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Synthesis and characterization of novel polyoxometalates with an inverted-Keggin structure as a new class of building unit

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ABSTRACT

Novel polyoxometalates with an inverted-Keggin structure were prepared and isolated as the tetra-alkylammonium salts from an aqueous organic solution. They were characterized using elemental analysis, X-ray analysis, UV–vis, IR and Raman spectroscopy. This study demonstrates that these novel polyoxometalates with an inverted-Keggin structure could be used as a new building block material because they have both a carboxy group and an alkene part, which could react with other organic substrates.

Polyoxometalates are well known as useful inorganic clusters because extensive attention has been paid to their application in various fields, such as catalysis, analytical chemistry and medicine [1–11]. In addition, polyoxometalates are beautiful artificial molecules. Polyoxometalates with various structures have been known. These structures include the Keggin and Wells-Dawson type. Recently, many types of large polyoxometalates were prepared and characterized. The mixed valence molybdenum containing polyoxometalates, such as $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}$ $[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}$ ca. $400H_2O$ and $Na_{48}[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]$ ca. $1000H_2O$, tend to have especially large structures [12,13]; some supermolecular structures are synthesized with dendrimers by using polyoxometalate building blocks that were prepared through the addition of an organic molecule (dendrimer) into the defect position of the polyoxometalates [14–16]. Additionally, functionalized polyoxometalates have been prepared by attaching various organic molecules onto the basic sites of the polyoxometalates [17,18]. Extensive attention has been paid to the synthesis and characterization of these organic-polyoxometalate hybrid complexes. Using the hydrothermal technique, two- or three-dimensional, hybrid polyoxometalates were prepared with various metal complexes [19,20].

Recently, we prepared molybdo-methylphosphate and molybdo-ethylphosphate with an inverted-Keggin structure [21]. It was the first report on the synthesis of inverted-Keggin-type, phosphorus-centered polyoxometalates, although arsenate- and fluorophosphate-based polyoxometalates with an inverted-Keggin structure had previously been prepared [22–25]. We then tried to prepare other types of organophosphate containing polyoxometalates. In this study, three new types of organophosphate-centered polyoxometalates (propylphosphate, 2-carboxyethylphosphate and vinylphosphate) were isolated and characterized using elemental analysis, X-ray analysis, IR, Raman and UV–vis.

A 2.42 g quantity of $MoO_4 \cdot 2H_2O$ [26] and a varying amount of organophosphonic acid (1.24 g for propylphosphonic acid, 1.54 g for 2-carboxyethylphosphonic acid or 1.08 g for vinylphosphonic acid) were dissolved in 100 ml of H_2O. One hundred milliliters of acetonitrile was poured into the solution followed by the addition of 3.5 ml of conc. HCl with stirring. After the solution stood at r.t. for 2 h, the tetra-alkylammonium salt, i.e., $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_3H_7)_4NBr$, or $(C_2H_5)_4NBr$, was added and initially gave a pale-yellow colored precipitate. The pale-yellow precipitate was removed and the resulting colorless solution was allowed to stand at r.t. for several days. After this period, a white precipitate was collected, washed with water and ethanol and recrystallized from acetonitrile to obtain a colorless single crystal (Yield: 30–40%) [27]. The bigger tetra-alkyl ammonium salts of these complexes tend to effloresce because of the evaporation of the acetonitrile in the single crystal. For the X-ray structural analysis [28], smaller tetra-alkyl ammonium salts were needed (although the bigger tetra-alkyl ammonium salts were used for the other measurements after drying in vacuo at ca. 60 °C). Fig. 1 shows the structure of the three complexes obtained from the X-ray analysis, which indicates that their structures should be nearly identical and of the so-called inverted-Keggin type [29]. Table 1 shows the selected mean bond lengths of the three new complexes and, for comparison, the already reported lengths for molybdo-methylphosphate and molybdo-ethylphosphate. Each bond length is almost the same, even if the carbon chains in the organophosphates are different. The bond length in Mo–Od (the terminal oxygen) is the shortest and the one in Mo–Oa (the oxygen bonded to a phosphorus atom) is the longest in each of

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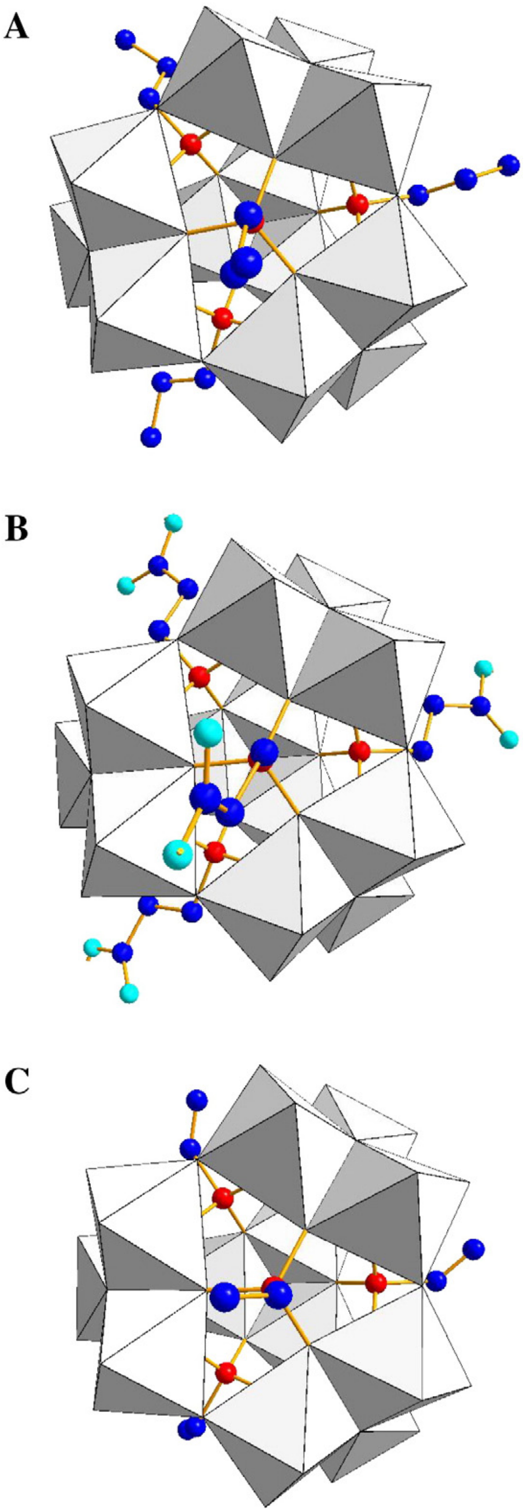

Fig. 1. Balls and stick description of the structure of (a) PrP_4Mo_{12}, (b) $CarP_4Mo_{12}$ and (c) $VinylP_4Mo_{12}$. Phosphorus, carbon and oxygen are described in red, blue and sky blue balls, respectively.

Table 1
Selected mean bond length of inverted-Keggin type polyoxometalates.

Bond type	MeP_4Mo_{12}	EtP_4Mo_{12}	PrP_4Mo_{12}	$CarP_4Mo_{12}$	$VinP_4Mo_{12}$
Mo–Od	1.70[a]	1.69[a]	1.70 ± 0.01	1.70 ± 0.02	1.70 ± 0.03
Mo–Ob	1.87[a]	1.86[a]	1.87 ± 0.01	1.87 ± 0.02	1.87 ± 0.02
Mo–Oc	2.02[a]	2.03[a]	2.02 ± 0.01	2.02 ± 0.03	2.02 ± 0.02
Mo–Oa	2.35[a]	2.35[a]	2.35 ± 0.03	2.35 ± 0.06	2.35 ± 0.05
P–Oa	1.54[a]	1.54[a]	1.55 ± 0.01	1.54 ± 0.02	1.54 ± 0.02
P–C	1.69[a]	1.79[a]	1.77 ± 0.01	1.79 ± 0.00	1.79 ± 0.01

Od: the terminal oxygen; Ob: the corner-shared oxygen; Oc: the oxygen coordinated to three molybdenum atoms; Oa: the oxygen bounded to a phosphorus atom.
[a] Obtained from Ref. [21].

the inverted-Keggin polyoxometalates. Bond lengths that alternate between long and short were observed between the molybdenum and the shared oxygen atoms, which is similar to many polyoxometalates [30]. The mean bond length between the phosphorus atoms and the oxygen atoms is the same (1.54 Å) for all the complexes, but it is shorter than the bond length between the phosphorus atoms and the carbon atoms (1.77–1.79 Å). The P–O bond length in all the inverted-Keggin anions is similar to the mean length of the reported P–O bond [31], while the P–C length is shorter than the one in methylphosphine [32]. The mean bond angles of O–P–C are 107.82(±3.88)° for $PropylP_4Mo_{12}$, 107.40(±3.60)° for $CarP_4Mo_{12}$ and 107.41(±3.27)° for $VinylP_4Mo_{12}$, and the angles of O–P–O are 110.05° for $PropylP_4Mo_{12}$, 111.41° for $CarP_4Mo_{12}$ and 111.21° for $VinylP_4Mo_{12}$. The structure around the phosphorus atom is distorted from an ideal tetrahedron for all the complexes. However, the separations between each of the phosphorus atoms are 4.52 Å ± 0.01 for $PropylP_4Mo_{12}$, 4.51 Å ± 0.02 for $CarP_4Mo_{12}$ and 4.52 Å ± 0.01 for $VinylP_4Mo_{12}$, and the angles from the phosphorus at the three different positions are 60° ± 0.2° for $PropylP_4Mo_{12}$, 60° ± 0.4° for $CarP_4Mo_{12}$ and 60° ± 0.2° for $VinylP_4Mo_{12}$, respectively, which indicate that the four phosphorus atoms are located at the apexes of an ideal tetrahedron (within a small error margin) for the three new complexes. It is noted that these complexes should have pseudo Td symmetry without taking into consideration the direction of the carbon chain of the organophosphates. These structural properties are very similar to those of molybdo-methylphosphate (MeP_4Mo_{12}) and molybdo-ethylphosphate (EtP_4Mo_{12}). ^{31}P NMR spectra for the three new complexes were measured in CD_3CN [33]. One peak was obtained at +29.3 ppm for PrP_4Mo_{12}, +27.3 ppm for $CarP_4Mo_{12}$ and +15.1 ppm for $VinylP_4Mo_{12}$. As previously reported, one peak appeared at +27.3 ppm and +31.0 ppm for MeP_4Mo_{12} and EtP_4Mo_{12}, respectively. The other mean bond lengths were found to be 1.51(±0.02) Å for –C–C– in PrP_4Mo_{12}, 1.50(±0.02) Å for –C–C–, 1.23(±0.01) Å for –C═O, and 1.29(±0.01) Å for –C–O– in $CarP_4Mo_{12}$ and 1.28(±0.02) Å for C═C in $VinylP_4Mo_{12}$. These bond lengths are normal judging from the reported mean carbon–carbon bond lengths, where –C–C–, –C–C and C═C bond lengths are 1.524 Å, 1.513 Å and 1.316 Å, respectively and the other types of mean bond lengths were reported to be 1.316 Å for C═C, 1.214 Å for –C═O, 1.308 for –C–O– [34]. Interestingly, in PrP_4Mo_{12} the mean bond length for the C–C bond whose carbon is bound to a phosphorus atom is 1.49 Å and the length of the other C–C bond is 1.54 Å, while two carbon–carbon bond lengths in $CarP_4Mo_{12}$ are 1.52 Å (phosphorus-bounded carbon–carbon bond) and 1.49 Å (carboxylic acid bounded carbon–carbon bond), although the difference of bond length is small.

Fig. 2 shows the UV–vis spectra of the three complexes in acetonitrile. Only one absorption maximum appeared at 245 nm for all the complexes [35], which should be ascribed to the metal to ligand charge transfer band (LMCT) from molybdenum to oxygen [36,37]. The absorption coefficients are 7.64×10^4 (dm^3/mol·cm) for $PropylP_4Mo_{12}$, 7.44×10^4 (dm^3/mol·cm) for $CarP_4Mo_{12}$ and 7.55×10^4 (dm^3/mol·cm) for $VinylP_4Mo_{12}$, respectively. Fig. 3 shows IR and Raman spectra of the three complexes, and each peak in the IR and Raman bands is described in Table 2 [38]. The shape of the spectra is almost the same for all the samples, but the frequencies of the peaks are slightly different. For most of the polyoxometalates, the IR spectra are known to show four parts: M-Od (terminal oxygen), M-Oc (corner-shared oxygen), M-Ob (edge-shared oxygen), and X-Oa (X = hetero atoms). In the case of the