OS})$ , $1\text{ C}_{34}\text{H}_{42}\text{Co}_3\text{Mo}_{12}\text{O}_{42}\text{PS}_2$

Phosphomolybdic acid hydrate (1 g, 0.54 mmol) was dissolved in acetone (15 mL) and precipitated with an excess of cobaltocenium hexafluorophosphate (0.8 g, 2.39 mmol) in acetonitrile (15 mL). The yellow precipitate was filtered, washed thoroughly with acetone and acetonitrile, and dried under vacuum. The precipitate was dissolved in a minimum volume of DMSO (about 8 mL) and layered with diethyl ether. After a few days, yellow crystals of **1** appeared. Alternatively, the crystals can be grown using the gas diffusion of diethyl ether into the reaction solution. For quantitative analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES, carbon analyzer), the ratio of Mo/Co/P/C in  $[\text{PMo}_{12}\text{O}_{40}]_3(\text{CoC}_{10}\text{H}_{10})_3 \cdot 2(\text{C}_2\text{H}_6\text{OS})$  was determined as 44.96 (expected 45.24)/6.77 (6.95)/1.26 (1.22)/15.57 (16.05).

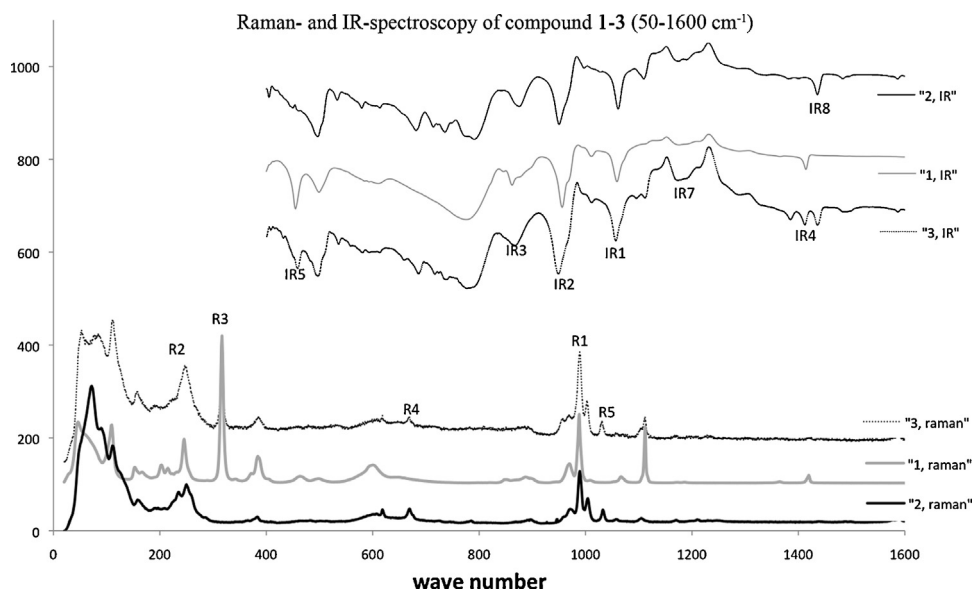


Fig. 7. IR and Raman spectra for compounds **1**, **2**, and **3**.

Single-crystals at different orientations were used for Raman spectroscopy. Raman ( $\text{cm}^{-1}$ ): 58 (m), 108 (m), 149 (w), 199 (w), 246 (m), 316 (s), 380 (m), 449 (w), 484 (w), 590 (broad, m), 881 (w), 967 (m), 987 (s), 1061 (w), 1110 (s), 1416 (w). Infrared spectroscopy on bulk material ( $\text{cm}^{-1}$ ): 1415 (w), 1188 (m), 1112 (w), 1063 (s), 955 (s), 865 (m), 783 (m), 505 (m), 458 (s).

After prolonged standing of the crystallization solution (about 1 months), another modification of compound **1** was observed. The asymmetric unit of **1a** contained two polyanions and six cobalt complexes; more details are available in the [Supporting informations](#).

#### 4.3. $[\text{PMo}_{12}\text{O}_{40}][\text{C}_{44}\text{H}_{38}\text{P}_2]_2[\text{Br}]^* \cdot 2(\text{C}_3\text{H}_7\text{NO})$ , $2\text{C}_{94}\text{H}_{90}\text{BrMo}_{12}\text{N}_2\text{O}_{42}\text{P}_5$

Phosphomolybdic acid hydrate (2 g, 1.1 mmol) was dissolved in acetone (20 mL) and precipitated with *o*-xylylenebis(triphenylphosphonium) bromide (1.5 g, 1.9 mmol) in acetonitrile (30 mL). The precipitate was filtered, washed thoroughly with acetone and acetonitrile, and dried under vacuum. The light yellow precipitate was dissolved in a minimum volume of DMF and layered with diethyl ether. After three days, plate-shaped yellow-greenish crystals of **2** appeared. The crystals easily lose solvent molecules and need to be measured using a cooling system. For quantitative

Table 4

Crystallographic data for compounds **1**, **2**, and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	$\text{C}_{34}\text{H}_{42}\text{Co}_3\text{Mo}_{12}\text{O}_{42}\text{P}_5\text{S}_2$	$\text{C}_{94}\text{H}_{90}\text{BrMo}_{12}\text{N}_2\text{O}_{42}\text{P}_5$	$\text{C}_{63}\text{H}_{69}\text{CoMo}_{12}\text{N}_3\text{O}_{43}\text{P}_3$
$M_r$	2545.84	3305.79	2859.33
Cryst. size, $\text{mm}^3$	$0.15 \times 0.10 \times 0.06$	$0.25 \times 0.20 \times 0.10$	$0.30 \times 0.25 \times 0.18$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> , Å	12.747(3)	35.578(4)	13.125(3)
<i>b</i> , Å	13.196(3)	14.052(13)	17.885(4)
<i>c</i> , Å	21.691(4)	24.097(2)	20.949(4)
$\alpha$ , deg	82.11(3)	90	93.11(3)
$\beta$ , deg	87.44(3)	91.456(2)	91.80(3)
$\gamma$ , deg	61.54(3)	90	111.38(3)
<i>V</i> , Å <sup>3</sup>	3176.3(11)	12043(2)	4565.5(16)
<i>Z</i>	2	4	2
$D_{\text{calcd}}$ , $\text{g cm}^{-3}$	2.691	1.847	2.080
$\mu(\text{Mo } K\alpha)$ , $\text{cm}^{-1}$	3.229	1.684	1.904
<i>F</i> (000), e	2426	6520	2776
Refl. measd./unique	55207/15176	37208/8724	68800/22351
Param. refined	857	699	1120
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0676/0.1490	0.0780/0.1953	0.0458/0.1032
GoF ( $F^2$ )	1.043	1.048	1.028
$\Delta\rho_{\text{fin}}$ (max/min), e Å <sup>-3</sup>	2.468/−2.279	1.191/−2.135	1.730/−1.715

analysis (ICP-OES, carbon analyzer), the bulk material was filtered and dried in vacuo to remove excess solvent. This afforded a ratio of Mo/P/C ( $[\text{PMo}_{12}\text{O}_{40}][\text{C}_{44}\text{H}_{38}\text{P}_2]_2[\text{Br}]$ , without solvent molecules) of: 36.22 (expected 36.44)/4.34 (4.89)/33.62 (33.45). For completeness, we performed powder X-ray diffraction (PXRD) with Pawley refinement on the dried bulk material. The cell volume ( $11646 \text{ \AA}^3$ ) was slightly smaller than the volume of the original cell ( $12043 \text{ \AA}^3$ ). This confirmed the loss of solvent molecules and, therefore, also supported the inaccurate results of the elemental analysis (refined parameters and spectra are included in the [Supporting informations](#)). Single-crystals at different orientations were used for Raman spectroscopy. Raman ( $\text{cm}^{-1}$ ): 70 (s, broad), 145 (w), 246 (m), 380 (w), 590 (w, broad), 607 (w), 665 (w), 902 (w, broad), 967 (m), 987 (s), 1002 (m), 1031 (m), 1087 (w), 1578 (w). Infrared spectroscopy on bulk material ( $\text{cm}^{-1}$ ): 1439 (w), 1186 (m), 1114 (w), 1063 (s), 958 (s), 880 (m), 792 (m), 686 (w), 500 (m).

#### 4.4. $[\text{PMo}_{12}\text{O}_{40}][\text{C}_{44}\text{H}_{38}\text{P}_2][\text{CoC}_{10}\text{H}_{10}] \cdot 3(\text{C}_3\text{H}_7\text{NO})$ , $3\text{C}_{63}\text{H}_{69}\text{CoMo}_{12}\text{N}_3\text{O}_{43}\text{P}_3$

Cobaltocenium hexafluorophosphate (0.09 g, 0.27 mmol), xylylenebis-triphenylphosphine dibromide (0.21 g, 0.27 mmol), and phosphomolybdic acid hydrate (0.5 g, 0.27 mmol) were dissolved in DMF (25 mL) and stirred for 2 h. Dark green crystals of **3** were grown after a few days, using gas diffusion with diethyl ether. The crystals were collected via filtration and washed with small amounts of DMF. The crystals were dried quickly and the analyses were performed as fast as possible to avoid fragmentation into the binary compounds, which occurred after drying and storage in air. For storage purposes, it was better to leave the crystals in their mother liquor. Quantitative analysis (ICP-OES, carbon analyzer) resulted in a Mo/Co/P/C ( $\text{C}_{63}\text{H}_{69}\text{CoMo}_{12}\text{N}_3\text{O}_{43}\text{P}_3$ ) ratio of: 40.39 (expected 40.32)/1.97 (2.06)/3.46 (3.25)/26.18 (26.5). Single-crystals at different orientations were used for Raman spectroscopy. Raman ( $\text{cm}^{-1}$ ): 70 (s, broad), 108 (s), 145 (w), 246 (s), 316 (s), 380 (w), 590 (broad, w), 607 (w), 881 (w), 967 (m), 987 (s), 1031 (m), 1110 (s), 1578 (w). Infrared spectroscopy on bulk material ( $\text{cm}^{-1}$ ): 1441 (w), 1417 (w), 1390 (w), 1188 (s), 1115 (w), 1059 (s), 952 (s), 876 (m), 792 (s), 500 (m), 462 (m).

#### 4.5. Single-crystal X-ray diffraction studies

All crystal structures were solved by direct methods (SHELX97) and subsequent difference Fourier maps, and refined on F2 (SHELXL) [29]. The measurements were made on an AXS Bruker Smart APEX diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.7103 \text{ \AA}$ ) in the  $\omega$  scan mode (compound **2**). Empirical absorption correction (SADABS) [30] was applied on **2**. Compounds **1** and **3** were measured on a Stoe IPDS 2 with Mo K $\alpha$  radiation. Numerical absorption correction (X-SHAPE) [31] was performed. Further details of the measurements can be found in [Table 4](#).

All the Keggin ions in compounds **1** and **2** show the same type of crystallographic disorder as found in many other crystal structures with the Keggin anion. The center atom is surrounded by a cube of eight oxygen atoms, with each oxygen site half occupied; the central atom and these

oxygen atoms formed two groups of tetrahedrons [32]. The disorder remains also while using non-centrosymmetric space groups.

Compound **1**: All atoms but H-atoms were refined with anisotropic displacement parameters. Hydrogen positions were calculated using the HFIX command.

Compound **2**: All atoms but H-atoms were refined with anisotropic displacement parameters. Diffuse solvent molecules could not be found properly in the difference Fourier map. Their contributions were eliminated by the SQUEEZE subprogram [33].

Compound **3**: All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were calculated using the HFIX command. Three DMF molecules per unit cell could be refined with anisotropic displacement parameters. The rest were treated by the SQUEEZE procedure.

CCDC-884550 (**1**), 886143 (**1a**, [Supporting informations](#)), 884551 (**2**), and 884552 (**3**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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#### Appendix A. Supplementary informations

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2012.10.017>.

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