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Chirality in Polyoxometalate Chemistry

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Dedicated to Prof. Pierre Gouzerh on the occasion of his retirement

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The increasing use of polyoxometalates in the fields of material sciences, catalysis, and biology has raised the interest in chirality of such systems. This review provides a summary of the different strategies followed: i) chirality in solid-state arrangements, ii) chiral polyoxometalate frameworks, and iii) chiral polyoxometalate–organic hybrids. Through the discussion of selected examples, an outline for future work is drawn.

1. Introduction

The growing importance of nanotechnology has generated a huge synthetic effort toward building customized particles. In particular, multimetallic compounds are highly valuable components in functional molecular systems.[1,2] Among these, polyoxometalates (POMs) – also called isopolyanions/heteropolyanions – are an extremely diverse family of metal–oxygen aggregates, but with a defined geometry, that can be synthetically controlled.[3–5]

POMs are composed of early transition metals in high oxidation states (mainly V^{V}, Mo^{VI}, or W^{VI}) and oxo ligands. They can include almost any other element within their backbones. Their sizes range from the subnanometer level to tens of nanometers. This large structural and elemental diversity allows chemists to control and tune POM properties and reactivities at the molecular level. Thus, designed POMs have been introduced for numerous applications in chemistry, physics, and biology.[6–8]

In catalysis, they are used as redox catalysts[9–13] and Brønsted or Lewis acids.[14–17] They are also suitable as supports for organometallic catalysts[18,19] or nanoparticles.[20,21] Because multielectron reduction without loss of the architecture is often reversible, they can be used as electron reservoirs.[22] Incorporation of paramagnetic or photochemically/photophysically active ions make the functional POMs valuable components of materials.[23–25] Finally, antitumoral, antiviral, and antibiotic properties have been evidenced for several POMs,[26–28] and specific POM–protein interactions have been established, which opens opportunities in biomedical studies.[29–32]

It is obvious that chirality is a crucial issue in all these fields, which range from chemistry to material sciences and biology. The preparation of chiral POMs, or chiral structures including POMs, is consequently a goal for many polyoxometalate chemists, as it would provide ultimate control of the synthesis of those nanosized objects. We wish to review here the state-of-the-art in the field and to draw some general conclusions that might point to new research directions.

Chirality of POMs can manifest itself in several distinct ways, and the development of organic hybrids creates even more possibilities. It can derive from stereogenic arrangements in the solid state or at the supramolecular level. The chiral polymetallic structure can be intrinsically chiral (chiral metal framework), or chirality can derive from functionalization of the ligands or from introduction of stereogenic side-chains in hybrid structures. All these aspects will be covered in the following pages by a selection of representative examples.

2. Chirality in Solid–State Arrangements

Flack recently compiled the essential points for the determination of absolute configuration in crystals,[33] which are summarized as follows. When considering chirality in a spatial arrangement of atoms in the solid state, one has to distinguish between the crystallographers' and the chemists' point of view. The former considers the absolute structure,

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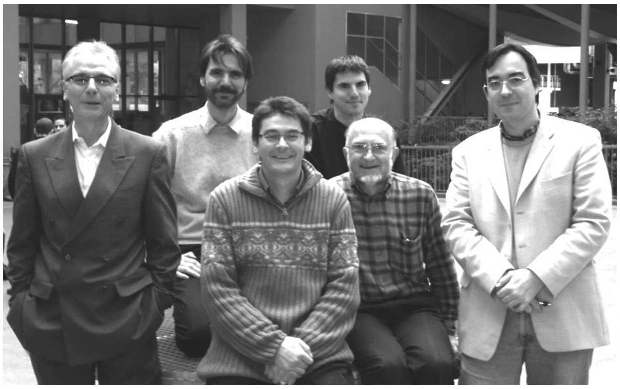
which applies to noncentrosymmetric crystal structures, whereas the latter considers the absolute configuration, which refers to chiral molecules. Thus, the point of view of crystallographers and chemists differ in the entity under consideration (crystal structure vs. molecule) and in the symmetry restrictions (noncentrosymmetric vs. lack of mirror, reflection, inversion through a point, rotoinversion). Noncentrosymmetry in a crystal can result from disorder, as shown by Murakami for a series of Keggin-type compounds with interesting nonlinear optical properties.[34] In this paper, we adopt the position of the chemists and consider the absolute configuration of a molecular entity in the crystal. If a molecule crystallizes in a space group containing symmetry operations of the second kind, the crystal is not enantiomorphous. If these operations are intramolecular, the individual molecules are achiral. However, if they operate intermolecularly, opposite enantiomers might be present. One must verify, in that case, that no noncrystallographic rotoinversion of rotoreflection symmetry operations are allowed in the molecular entity under consideration. If none is found, the molecule is chiral.

Several authors have reported organic–inorganic hybrids in which the components are coordinated or closely packed along helical axes.[35–38] However, in these cases, additional symmetry planes or inversion centers are also present, and the resulting crystals are not enantiomorphic.

Chiral cationic transition-metal complexes have been associated with POMs to build original 2D or 3D networks.[39] In most of the examples, the metallic cation was complexed by chelating diamines to yield ML_3^{n+} complexes.[40] The resulting Δ or Λ configuration was generally not controlled and racemic salts $[\Delta,\Lambda\text{-}ML_3]_x[POM]_y$ were isolated.

Yet, there are several cases of POMs crystallizing in enantiomorphic space groups. When the POM motif itself is asymmetric, such as the distorted POM structures in α-$[CuW_{12}O_{40}]^{6-}$,[41] α-$[SiNaW_{11}O_{39}]^{7-}$,[42] γ-$[GeW_{10}O_{36}]^{8-}$,[43] or $[H_6S_4V_6O_{24}]^{2-}$,[44] the crystalline compound is a con-



Bernold Hasenknopf (back row, left) was born in Berchtesgaden, Germany, in 1965. He studied chemistry in Germany, France, and Great Britain, and obtained his Ph.D. in 1996 under the supervision of Jean-Marie Lehn at the University of Strasbourg for his work on circular helicates. He then joined the group of Peter Schultz in Berkeley for one year to work on unnatural biopolymers and catalytic antibodies. In 1997, he became faculty member of the University Pierre and Marie Curie in Paris, where he is now associate professor. His research interests focus on supramolecular chemistry of multimetallic assemblies and their interactions with biomolecules. After more than ten years of fruitful work in the group of Pierre Gouzerh and Anna Proust, he founded a team for supramolecular chemistry at the Institut Parisien de Chimie Moléculaire.

Kevin Micoine (back row, right) was born in Rennes, France, in 1983. He graduated from the École Supérieure de Physique et de Chimie Industrielles (ESPCI, Paris) in 2006. A 6 months internship at Novartis (Basel, Switzerland) in 2004 was part of his studies. Since 2006, he is working towards his Ph.D. thesis at UPMC, focusing on the functionalization of polyoxometalates for biological applications and optical resolution.

Emmanuel Lacôte (front row, right) was born near Lyon in 1972. After graduating from the École Normale Supérieure, he joined the group of Max Malacria at UPMC. He then moved to Fribourg (Switzerland) for an extended stay in the group of Philippe Renaud, which led to a double Ph.D. from UPMC and the University of Fribourg (1999). After a postdoctorate position at Stanford with Paul Wender, where his work was devoted to the total synthesis of bryostatin analogues, he was appointed at CNRS in 2000, where he is now Directeur de Recherche. His current interests involve finding new heteroatom-based organic reactions and the elaboration of organic hybrids of polyoxometalates toward applications in biology and catalysis.

Serge Thorimbert (front row, center left) was born in Chelles, France, in 1965. He prepared his Ph.D. under the supervision of Professor J.-P. Genêt and moved in 1993 to the MPI in Mülheim/Rhur to work with Professor W. F. Maier on the preparation of heterogeneous catalysts for olefin epoxidation. From Sept. 1998 to Sept. 1999, he joined the Craig group at the Imperial College of London (UK) as an academic visitor and worked on the functionalization of chiral tetrahydropyridines. Since 1994, he is Associate Professor at UPMC, and his research focuses on organometallic catalysis for stereoselective synthesis as well as preparation of hybrid polyoxometalates.

Max Malacria (front row left) was born in 1949 in Marseille, France. He obtained his Ph.D. from the University of Aix-Marseille III with Professor Marcel Bertrand in 1974. He was appointed as Assistant in 1974 at the University of Lyon I. After a postdoctoral stay with Professor K. Peter Vollhardt at Berkeley, he went back to the University of Lyon as a Maître de Conférences in 1983. In 1988, he was appointed Full Professor at UPMC. In 1991, he was appointed as a junior member of the Institut Universitaire de France, from which he has been promoted to senior member in 2001. Prof. Malacria has been active in the development of new domino processes in both organometallic and radical chemistry.

René Thouvenot (front row, center right) was born in 1946 in Le Val d'Ajol in the East of France. After graduating from the Ecole Normale Supérieure de Saint-Cloud, he prepared a thesis on vibrational investigations of polyoxometalates in the POM group of Pierre Souchay at UPMC. He defended it in 1978 with Yves Jeannin as supervisor after Souchay's untimely death. During a postdoctoral stay at ETH in Zürich with Luigi Venanzi, he became interested in organometallic chemistry and multinuclear NMR spectroscopy. He is currently Directeur de Recherche at CNRS and his research interests are multinuclear NMR spectroscopy of polyoxo compounds, including chiral and paramagnetic POMs, as well as the synthesis and characterization of organo-Si and organo-P derivatives of POMs.

glomerate, although the deviation from an achiral structure is very small in these cases. In other organic–inorganic hybrids crystallizing in enantiomorphic space groups, chiral packing could be observed.[45,46]

A chiral framework composed of achiral building units in enantiomorphic crystals was reported recently by Wang. The compound $[Cu(bbi)_2V_{10}O_{26}][Cu(bbi)]_2$ [bbi = 1,1′-(1,4-butanediyl)bis(imidazole)] crystallized as a conglomerate in the enantiomorphic space group I_{222}.[47] It contains helical chains of a Cu–bbi coordination polymer, which are connected into a 3D network. The two enantiomeric forms were separated manually. When redissolved in dmso, the compound decomposed into fragments that maintained chirality, as shown by their opposite CD (circular dichroism[48,49]) spectra.

Chirality can be transferred to the framework by using dissymmetric POMs. Yang reported linear chains of homochiral $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6L_3(B\text{-}\alpha\text{-}PW_9O_{34})]$ (L = ethylenediamine or 1,2-diaminopropane) linked by aromatic dicarboxylic acids that crystallized as a conglomerate.[50] The coordination of the three bidentate diamines confers chirality to the POM cluster (Figure 1a).[51] A chiral 3D framework based on the same $\{Ni_6PW_9\}$ core but without the bidentate diamines was also obtained.[50] In this case, the chirality results from the connection of the POM units by an aromatic tricarboxylic acid (Figure 1b). This compound also crystallized as a conglomerate.

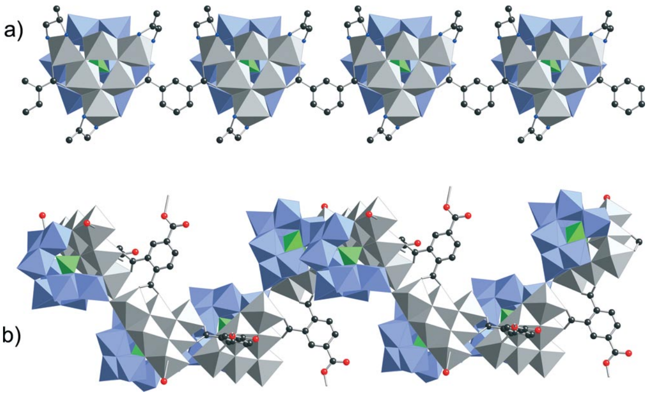


Figure 1. a) Linear chain of homochiral $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(pn)_3\text{-}(B\text{-}\alpha\text{-}PW_9O_{34})]$ (pn = 1,2-propylenediamine) bridged by 1,3-benzenedicarboxylic acid. b) A right-handed helix that is part of the 3D framework of $\{[Ni_6(\mu_3\text{-}OH)_3(H_2O)_5(B\text{-}\alpha\text{-}PW_9O_{34})](1,2,4\text{-}Hbtc)\}^{2-}$ (btc = benzenetricarboxylic acid). Adjacent helices are connected through the open bonds at the 4-carboxylic group.[50]

Similarly, Wang, Su and co-workers have linked the chiral Waugh-type polyoxomolybdate $[MnMo_9O_{32}]^{6-}$ with Zn^{II} ions into a chiral network $[(Zn(H_2O)_3)_3(MnMo_9O_{32})]$,[52] and separated the enantiomers manually. Interestingly, the enantiomers redissolved in water displayed opposite CD spectra, which indicates a stable chiral arrangement. The authors also presented a CD spectrum for the precursor $K_3(NH_4)_3[MnMo_9O_{32}]$ in aqueous solution. This optical activity calls for further investigation. Earlier reports on $(N(C_4H_9)_4)_6[MnMo_9O_{32}]$ have shown a Pfeiffer effect in acetonitrile in the presence of L-brucine, i.e. a fast conversion of the enantiomers.[53] The anion $[MnMo_9O_{32}]^{6-}$ is unstable in dilute aqueous solution, and attempts to resolve the racemate with chiral cations or to induce a Cotton effect in water were unsuccessful.[54] However, enantiomorphous crystals of $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ were reported.[55]

The complementary approach to transfer chirality to the framework is to use optically pure chiral cations with achiral POMs. Cronin et al. used diprotonated (–)-spartein as a chiral cation for the preparation of an optically pure chiral framework based on the polyoxomolybdenum(V) anion $[H_{15}Mo_{12}NaO_{62}P_8]^{8-}$ and 1,3,5-benzenetricarboxylic acid as linker.[56] Wang used enantiopure copper/proline complexes to obtain homochiral frameworks with Keggin ions $[BW_{12}O_{40}]^{5-}$.[57] The chiral configuration of the proline determines the chirality of the total framework. Such constructs and their building principles represent a first step to high-dimensional chiral compounds based on POMs, which might be useful for asymmetric catalysis or chiral separation.

3. Chiral POM Structures

Chiral POM molecules attract particular interest of chemists, because most applications, including potential medical and catalytic ones, require and are defined by soluble complexes, not complexes in crystals.

3.1. Chirality from Alternating Bond Lengths

Pope and d'Amour concomitantly pointed out the dissymmetry of some polyoxomolybdate structures as a result of alternating Mo–O bond lengths.[58,59] Indeed, careful analysis of the X-ray structure of $[\alpha\text{-}P_2Mo_{18}O_{62}]^{6-}$[59,60] revealed that this compound does not have an overall D_{3h} symmetry, as is conventionally represented (Dawson structure). Instead, the Mo–O bond lengths regularly alternate between short (ca. 1.80 Å) and long bonds (ca. 2.05 Å). This removes the mirror planes, which results in a chiral structure (Figure 2b).

It is interesting to note that this bond length alternation can be traced back to the trilacunary species $[\alpha\text{-}PMo_9O_{31}(OH_2)_3]^{3-}$ (Figure 2a) whose crystal structure was described previously by Strandberg[61] and d'Amour.[62] The longer bond length to the aqua ligand shortens the *trans* Mo–O bond, which in turn lengthens the next O–Mo bond, and so on. As a result, two enantiomers of $[\alpha\text{-}PMo_9O_{31}(OH_2)_3]^{3-}$ exist. Two homochiral complexes combine to the $[\alpha\text{-}P_2Mo_{18}O_{62}]^{6-}$, whereas the heterochiral combination yields the α* isomer of the Dawson compound ($\pi/3$ rotation of a half-anion). Pope resolved the racemic mixture of $[\alpha\text{-}P_2Mo_{18}O_{62}]^{6-}$ in an organic solution through the Pfeiffer effect, i.e. without isolating the enantiopure POM, by addition of L-brucine [yielding the $(+)_{380}$ enantiomer] and D-cinchonine [yielding the $(-)_{380}$ enantiomer].[63] The chiral ammonium ions form stronger ion pairs with one of the POM enantiomers, which leads to the conversion of the less favorable isomer into the more favorable one. Three L-

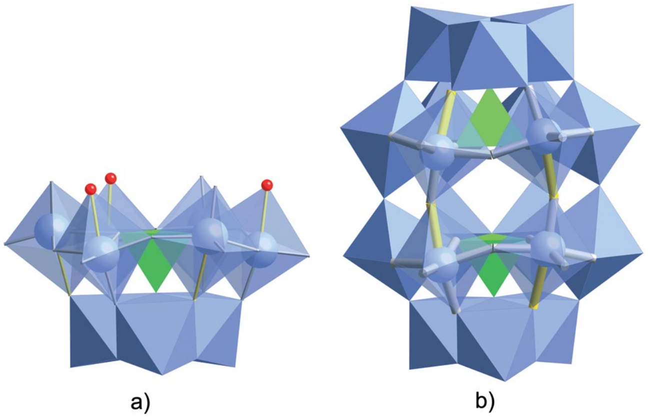


Figure 2. a) Structure of $[PMo_9O_{31}(OH_2)_3]^{3-}$.[61] The yellow bonds are longer than the grey bonds. The red balls correspond to H_2O ligands. b) Structure of α-$[P_2Mo_{18}O_{62}]^{6-}$.[60] Some longer bonds are highlighted in yellow to show the loss of mirror symmetry. The enantiomer shown corresponds to the homochiral condensation of two of the $[PMo_9O_{31}(OH_2)_3]^{3-}$ anions shown in a).

brucine molecules per α-$[P_2Mo_{18}O_{62}]^{6-}$ polyanion seem sufficient to cause complete conversion of the racemate to only one enantiomer. This indicates the lability of the structure and the relatively fast racemization rate. Pope also noted a more symmetric coordination environment of the Mo^V ions in the two-electron reduced compound $[H_2P_2Mo^V{}_2Mo_{16}O_{62}]^{6-}$.

Seven years later, Miwa reported the possible use of such chiral Dawson-type heteropolyacids associated with L-brucine for the enantioselective formation of polybenzyl polymers.[64] In the same year, he also demonstrated that Keggin-type heteropolyanions of the general formula $[XM_{12}O_{40}]^{n-}$ with X = Co^{II}, Zn^{II}, $2H^+$, Al^{III} presented induced Cotton effects in the presence of L-brucinium cations.[65] Protonated amino acids were selected as chiral cations for optical resolution in the solid state, and successful crystallographical data were collected for the enantiomerically pure 18-molybdodiphosphate associated with two lysine molecules in $(Lys)_2H_2[P_2Mo_{18}O_{62}]\cdot 16H_2O$.[66]

The corresponding heteropolytungstates do not display this dissymmetry from alternating bond lengths. However, chiral structures resulting from bond length alternation were observed in the Preyssler heteropolytungstate $[NaP_5W_{30}O_{110}]^{14-}$[67] and in $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$.[68] Interestingly, achiral $[PW_{12}O_{40}]^{3-}$ with chiral ammonium cations was used as a chiral Brønsted acid catalyst in asymmetric enamine condensations.[69]

Poblet et al. very recently completed a comprehensive statistical analysis of alternating bond lengths in POMs and provided an explanation on the basis of DFT calculations.[70] They showed that these distortions are more pronounced when the HOMO–LUMO gap in the POM is decreased. Thus, the effect of bond alternation is more manifest in larger POMs (Lindqvist < Keggin < Dawson structure) and, when considering an isostructural series (Dawson), with a heteroatom of lower oxidation number ($[S_2Mo_{18}O_{62}]^{4-}$ < $[P_2Mo_{18}O_{62}]^{6-}$ < $[Si_2Mo_{18}O_{62}]^{8-}$). As the HOMO–LUMO gaps in tungstates are substantially larger than in molybdates, the distortions in equivalent structures are less marked. The DFT calculations also confirmed that reduced POMs have a more symmetric structure than the fully oxidized parent structure.

A particular case of asymmetry due to alternating bond lengths is present in borotungstates.[71] The heteropolytungstate core $\{H_3BW_{13}O_{46}\}^{8-}$ can be found in condensed structures $[H_6B_2W_{26}O_{90}]^{12-}$ and $[H_6B_3W_{39}O_{132}]^{15-}$ (Figure 3). The $\{H_3BW_{13}O_{46}\}^{8-}$ moiety has a ditungstate group $\{W_2O_7\}$ condensed to a monolacunary Keggin borotungstate, and in this ditungstate group, one terminal oxygen is doubly protonated (H_2O as ligand). As a result, the bond lengths along the O=W–O=W–OH_2 chain alternate between short and long, and the mirror plane of the monolacunary Keggin ion is lost. The resulting building block is therefore chiral. In $[H_6B_2W_{26}O_{90}]^{12-}$, two homochiral $\{H_3BW_{13}O_{46}\}^{8-}$ moieties are condensed, whereas $[H_6B_3W_{39}O_{132}]^{15-}$ corresponds to a heterochiral assembly. The ^{183}W NMR spectrum of the latter shows 39 lines, which proves that the chiral structure is maintained in solution. The compound crystallized as a racemate.

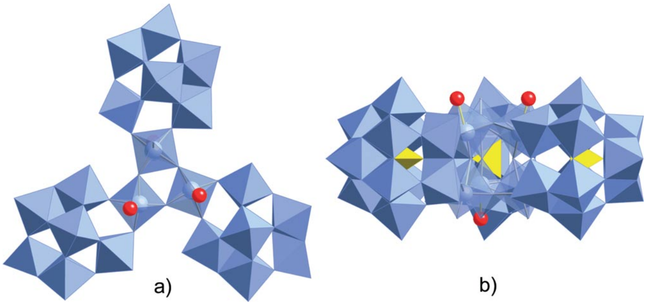


Figure 3. Views along (a) and perpendicular (b) to the C_3 axis in $[H_6B_3W_{39}O_{132}]^{15-}$.[71] The longer bonds to the H_2O ligands (red balls) make the structure chiral. In solution, the polyanion lacks symmetry.

3.2. Chiral Primary POM Structure

The chiral heteropolyoxomolybdate $[H_4Co_2Mo_{10}O_{38}]^{6-}$ (Figure 4)[72] was resolved by Ama, Hidaka, and Shimura with traditional resolution techniques, i.e. through formation of diastereomeric salts with $[Co(en)_3]^{3+}$.[73] It was historically the first chiral POM to have been isolated in an enantiopure manner, and it has opened the field to all the contributions that are reviewed herein. Gimenez-Saiz used it for several applications in material sciences, although no macroasymmetry was induced.[74]

An original helical-shaped POM $[P_6W_{18}O_{79}]^{20-}$ (Figure 5) was reported in 1988 by Fuchs[75] (Na^+ salt) and in 1990 by Acerete[76] (Na^+/H^+ salt),[77] and this compound can be considered as the first characterized heteropolytungstate with a chiral primary structure. The derivative $[P_5W_{18}O_{75}(OH)_3]^{20-}$ lacking one of the peripheral phosphates was also described.[75] This heteropolyanion with a relatively high phosphorus content was formed in a slightly

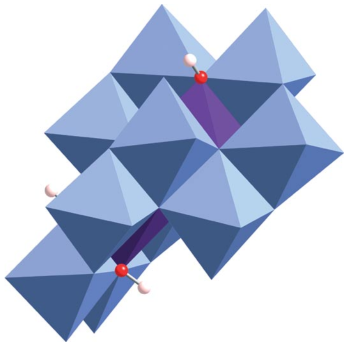


Figure 4. The heteropolyoxomolybdate $[H_4Co_2Mo_{10}O_{38}]^{6-}$.[73]

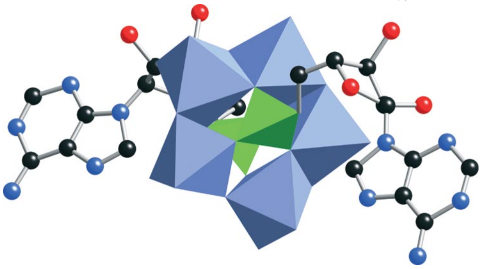


Figure 6. The Strandberg ion incorporating two molecules of adenosine-5′-monophosphate.[84]

acidic aqueous solution of a 1:3 mixture of phosphate and tungstate. The X-ray structure determinations revealed the intrinsic dissymmetric structure. The C_2 symmetric POM consists of two $\{\beta_3\text{-A-PW}_8O_{33}\}^{13-}$ moieties capped by two phosphate groups and joined by a ditungstate group (Figure 5). A twist in this ditungstate unit imparts the overall appearance of a helix. The compound was obtained as a racemate, and both enantiomers were present in the crystals. Acerete pioneered the use of ^{183}W NMR spectroscopy to investigate the chirality of the compound in solution. The spectrum of $[P_6W_{18}O_{79}]^{20-}$ consists of 9 signals, which split into two sets on the addition of L-lysine·HCl, as a result of diastereomer formation. It can be concluded that the chiral structure is maintained in solution, and that the racemization is slow on the NMR timescale.

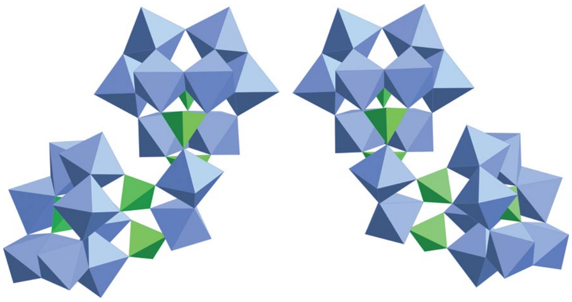


Figure 5. The two enantiomers of the helical-shaped $[P_6W_{18}O_{79}]^{20-}$.[75,76]

The Strandberg structure in $[P_2Mo_5O_{23}]^{6-}$[78] consists of a ring of five $Mo^{VI}O_6$ octahedra with four edge junctions and one corner junction, and phosphate tetrahedra capping each side of the ring. It is also known for the W analogue.[79] The highest possible symmetry is C_2, thus the structure is chiral. Spontaneous resolution was observed in one system.[80] The same Mo_5 ring can be capped with phosphonate groups[81,82] or by sulfate.[83] Yamase prepared the adenosine-5′-monophosphate capped structure (Figure 6).[84] The crystal contained only a single enantiomer, and the ^{13}C and ^{31}P NMR spectra are in agreement with the enantiomeric purity in solution. Carraro, Bonchio, and Kortz used Strandberg-type POMs with pendant ammonium groups to produce gels composed of twisted fibrils.[85]

The sulfate-capped $[S_2Mo_5O_{23}]^{4-}$ was resolved by the Pfeiffer effect with arabinose.[86] Both enantiomers of the POM were accessible by choosing the suitable enantiomer of the sugar, although the enantiopure POMs were not isolated. From the data presented, one can conclude that the rate for racemization of this type of POM is in the order of hours.

Kabanos prepared the Strandberg structure $[Mo^{VI}{}_5S_2O_{21}]^{4-}$ with sulfite as capping groups and crystallized it with diprotonated 4,4′-H_2bipyridine^{2+} as counterion.[87] The isolated crystal contained only one enantiomer, whereas the solid-state CD spectrum did not show any band. This observation is compatible with spontaneous resolution of the racemate and measurement of the CD spectrum on the conglomerate. The cations are strongly hydrogen bonded and transfer the chirality to the entire structure, which results in NLO properties.

Several original chiral POMs have been reported this year. A mixed-valence antimony polyoxomolybdate $[Mo_{18}Sb^{V}{}_4Sb^{III}{}_2O_{73}(H_2O)_2]^{12-}$ was prepared and characterized by Xue (Figure 7a).[88] The C_1 symmetric compound demonstrates a high nucleophilicity and can act as a basic building block to form larger derivatives. It can be connected by a divalent transition-metal ion (Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}) to form a meso dimer in which the M^{II} center is located at the inversion center. Cao reported an approximately C_3 symmetric pentadecatungstate incorporating two Ce^{III} ions $[H_6Ce_2(H_2O)Cl(W_{15}O_{54})]^{7-}$ (Figure 7b).[89] This compound and the previous $[Mo_{18}Sb^{V}{}_4Sb^{III}{}_2O_{73}(H_2O)_2]^{12-}$ compound are remarkable because they are not derived from a classical POM structure, which shows that the family of original POM structures is still growing.

Similarly, Young very recently published the structure of a new C_2-symmetry mixed-valence hexadecamolybdate with unprecedented Mo topology.[90] Organic ligands (twelve isopropylpyrazoles) are crucial for the cluster assembly. In the authors' words, "the pyrazole groups coat much of the surface of the molecule, apart from a number of oxo-rich seams that trace a chiral pattern across the surface".

Chiral sandwich polyoxotungstates $[WM_3(H_2O)_2(B\text{-}\alpha\text{-}XW_9O_{34})_2]^{12-}$ (X = M = Zn^{II} or Co^{II}) were prepared in 1991 by Tourné by aging solutions of Keggin-type polytungstozincates and polytungstocobaltates $[M(H_2O)(XW_{11}O_{39})]^{8-}$.[91] They also prepared derivatives by replacement of two or three metal ions by others such as Mn$^{II/III}$,

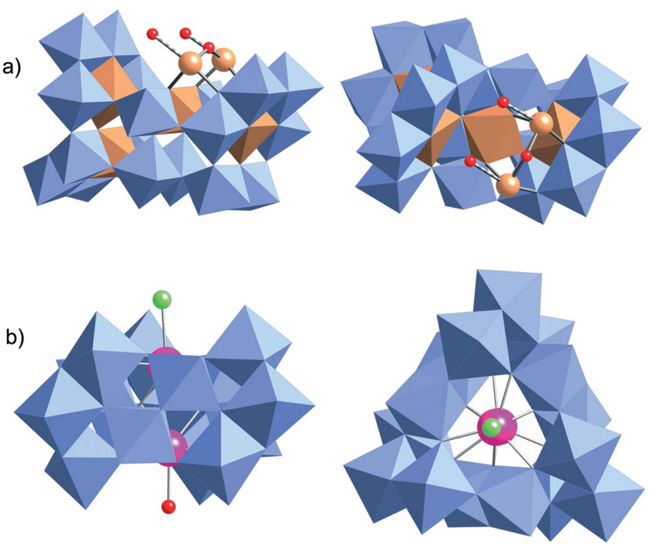


Figure 7. a) Two perpendicular views of $[Mo_{18}Sb^{V}{}_4Sb^{III}{}_2O_{73}(H_2O)_2]^{12-}$.[88] The Sb^{III} atoms are represented as brown balls, the Sb^{V} atoms as brown polyhedra. b) Side and top view of $[H_6Ce_2(H_2O)Cl(W_{15}O_{54})]^{7-}$.[89] Ce = purple, Cl = green, H_2O = red sphere.

$Fe^{II/III}$, Ni^{II}, Cu^{II}, Pd^{II}, Pt^{II}, or V^{IV}. The crystal structures of $[WZn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, $[WCu_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, and $[WZnV_2O_2(ZnW_9O_{34})_2]^{12-}$ (Figure 8a) were reported. They contain a positional disorder $W_{0.5}M_{0.5}$ (M = Zn or Cu) group, which makes the POM framework appear to be C_{2h} symmetric in the crystal. However, the crystals correspond to a racemate, and the true molecular symmetry is C_2. This was confirmed by the 10-line ^{183}W NMR spectra for diamagnetic $[WZnM_2(ZnW_9O_{34})_2]^{12-}$ (M = Zn, Pd, Pt). The same observations were reported by Pope for the organotin-substituted derivatives $[WM(SnR)_2(B\text{-}\alpha\text{-}MW_9O_{34})_2]^{12-}$ (M = Zn^{II} or Co^{II}, R = alkyl).[92] Kortz reported the structurally related indium(III)-substituted tungstophosphates.[93] Single crystals of $[In_3Cl_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{11-}$ and $[In_3Cl_2(B\text{-}\alpha\text{-}P_2W_{15}O_{56})_2]^{17-}$ were analyzed and, surprisingly, only three indium atoms are incorporated into the structure, leaving one vacant inner position in both structures (Figure 8b). The ^{183}W NMR spectrum shows less than the expected number of lines for a C_2 symmetric compound (9 and 15, respectively, for the Keggin and Dawson compound). This was explained by accidental degeneracy.

Neumann used these sandwich POMs extensively as oxidation catalysts, and he also prepared new metal derivatives.[94,95] A striking example of the broad potential was put forward together with Adam, Seebach and Zhang.[96,97] The authors showed that sandwich POM $[ZnW(VO)_2(ZnW_9O_{34})_2]^{12-}$ was an outstanding asymmetric oxidant when coupled with TADDOL-derived hydroperoxide. TONs as high as 42000 could be obtained with *er* values reaching 95:5. The key was the formation of a transient POM-V peroxide that installed the chirality of the peroxide on the POM, as the V atom was shown to be directly involved in the oxygen transfer (Figure 9). The advantages of using the POM were derived from the rigid bulk of these structures that provided the optimal template for steric interactions during the oxygen transfer of the peroxide to the alkene. The robustness of the POM toward hydroperoxides ensured high TONs. Yet, the POM was used as a racemate, and the enantioselectivity stems from the organic hydroperoxide.

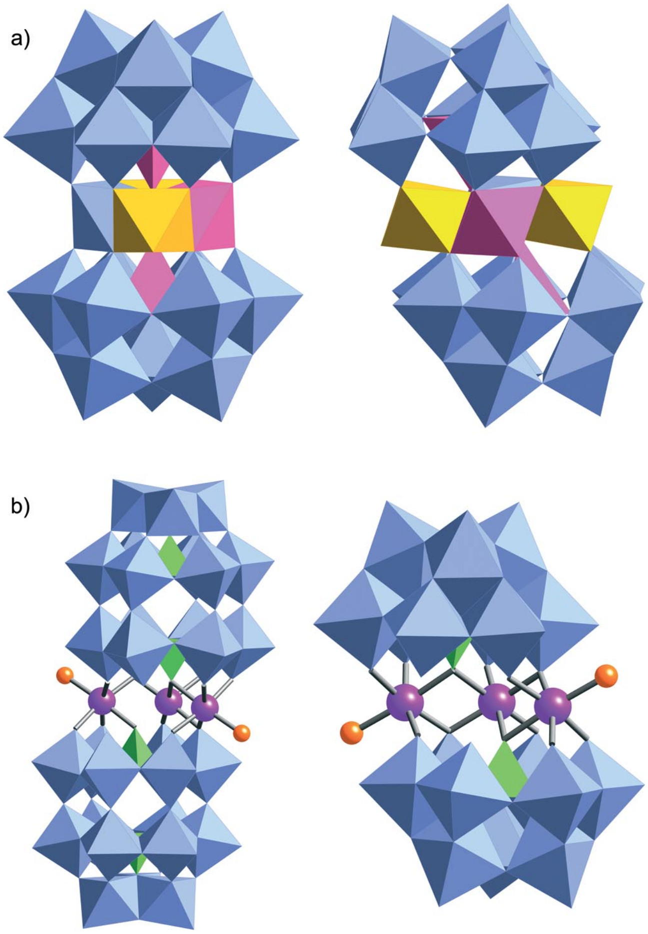


Figure 8. a) Two perpendicular views of $[WZnV_2O_2(ZnW_9O_{34})_2]^{12-}$.[91] Zn = pink, V = yellow. b) Representations of $[In_3Cl_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{11-}$ and $[In_3Cl_2(B\text{-}\alpha\text{-}P_2W_{15}O_{56})_2]^{17-}$.[93] In = purple, Cl = orange. In all these cases, chirality stems from the dissymetry in the sandwich layer, which reduces the overall symmetry to C_2.

Other chiral sandwich polyoxotungstates were prepared from trilacunary Keggin tungstophosphate and tungstosilicate of the general formula $[A\text{-}XW_9O_{34}]^{n-}$ with tin(II) sulfates.[98] The structures of $[Sn_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$ and $[Sn_3(A\text{-}\alpha\text{-}SiW_9O_{34})_2]^{14-}$ were fully resolved and that of $[Sn_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{14-}$ was partially resolved. These complexes are all formed by two $[A\text{-}XW_9O_{34}]^{n-}$ anions linked by three Sn^{II} cations. The chirality of the entire structure is due to a small twist between the $[XW_9O_{34}]^{n-}$anions, which lowers the symmetry from D_{3h} to D_3. In solution, both enantiomers interconvert rapidly, but their discrimination by formation of diastereomers with various chiral amino acids is possible by ^{183}W NMR spectroscopy.

Sandwich clusters derived from achiral monolacunary Keggin or Dawson polyanions of type $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ or $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and Hf^{4+}, Zr^{4+}, or Ln^{3+} (Ln = lanthanide)

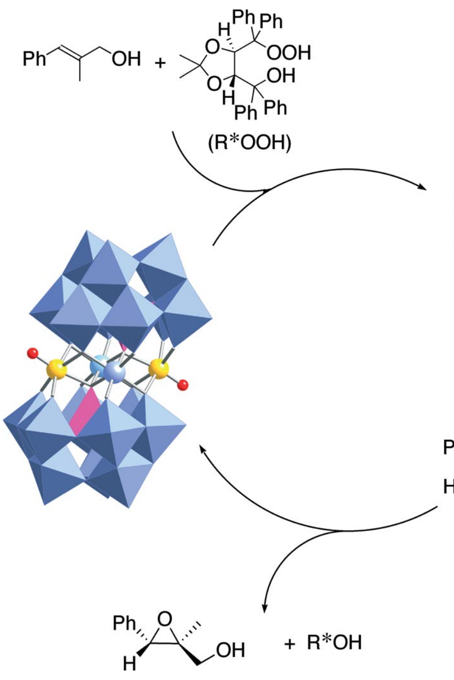


Figure 9. Catalytic cycle of alkene epoxidation with $[ZnW(VO)_2(ZnW_9O_{34})_2]^{12-}$ and TADDOL-derived hydroperoxide.[96]

metal ions were first prepared by Peacock and Weakley.[99] The resultant dimeric structures are chiral because of the distorted square antiprism geometry of the 8-coordinated cation sandwiched between the two lacunary anions. This can be evidenced by ^{183}W NMR spectroscopy[100,101] or the induced Cotton effect.[102] Crystallization usually occurred in a centrosymmetric space group, such as, for example, $Cs_{11}[Eu(\alpha\text{-}PW_{11}O_{39})_2]$[103] or $K_{17}[Lu(\alpha_2\text{-}P_2W_{17}O_{61})_2]$.[104] Similar structures are known for tungstosilicates and tungstogermanates.[101,105] Nomiya crystallized $[(C_2H_5)_2NH_2]_{10}[Hf(\alpha\text{-}PW_{11}O_{39})_2]$ as a racemate.[100] On the other hand, spontaneous resolution of $[(CH_3)_2NH_2]_{10}[Hf(\alpha\text{-}PW_{11}O_{39})_2]$ (Figure 10a) was reported by Hill.[106] It seems that the counterion and perfect control of the acidic pH during preparation and crystallization is crucial to separate the chiral polyanions.

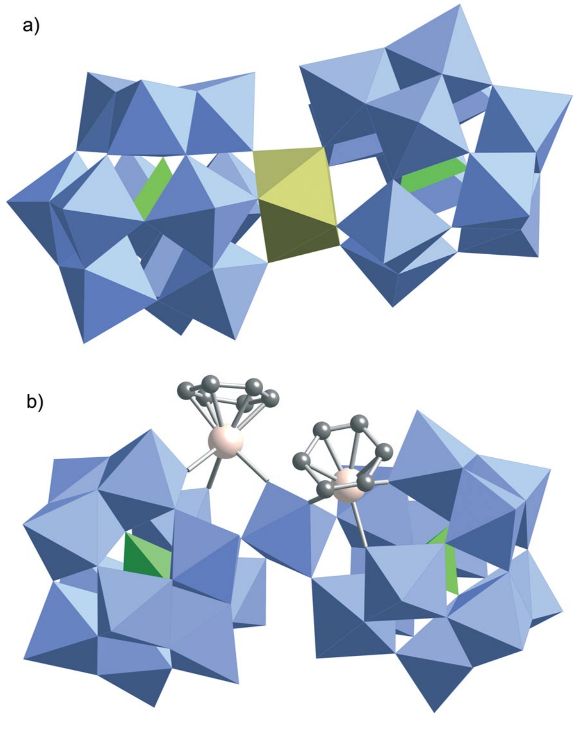


Figure 10. a) $[Hf(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ that was isolated in an enantiomerically pure manner.[106] b) $[\{\alpha\text{-}PW_{11}O_{39}RuAr\}_2WO_2]^{8-}$.[107] Two Ru–arene-substituted monolacunary Keggin ions are twisted around the central $\{WO_2\}^{2+}$ unit.

An original chiral assembly of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ was reported by Proust.[107] In $[\{\alpha\text{-}PW_{11}O_{39}RuAr\}_2WO_2]^{8-}$ (Ar = C_6H_6, $C_6H_5CH_3$) (Figure 10b), two organometallic Keggin derivatives are joined by a $\{WO_2\}^{2+}$ unit. The chirality stems from complexation of the ruthenium fragment to two inequivalent oxo atoms of the lacuna. As a result, the assembly has a twisted shape with idealized C_2 symmetry.

3.3. Chiral Monolacunary POMs

If in a monolacunary POM the vacancy is outside a mirror plane, the structure is chiral. The most prominent examples of this type are the monolacunary Keggin ion $[\beta_2\text{-}XW_{11}O_{39}]^{8-}$ (X = Si, Ge) and Dawson ion $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$. Tézé and Hervé comprehensively studied their preparations as racemates, studied their properties (acidity, redox behavior, etc.), and reported some reactions of undecatungstosilicate with other metals such as Cu^{II}, Fe^{II}, or V^{III}.[108–110] The corresponding undecatungstogermanate $[\beta_2\text{-}GeW_{11}O_{39}]^{8-}$ was characterized by its 11-line ^{183}W NMR spectrum.[43] This is consistent with a chiral lacunary species in which the vacancy is situated in the belt adjacent to the rotated triad as in structurally characterized $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ (Figure 11a).

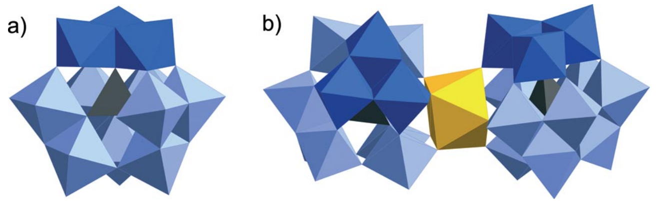


Figure 11. a) $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$. b) $[La(\beta_2\text{-}SiW_{11}O_{39})]^{13-}$. The rotated triad is a darker blue.[111]

Kortz recently prepared and characterized dimeric monolanthanide-containing silicotungstates $[Ln(\beta_2\text{-}SiW_{11}O_{39})]^{13-}$ with Ln^{3+} = La, Ce, Sm, Eu, Gd, Tb, Yb, Lu (Figure 11b).[111] Since each monolacunary Keggin structure $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ is chiral, the resulting dimeric polyanions could be either homochiral (enantiomeric pair) or heterochiral (meso). Interestingly, the size of the bridging lanthanide ion seems to be crucial. Indeed, for early (large) lanthanide ions, the homochiral structure is favored, whereas late lanthanide ions Yb^{3+} and Lu^{3+} strongly favor the meso dimeric complex. A NMR study in water reveals the rapid transformation of the chiral β_2 structures into the more stable $[Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{13-}$. The chiral structures are stabilized in 2 M aqueous NaCl at pH 5.5.

A manganese-substituted analogue crystallized as a homochiral trimer $[(\beta_2\text{-}SiMnW_{11}O_{38}OH)_3]^{15-}$.[112] In this case, partial spontaneous resolution was observed in the solid state.

The monolacunary Dawson derivative $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ is a particularly appealing chiral POM, since it allows versatile functionalization and varied potential applications. This feature has attracted renewed interest – including our own – over the last few years.

Among the two monolacunary structures derived from $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, the α_1 isomer is formally obtained by the removal of one W=O from the belt (Figure 12), whereas a cap W=O is removed in the α_2 isomer. Its first synthesis has been described by Contant.[113,114]

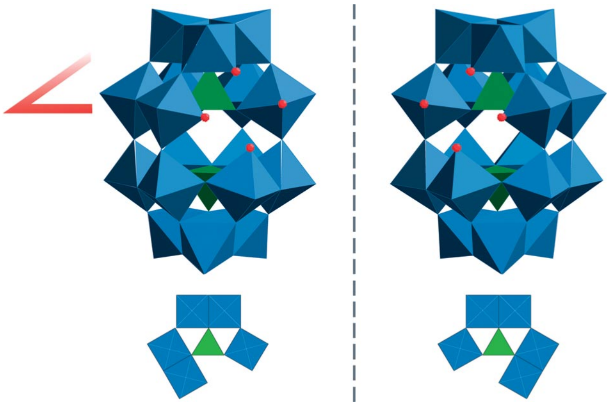


Figure 12. Chirality of monolacunary α_1-Dawson structure. Below each enantiomer a horizontal plane through the lacuna is drawn, as indicated in red.

The metal derivatives $[\alpha_1\text{-}M(H_2O)_xP_2W_{17}O_{61}]^{n-}$ (M = Ca^{2+}, VO^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, MoO^{4+}) were reported.[115,116] Francesconi examined the speciation of lanthanide complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ in depth to develop their luminescence properties. $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and lanthanide ions Ln^{3+} form predominantly 1:1 POM/Ln complexes, in particular, with later, smaller lanthanides.[117] This behavior was further confirmed in organic solution during a collaboration of our groups.[118] Complexes with a 2:1 stoichiometry are also known, and the multiple diastereomers occurring have been reviewed.[119]

We used this predominance of 1:1 complexes in organic solution to introduce POM-based Lewis acid catalysts.[15] Other Lewis acid cations can be used, such as Hf.[16] The main advantages offered by POMs are their easy recyclability and the complete chemoselectivity for imines over aldehydes in Mannich/Mukaiyama aldol competitions. The catalytic properties of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$-derived POMs illustrate the relevance of chiral POMs beyond the academic challenges associated with the understanding of this original stereochemistry. Resolution of their enantiomers would lead to a completely new type of chiral catalyst featuring an *inorganic* chiral ligand. The starting point for this endeavor was reported by Pope in 2001.[120] Complexation of $[\alpha_1\text{-}Ce(OH_2)_xP_2W_{17}O_{61}]^{7-}$ by L-proline in water induced splitting of the ^{31}P NMR signals, although the complexation equilibrium was fast on the NMR timescale. This experiment unambiguously proved the chirality of the α_1-Dawson family, and we examined this further for catalytically active $[\alpha_1\text{-}Yb(OH_2)_4P_2W_{17}O_{61}]^{7-}$.

The first step toward that end was the complete assignment of the ^{183}W NMR signals of the lacunary compound and the Yb complex, which was based on careful analysis of the J_{WW} coupling constants.[121] Further studies showed that complexation of optically pure amino acids or phosphonic acids with $[\alpha_1\text{-}Yb(OH_2)_4P_2W_{17}O_{61}]^{7-}$ occurred by reversible binding of these organic ligands to Yb.[122] This equilibrium had an influence on the whole POM structure, but some specific sites were more affected by the complexation and the chirality of the ligand. All these interactions were efficiently mapped by ^{31}P and ^{183}W NMR spectroscopy (Figure 13), which should help us to rationally design optimal organic ligands for the resolution of the chiral lanthanide complexes.

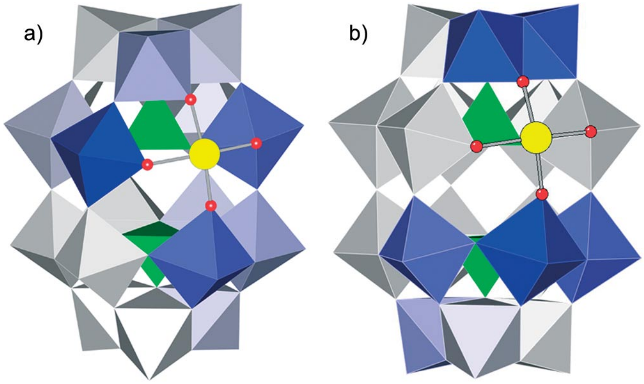


Figure 13. Mapping of chiral interactions: diastereomeric discrimination by ^{183}W NMR spectroscopy of W sites in $[\alpha_1\text{-}Yb(OH_2)_4\text{-}P_2W_{17}O_{61}]^{7-}$ on addition of a) L-serine (10 equiv.) and b) *N*-phosphonomethyl-L-proline (0.5 equiv.).[122] The chemical shift difference between the diasteromers is highlighted by the darkness of the blue color – the darker the color, the larger the chemical shift difference.

Yet, what is observed is an average signal reflecting the multiple equilibria in solution caused by rapid ligand exchange. We wished to obtain stable POM diastereomers. The introduction of organic hybrids in the organotin-substituted Dawson ion $[\alpha_1\text{-}P_2W_{17}O_{61}\{SnR\}]^{7-}$ (R = organic residue) was our key to address this problem. Organotin derivatization had been introduced by Pope for the Dawson $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and Keggin $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ compounds.[123,124] We extended this methodology to chiral $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and developed a series of tin-substituted polyoxotungstate platforms and methods to further modify them by using adapted organic methodologies.[125–127] In particular, we could insert chiral information (sugars, amino acids, peptides, etc.). It allowed us to prepare a stable pair of diastereomers arising from the stereogenic inorganic framework. Contrary to Yamase's,[128] Müller's,[129] and Kortz's[130] cases (see below), attachment of the amino acid was carried out through the N-terminus, not through the

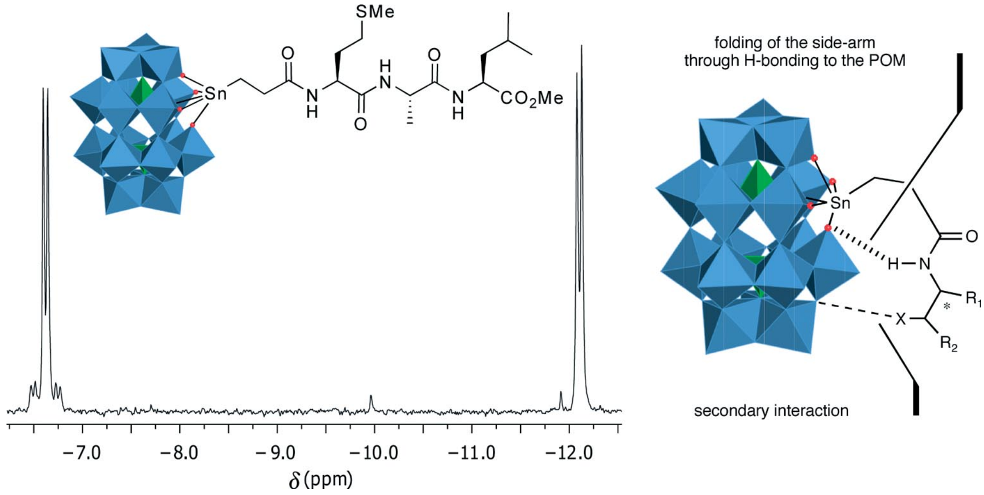


Figure 14. ^{31}P NMR spectrum of diastereomers $[\alpha_1\text{-}P_2W_{17}O_{61}\{SnR^*\}]^{7-}$, in which the inorganic part derives from a racemic POM and the organic side chain contains only L-amino acids.

carboxyl function.[125,131] Coupling of chiral amines to a ω-carboxyl function of our hybrid platform installed stereogenic elements on the side chain of the POM and led to splitting of the ^{1}H and ^{31}P NMR signals (Figure 14). This coupling could then be carried out without an activating agent owing to a regioselective intramolecular activation of the carboxyl group by an oxo ligand of the POM.[127] The chiral cyclized inorganic lactone can react easily with a more varied range of organic molecules, bearing diverse functionalizations, which could reward our efforts towards separation of enantiomers.

Differentiation of the diastereomers is highly dependent on the electrostatic interactions and hydrogen-bonding patterns that develop between the organic side-chain and surface oxygen atoms of the cluster. The understanding of that molecular recognition process is crucial for the effective resolution of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ enantiomers and their derivatives.

4. Chirality in Functionalized POMs

4.1. Chirality from Oxo Ligand Substitution

Functionalization of POMs, i.e. the replacement of oxo ligands by other groups, is also a way to create stereogenicity in the inorganic framework, even when the "naked" parent polyoxometallic structures are highly symmetric.

Lindqvist niobotungstate *cis*-$[Nb_2W_4O_{19}]^{4-}$ is a versatile platform for derivatization, which has been extensively explored by Klemperer. In particular, its methylation with dimethylsulfate delivered a mixture of five distinct diastereomeric *cis*-$[Nb_2W_4O_{18}(OMe)]^{3-}$ POMs, two of which are chiral (Figure 15).[132] Unfortunately, the chiral polyoxoanions were only minor components of the mixture and could not be isolated pure. Similar results were obtained for organometallic derivatives [Cp*Rh(*cis*-$[Nb_2W_4O_{19}])]^{2-}$,[133] $[(CO)_3Mn($*cis*-$[Nb_2W_4O_{19}])]^{3-}$, and $[(CO)_3Re($*cis*-$[Nb_2W_4O_{19}])]^{3-}$.[134]

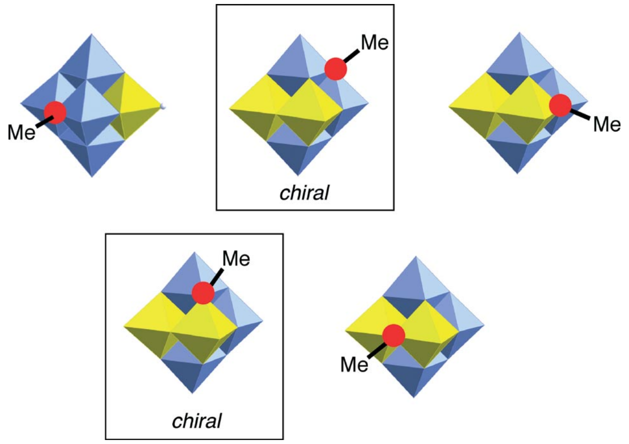


Figure 15. The diastereomers obtained by methylation of *cis*-$[Nb_2W_4O_{19}]^{4-}$ (Nb = yellow).[132]

4.2. Chirality Transfer from Organic Molecules

Zr- and Hf-containing POMs have been the focus of important studies over the last few years.[16,17,100,106,135–140] This has partly been fueled because these transition elements can lead to novel architectures. In particular, they can be used as cornerstones for the assembly of more complex structures. Kortz reacted $ZrCl_4$ with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ to obtain asymmetric dimeric $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ and trimeric $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ species with C_1 symmetry.[141] The Zr clusters link $\{\beta\text{-}SiW_{10}O_{37}\}$ units. Hill impressively used the assembly of $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ and $[\alpha\text{-}P_2W_{16}O_{59}]^{12-}$ with Zr^{4+} to rationally build two chiral POMs shown in Figure 16. The key feature of his strategy is the transferring of chirality of the small organic molecules to the inorganic structure. The versatile Zr^{4+} cations act as a chirality transmitter bridging the partners. With tartrates, the pseudo-dimer is configurationally stable in solution.[138] Its structure can be tweaked by proper change of the organic molecule and/or the POM.[139]

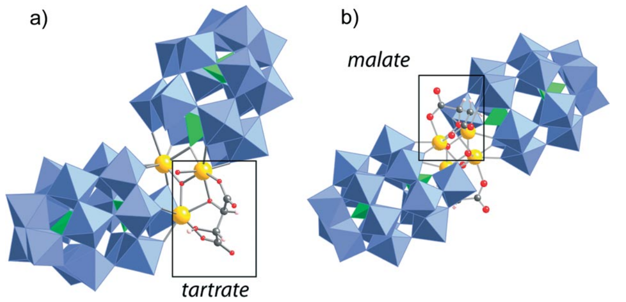


Figure 16. Chirality transfer from tartrate or malate via Zr^{4+} to the POM structures. a) $[\{\alpha\text{-}P_2W_{15}O_{55}(H_2O)\}Zr_3(\mu_3\text{-}O)(H_2O)(\text{L-tartH})\{\alpha\text{-}P_2W_{16}O_{59}\}]^{15-}$.[138] b) $[\{\alpha\text{-}P_2W_{16}O_{59}\}Zr_2(\mu_3\text{-}O)(\text{L-malate})]_2^{18-}$.[139]

Pope pioneered the incorporation of chelated transition metal ions $[Co(en)]^{3+}$ (en = ethylenediamine) into lacunary POMs.[142] This is an interesting achievement on the way to control the chirality of POM structures, because, conceptually, one might envisage to replace some octahedral Mo or W atoms by optically pure octahedral metal chelates. The same author was able to prepare an asymmetric bis-Keggin-derived POM $[K\subset\{Co(en)WO_4\}WO(H_2O)(PW_9O_{34})_2]^{7-}$. However, that POM is highly fluxional and thus rapidly loses all chirality. A second compound $[\{Co(en)(\mu\text{-}OH)_2\text{-}Co(en)\}\{PW_{10}O_{37}Co(en)\}_2]^{12-}$ contains the two enantiomers of the chiral $[PW_{10}O_{37}Co(en)]^{6-}$ unit.

4.3. Stereogenic Centers in the Attached Groups

Organic–inorganic hybrids offer great opportunities to install stereogenic elements on added side chains, since the broad diversity of organic structures can potentially be grafted to inorganic backbones and contribute to the overall chirality of the structures. We already discussed above the utility of diastereomer formation by covalently linking racemic $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ to optically pure organic groups.

Amino acids are powerful tools for introducing stereogenicity on otherwise achiral POMs. Yamase prepared γ-octamolybdates coordinating two lysine ligands, such as $Na_2[Mo_8O_{26}(\text{D-Lys})_2]\cdot 8H_2O$ and $Na_2[Mo_8O_{26}(\text{L-Lys})_2]\cdot 8H_2O$ (Figure 17a).[128] The compounds were designed to investigate the biological properties of molybdates, which were thought to involve protein–POM interactions. The hybrid octamolybdate anion is derived from the $\gamma\text{-}[Mo_8O_{26}]^{4-}$ structure, in which two terminal positions are occupied by the chiral lysine ligands bound through their carboxyl part, which results in optically active chiral hybrids, though the inorganic part is not a stereogenic element.

An outstanding new development in this direction was recently reported by Müller and Ermler, who elucidated the structure of the Mo/W storage protein of *A. Vinelandii*. They evidenced a large cavity with pockets that stabilize polynuclear tungsten oxide clusters through coordination and H bonds to the imidazole nitrogen atoms on the side chains of histidine residues. Assembly of the POMs is very likely directed by the protein, and it should be pointed out that the POMs are not stable outside of the pocket.[143]

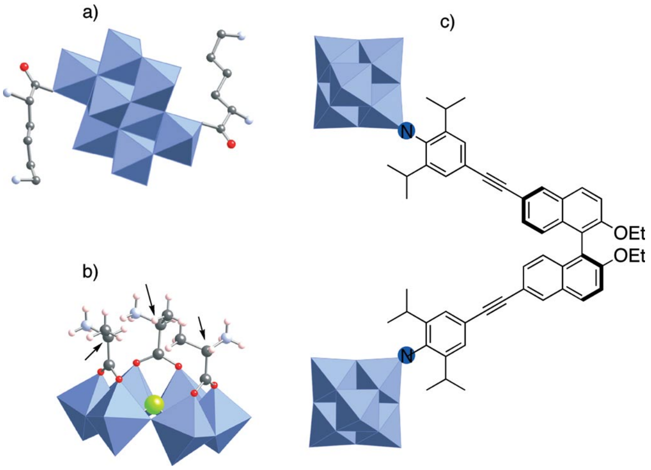


Figure 17. POMs with chiral organic side chains. a) $[Mo_8O_{26}(\text{L-Lys})_2]^{2-}$,[128] b) $[SeMo_6O_{21}(Ala)_3]^{n-}$,[130] c) binaphthyl-bridged imido-Lindqvist $[(Mo_6O_{18}N)_2R]^{4-}$.[146]

Kortz has introduced a broad family of heteropolymolybdates $[XMo_6O_{21}(AA)_3]^{n-}$ ($X = As^{III}, Sb^{III}, Bi^{III}, n = 3$; $X = Se^{IV}, Te^{IV}, n = 2$) functionalized by covalently bound amino acids (AA, Figure 17b).[130] Three of the hybrids were derived from chiral α-amino acids (alanine and lysine). The polyanions consist of the heteroatom surrounded by alternating edge-/corner-sharing MoO_6 octahedra. Two edge-sharing Mo units are further bound by the carboxyl group of the amino acids. Thus, three amino acids are included in the hybrid, all on the same side of the inorganic ring. However, the chiral information seems to be lost through ligand lability in water.

McCann has reported the introduction of *cinchona* alkaloids into a β-octamolybdate framework.[144] Attachment of the chiral organic molecule is expected through its pyridine nitrogen atom, although no crystal structure has been reported. The POMs were used as precatalysts for ROMP of norbornene.[145]

Giant POMs could also be functionalized with chiral elements. Müller reported the synthesis of a giant wheel-type species with cysteine ligands coordinated to the inner wall of the cluster, thus potentially providing entry into chiral cavities and pores.[129] Again, coordination to the molybdenum ions is achieved through the carboxyl end of the amino acid. Cysteine is crucial since its thiol side-chain acts as the reducing agent required for the assembly of the Mo_{154} polyanion.

Keana developed functionalized TEM labels for potential bioimaging applications from achiral Ti-substituted Dawson lacunary phosphotungstate $[\alpha_2\text{-}P_2W_{17}O_{61}TiCp]^{7-}$ (Cp = cyclopentadienyl).[147,148] The chiral molecules of interest to Keana were biotin and a derivatized ATP connected through the Cp ligand, even if the chirality of the objects was not the primary focus of the research. Our own work mirrors this approach, but relies on a tin anchor.

Following the same trend, Augustine used commercially available Keggin heteropolyoxometalates to anchor Rh^{I} complexes featuring chiral ligands.[149] A bond between the chiral system and the POM is claimed to explain the differences observed in the catalytic properties of heterogeneous mixtures. Yet, no evidence or structural characterization has been reported to date.

Peng used a C_2-symmetric binaphthyl as spacer to generate a rigid and chiral hybrid *bis*-Lindqvist iminomolybdate (Figure 17c).[146] The proximity of the two clusters grafted onto the organic backbone seems to modify the properties of the naphthyl nucleus.

5. Conclusion

All the examples reported above illustrate that chirality in polyoxometalate chemistry manifests itself in various forms: through chiral arrangements of POMs, chiral POM frameworks, or chiral organic side chains on POMs, and by combination of these. Some of the structures reported are unstable towards decomposition or racemization, but others have been proven to be stable so that the chirality can potentially be exploited in useful applications. One might be tempted to qualify the differences between two POM enantiomers as rather subtle, and thus question their utility. Indeed, these mostly nanometer-sized structures bear closed packed oxygen layers at the surface. However, the above-reported experiments of chiral differentiation prove that recognition of the POM chirality is possible at the molecular level. Furthermore, amplification of chirality is possible by assembling chiral POMs into supramolecular structures or networks. Therefore, applications for chiral POMs should be developed in those fields where intermolecular interactions play a key role. This should be the case in biology, because biomolecules are optically pure and present numerous functional groups that can interact with POMs in different ways. Another important field for further development should be catalysis. In this case, chiral catalytically active POMs should have an advantage when the substrate presents specific groups that recognize the chiral oxo surface. Work along these lines is ongoing in our laboratories.

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