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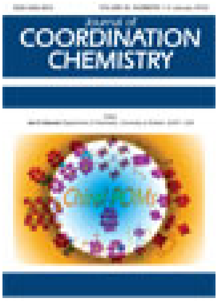

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Review: The chirality and bionic studies of polyoxometalates: the synthetic strategy and structural chemistry

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Published online: 16 Dec 2011.

To cite this article: Wei-Lin Chen, Hua-Qiao Tan & En-Bo Wang (2012) Review: The chirality and bionic studies of polyoxometalates: the synthetic strategy and structural chemistry, Journal of Coordination Chemistry, 65:1, 1-18, DOI: 10.1080/00958972.2011.645812

To link to this article: http://dx.doi.org/10.1080/00958972.2011.645812

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Journal of Coordination Chemistry
Vol. 65, No. 1, 10 January 2012, 1–18

Review: The chirality and bionic studies of polyoxometalates: the synthetic strategy and structural chemistry

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(*Received 11 October 2011; in final form 18 November 2011*)

Chiral polyoxometalates (POMs) have been a hot topic because of their potential applications in the fields of stereoselective catalysis, bio-simulation, sensing, nonlinear materials, and medicine. In view of the extensive work on chiral POMs, four parts are included in this review to give a broad overview on recent developments of chiral POMs: first, the synthetic strategy and molecular design of chiral POMs; second, research progress of chiral POMs including the structure chemistry, chiral resolution, and theoretical calculations; third, the bionic research of chiral POMs involving the studies of the chiral helix structures and bionic molecules. The final part shows the research outlook of chiral POMs including their applications in chiral catalysis and biomedical studies, which are the ultimate goals of chiral POMs investigations.

Keywords: Polyoxometalates; Chirality; Chiral resolution; Synthetic strategy; Bionic studies

1. Introduction

Chirality is basic in life processes. Chirality and bionics have been widely applied in the fields of asymmetric catalysis, chiral medicine, bio-simulation, sensing, and nonlinear materials [1]. Polyoxometalates (POMs), as important inorganic metal-oxide clusters, are composed of $\{MO_6\}$ octahedra and $\{MO_4\}$ tetrahedra, which are connected with shared sides, angles and planes [2]. POMs usually possess high symmetry and chemists are urgent to break the symmetry to get chiral POMs, which can be applied in catalysis and bio-medicine [3]. POMs chemistry has brought new development peak during 200 years of developments [4]. With rapid development of catalysis, medicine, and bio-inorganic chemistry, chirality and biomimetic chemistry have become a new growth point in inorganic chemistry [5].

The main synthesis difficulties of chiral POMs are focused on rapid racemization of many chiral POMs in solution, usually existing as racemic mixtures in solution and solid state [6, 7]. Chiral explanations of the racemization are very complex because of their solubility, instability, and structural similarity. In 1993, Zubieta reported the first chiral double helix POM structure $(Me_2NH_4)K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7] \cdot 4H_2O$

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2011.645812

(Me = Methyl) synthesized under hydrothermal conditions [8], which opened a new page for studies of chiral POMs. Although the studies in this field are ongoing, some important progress has been made [5–30].

In this review, research progress of chiral POMs is systematically summarized. The following are covered: the basic concepts of chirality, the synthetic strategy of chiral POMs, the structural chemistry, chiral separations, and theoretical calculations of chiral POMs. Furthermore, chiral helix structures and bionic molecules of chiral POMs and the research outlook of chirality in POMs chemistry are also introduced in the review. The ultimate goal of chiral POMs studies is their applications in chiral catalysis, biomedical studies, etc.

2. Synthetic strategy and molecular design of chiral POMs

As most polyoxoanions possess high symmetry, many chiral POMs in acidic solutions are unstable, easily partial hydrolyzed in solutions, and also, they are rapidly racemic to lose optical activities, existing as the racemic mixtures in the crystals; therefore, synthesis of chiral POMs is very difficult [8], seriously limiting the application of chiral POMs [1]. Hence, it is a challenge in materials chemistry and synthetic chemistry. Recently, with development of the synthesis theories and techniques of chirality, three synthetic strategies have been widely used in the synthesis of chiral POMs.

The first method is self-assembly of achiral molecules, which indicates that the absence, substitution, rotation, and distortion of some building units in polyoxoanions may result in asymmetry of POMs [8]. The second is reactions of chiral POMs and achiral ligands, if chiral POMs are modified by organic achiral ligands, whose chirality may transfer to the whole crystals to obtain some new chiral POMs [6a]. The third is the reactions of achiral POMs and chiral ligands, the chiral ligands are coordinated to the surface oxygen atoms of achiral POMs, which deliver their chirality to the whole crystals; this is the most used method since the chirality is transferred to the polyoxoanions with high symmetry, and also, the chiral ligands are connected to the inorganic POMs, which makes the polyoxoanions possess unusual characteristics [5, 6b].

3. Progress in chiral POMs

3.1. *The structural chemistry of chiral POMs*

Some classic chiral polyoxoanions have been reported, such as $[Co_2Mo_{10}O_{38}H_4]^{6-}$ [9a], $[Mn^{IV}Mo_9O_{32}]^{6-}$ [9b], $[Ni^{IV}Mo_9O_{32}]^{6-}$ [9b], α-$[P_2Mo_{18}O_{62}]^{6-}$ [9c, 9d], α_1-$[P_2W_{17}O_{61}]^{10-}$ [9e], β_2-$[SiW_{11}O_{39}]^{8-}$ [9f], β_2-$[GeW_{11}O_{39}]^{8-}$ [9g], $[PMo_9O_{31}(OH)_3]^{3-}$ [9c] (figure 1), α_1-$[P_2W_{17}O_{61}]^{10-}$ β_2-$[SiW_{11}O_{39}]^{8-}$, and [9e, 9f]. The chiral polyanions all exist as structural units, which limit their applications, so series of chiral POMs with higher multi-dimensions have been synthesized in order to expand their functionalities. Many chemists have made major contributions to the studies of chiral POMs [13–18].

The classic synthesis method to obtain chiral POMs is self-assembly of achiral substances, by which several chiral POMs are synthesized [10]. The chiral

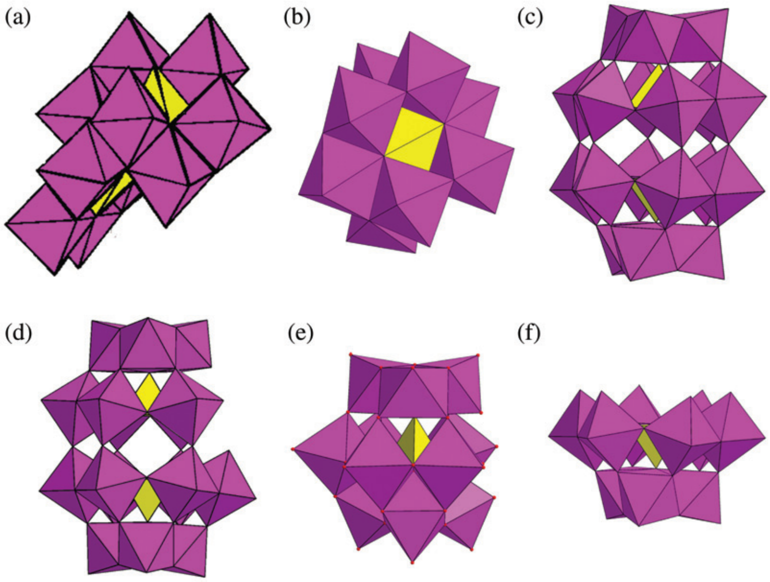

Figure 1. Structures of (a) $[Co_2Mo_{10}O_{38}H_4]^{6-}$, (b) $[Mn^{IV}Mo_9O_{32}]^{6-}$ (c) α-$[P_2Mo_{18}O_{62}]^{6-}$, (d) α_1-$[P_2W_{17}O_{61}]^{10-}$, (e) β_2-$[SiW_{11}O_{39}]^{8-}$, and (f) $[PMo_9O_{31}(OH)_3]^{3-}$.

polyoxotungstate $[P_6W_{18}O_{79}]^{20-}$ [10a], the chiral structures of D/L-$Na_{12}[WCu_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 48H_2O$, and D/L-$K_{12}[WZnV_2O_2(ZnW_9O_{34})_2]\cdot 30H_2O$ (L = Levorotatory; D = Dextrorotatory) [10b] were synthesized with this method. Such chirality may result from alternating bond lengths or the absence, substitution, rotation, and distortion of some building units. Pope and D'Amour indicated that chirality in α-$[P_2Mo_{18}O_{62}]^{6-}$ with D_3 symmetry was derived from alternations of different Mo–O bond lengths, eventually leading to distortion of the structure (figure 1c) [9c, 10c]. A series of chiral POMs have been prepared based on alternations of the bond lengths, such as the Preyssler polyoxoanions $[NaP_5W_{30}O_{110}]^{14-}$ [10d], $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$ [10e], $[H_6B_2W_{26}O_{90}]^{12-}$ [10f], and $[H_6B_3W_{39}O_{132}]^{15-}$ [10f]. In $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$, each $\{P_2W_{15}Ti\}$ fragment possesses a chiral distortion (figure 2a) [10e]. The polyoxoanions $[H_6B_2W_{26}O_{90}]^{12-}$ and $[H_6B_3W_{39}O_{132}]^{15-}$ are composed of dimers or trimers of $[H_3BW_{13}O_{46}]^{8-}$, the diprotonated terminal oxygen atoms of $\{W_2O_7\}$ in $[H_3BW_{13}O_{46}]^{8-}$ leading to alternating W–O bond lengths, resulting in chirality of the polyanions (figure 2b) [10f]. Thorimbert and Lacôte synthesized a series of rare-earth substituted α_1-$[P_2W_{17}O_{61}]^{10-}$ complexes, which show excellent catalytic activity and selectivity in Lewis acid catalyzed aldol reaction [10g]; they investigated the interactions between chiral $[\alpha_1\text{-}YbP_2W_{17}O_{61}]^{7-}$ and chiral amino acids with their derivatives characterized by ^{31}P and ^{183}W NMR (figure 2c) [10h], providing important basis for resolutions of the rare-earth-substituted chiral polyanions.

In 2001, Kortz reported the enantiomers of $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{15-}$, which consist of trimeric $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ linked by Mn^{2+} cations; the abundances of enantiomers are 60% and 40% (figure 3) [11a]. Three $[\beta_2\text{-}SiW_{11}O_{39}]^{8-}$ fragments coordinated to Mn^{2+} are not in the same plane, which leads the anion to possess three screw axes, giving the chiral cyclic trimer structure [11a]. Furthermore, $[Mo_{18}Sb^{V}_4Sb^{III}_2O_{73}(H_2O_2)]^{12-}$ with C_1 symmetry [11b], $[H_6Ce_2(H_2O)Cl(W_{15}O_{54})]^{7-}$ with C_3 symmetry [11c], and

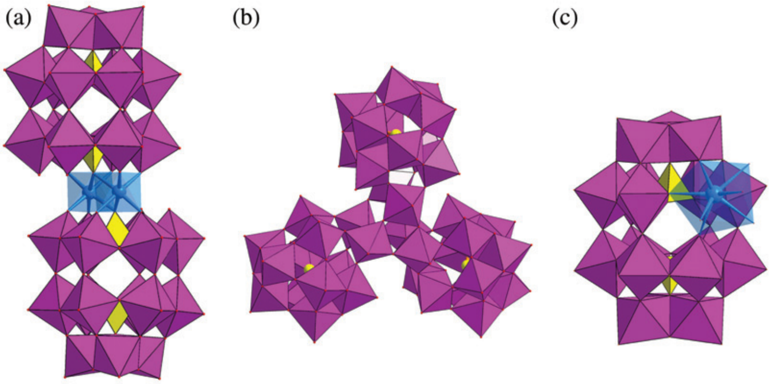

Figure 2. Structures of (a) $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$, (b) $[H_6B_3W_{39}O_{132}]^{15-}$, and (c) $[\alpha_1\text{-}YbP_2W_{17}O_{61}]^{7-}$.

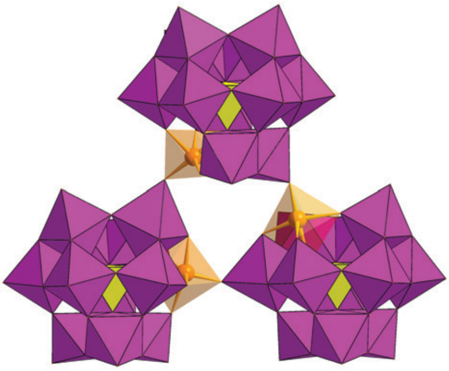

Figure 3. The structure of $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{15-}$.

$[Mo_{16}O_{42}(OH)_2(3\text{-}i PrC_3H_3N_2)_{12}] \cdot nH_2O$ (*i*Pr = isopropyl) with C_1 symmetry [11d] have also been reported.

Lone pair electrons of tin(II) may induce chirality of polyoxoanions [12]. In 1996, Pope synthesized three POM-based sandwich tin(II) derivatives, $[Sn_3^{II}(\alpha - PW_9O_{34})_2]^{12-}$, $[Sn_3^{II}(\alpha - SiW_9O_{34})_2]^{14-}$, and $[Sn_3^{II}(\beta - SiW_9O_{34})_2]^{14-}$, with lone-pair-induced chirality existing in the polyoxotungstate structures [12a]. Malacria developed an efficient and high-yield phase transfer method to prepare tin-substituted α_2-Wells–Dawson polyoxotungstates $[\alpha_2\text{-}P_2W_{17}O_{61}\{Sn(CH_2)_2CO_2H\}]^{7-}$, but the crystal products were not obtained [12b, 12c]. Kortz synthesized a tetrameric chiral tungstoarsenate(III), $[\{Sn(CH_3)_2(H_2O)\}_2\{Sn(CH_3)_2\}As_3(\alpha\text{-}AsW_9O_{33})_4]^{21-}$, which consists of four $\{B\text{-}\alpha\text{-}AsW_9O_{33}\}$ fragments functionalized by diorganotin groups and three As(III), resulting in a chiral polyoxoanion with C_1 symmetry [12d].

Recently, self-assembly reactions of polyoxoanions and organic ligands have also been used to synthesize some chiral POMs. Cronin synthesized a chiral polymolybdate-based framework $(C_{15}H_{28}N_2)_4(C_9H_6O_6)_1[H_{15}Mo_{12}NaO_{62}P_8] \cdot 10H_2O$, using di-protonated (–)-sparteine as the template *via* hydrogen-bonding and electrostatic interactions (figure 4) [13a]. In 2008, Yang reported three POMs, $\{[Ni_6(OH)_3(H_2O)_2(enMe)_3$

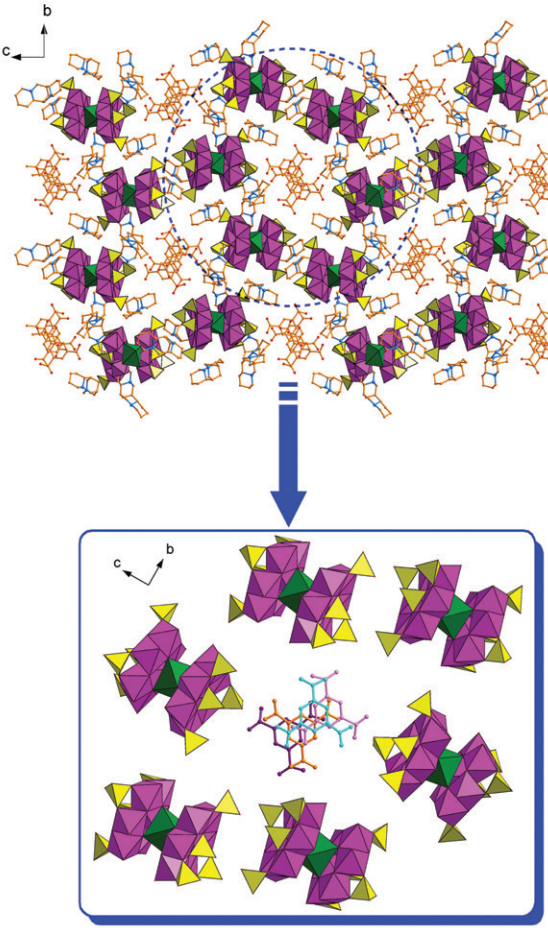

Figure 4. Chiral polymolybdate-based framework using di-protonated (−)-sparteine as the template.

$(PW_9O_{34})](1,3\text{-bdc})\}[Ni(enMe)_2]\cdot 4H_2O$, $\{[Ni_6(OH)_3\text{-}(H_2O)_2(en)_3(PW_9O_{34})](Htda)\}\cdot H_2O$, and $\{[Ni_6(OH)_3(H_2O)_5(PW_9O_{34})](1,2,4\text{-Hbtc})\}\cdot H_2enMe\cdot H_2O$ (enMe = 1,2-diaminopropane; 1,3-bdc = 1,3-benzene dicarboxylic acid; en = ethylenediamine; Htda = 2,5-thiophene dicarboxylic acid; 1,2,4-Hbtc = 1,2,4-benzene tricarboxylic acid), which are composed of $[PW_9O_{34}]^{9-}$ and Ni-amine or carboxylic acid complexes synthesized under hydrothermal conditions [13b]. The chirality is derived from the asymmetric units or the new helix structures composed of $\{Ni_6(PW_9O_{34})\}$ units stabilized by the diamine or carboxylic acid (figure 5) [13b].

Su synthesized two enantiomers L/D-$[Cu(bbi)_2V_{10}O_{26}][Cu(bbi)]_2\cdot H_2O$ (bbi = 1, 1′-(1,4-butanediyl)bisimidazole) in 2008, constructed from Cu-bbi wave layers pillared by $[V_{10}O_{26}]^{4-}$ (figure 6) [13c]. The chirality of the Cu-bbi chains is transferred to the whole compound. Wang reported another two enantiomeric chiral 3-D frameworks $[Ni_2(H_2O)(HL_4)][HP_2Mo_5O_{23}]\cdot 7H_2O$ (L = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene), which are chiral self-threading frameworks based on $[HP_2Mo_5O_{23}]^{5-}$ including the unprecedented tri-flexure helix; figure 7 shows its structural unit [13d]. Recently, chiral POM-based enantiomers D/L-$[Cu(en)_2]_3[PW_{11}NaO_{39}]\cdot 7H_2O$ (en = ethylenediamine)

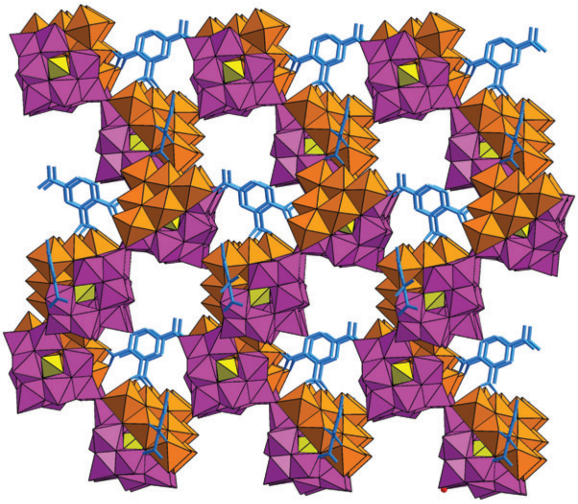

Figure 5. The structure of $\{[Ni_6(OH)_3(H_2O)_5(PW_9O_{34})](1,2,4\text{-Hbtc})\}\cdot H_2enMe\cdot H_2$.

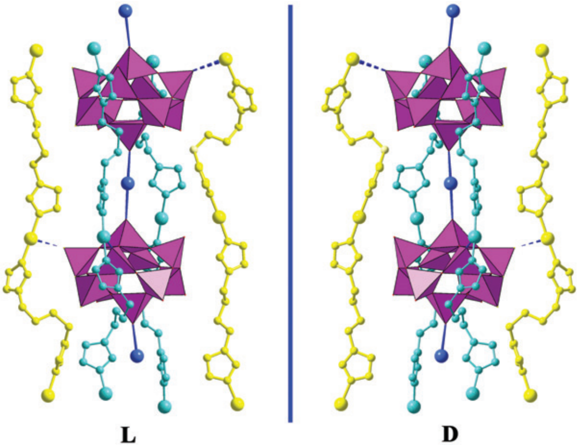

Figure 6. Enantiomers of chiral Cu-bbi chains and $[V_{10}O_{26}]^{4-}$.

were synthesized by Luo, which were linked by $[Cu(en)_2]^{2+}$ fragments and monolacunary POMs obtained by spontaneous resolution. The $[Cu(en)_2]^{2+}$ is anchored to opposite sides of the POM chains, resulting in the final chiral chain-like architecture (figure 8) [13e]. Wang also reported two chiral POM chains $[Cu(en)_2][Cu(en)_2(H_2O)]_2[SiW_{11}CuO_{39}]\cdot 5H_2O$, constructed from the achiral $[SiW_{11}CuO_{39}]^{6-}$ and $[Cu(en)_2(H_2O)_n]^{2+}$ ($n = 0$ or 1) fragments. The structural chirality is induced by the asymmetric $[Cu(en)_2(H_2O)_n]^{2+}$ units [13f]. Additionally, Sokolov synthesized stable chiral POMs $(NH_2Me_2)_8[M(L\text{-}OOCCH(OH)CH_2COO)P_2W_{17}O_{61}]\cdot 7.9H_2O$ ($M = Zr$ or Hf) under hydrothermal conditions, in which L-malic acid replaced water in $[(H_2O)_3M(P_2W_{17}O_{61})]^{6-}$ to obtain the chirality [13g].

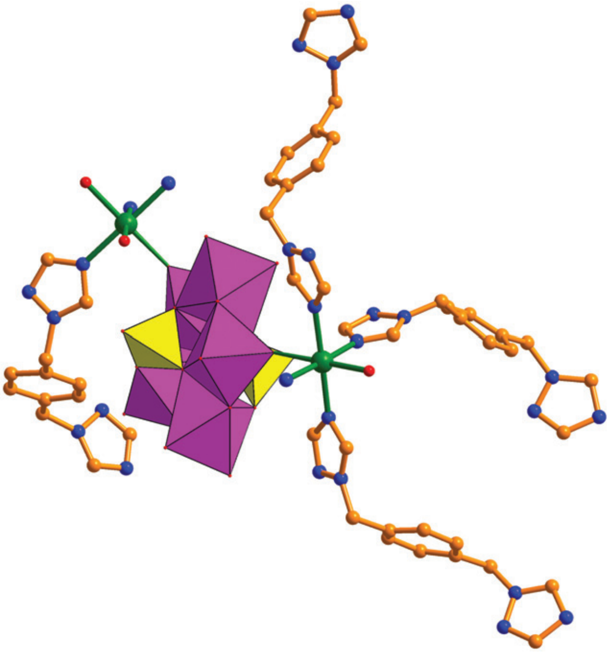

Figure 7. The structural unit of L-$[Ni_2(H_2O)(HL_4)][HP_2Mo_5O_{23}]$.

Series of amine-modified chiral POMs have been reported. Wei synthesized pure chiral POM nanorods $[Mo_6O_{18}NC(OCH_2)_3MMo_6O_{18}(OCH_2)_3CNMo_6O_{18}]^{7-}$ ($M = Mn^{III}$ or Fe^{III}), which crystallized in chiral space groups $P3_121$ and $P3_221$, respectively [14a]. The Anderson-type polyoxoanion and two Lindqvist-type hexamolybdates are bridged by two diimido ligands to form a chiral triad (figure 9) [14a]. Furthermore, they reported POM-based chiral macrocycles $[N(n\text{-}Bu)_4]_2[Mo_6O_{17}(2,2'\text{-}NC_6H_4OC_6H_{12}OC_6H_4N)]$ (n-Bu = n-butyl), constructed from the achiral Lindqvist hexamolybdates and bisarylamines bearing o-alkoxy chain substituents. It is interesting that the macrocyclic anions are packed to produce the supramolecular chiral nanochannels (figure 10) [14b]. Klemperer explored five diastereomeric mixtures of *cis*-$[Nb_2W_4O_{18}(OMe)]^{3-}$, in which only two polyanions were chiral, but they were not separated [14c], and Peng obtained the chiral binaphthyl-bridged polyanion $[(Mo_6O_{18}N)_2R]^{4-}$ (R = binaphthyl) [14d].

In 2005, Hill reported the enantiomerically pure polyoxotungstates $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]\text{-}Zr_3(\mu_3\text{-}O)(H_2O)(L\text{-tartH})[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$ and $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]\text{-}Zr_3(\mu_3\text{-}O)(H_2O)(D\text{-tartH})[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$ (tartH = tartaric acid) prepared by reactions of achiral polyoxoanions $\alpha\text{-}[P_2W_{15}O_{56}]^{12-}$, chiral ligands L/D-tartrates and Zr^{4+}, which crystallized in the chiral orthorhombic space group $P2_12_12_1$ [5a]. They used the same method to obtain the pure enantiomers $[(\alpha - P_2W_{16}O_{59})Zr_2(\mu_3 - O)(L/D - mal)]_2^{18-}$ (mal = malate), which consist of Zr-substituted polytungstates coordinated to two malates of the same handedness [15]. The chirality of the tartrates and malates has been transferred to the whole polyoxoanion (figure 11).

In 2006, Wang obtained two new enantiomerically pure 3-D POM-based frameworks with helical channels $KH_2[(L\text{-}C_5H_8NO_2)(H_2O)Cu_3][BW_{12}O_{40}] \cdot 5H_2O$ crystallized in $P4_32_12$ and $KH_2[(D\text{-}C_5H_8NO_2)(H_2O)Cu_3][BW_{12}O_{40}] \cdot 5H_2O$ crystallized in $P4_32_12$ [5b],

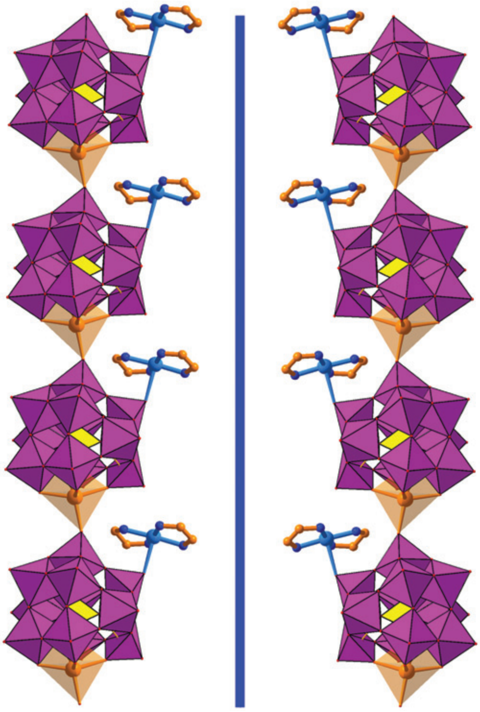

Figure 8. The chiral chain-like architecture of D/L-$[Cu(en)_2]_3[PW_{11}NaO_{39}] \cdot 7H_2O$.

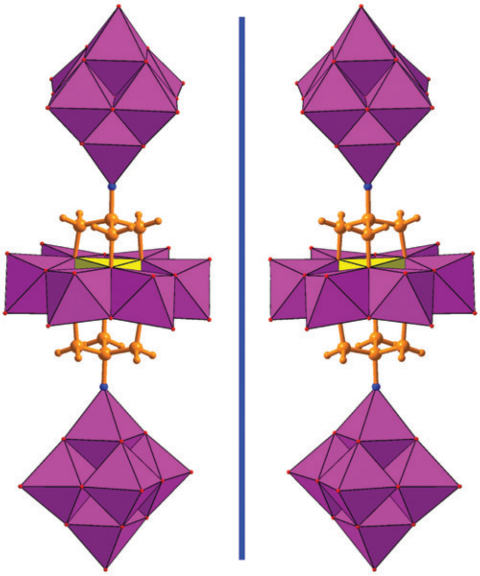

Figure 9. The structure of $[Mo_6O_{18}NC(OCH_2)_3MMo_6O_{18}(OCH_2)_3CNMo_6O_{18}]^{7-}$ (M = Mn^{III} or Fe^{III}).

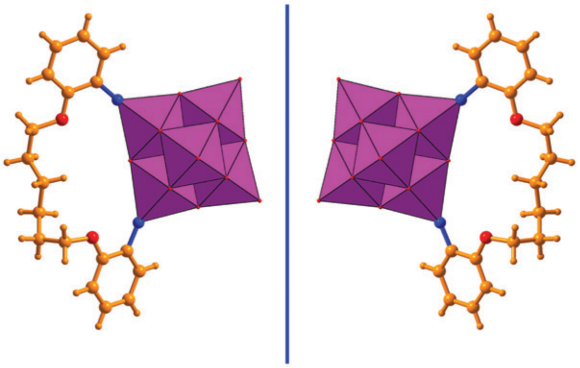

Figure 10. The structure of $N(n\text{-}Bu)_4]_2[Mo_6O_{17}(2,2'\text{-}NC_6H_4OC_6H_{12}OC_6H_4N)]$.

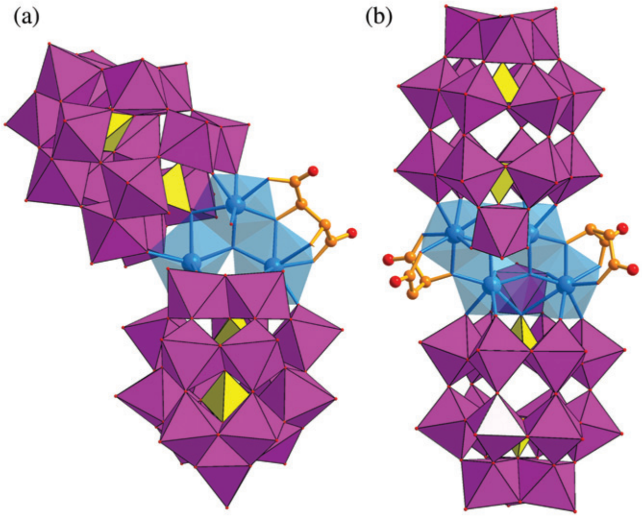

Figure 11. (a) Structure of $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]Zr_3(\mu_3\text{-}O)(H_2O)(L\text{-}tartH)[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$; (b) structure of $[(\alpha\text{-}P_2W_{16}O_{59})Zr_2(\mu_3\text{-}O)(L\text{-}mal)]_2^{18-}$.

composed of $[BW_{12}O_{40}]^{5-}$ units and Cu-proline complexes to form 3-D chiral frameworks (figure 12). The chirality of the carbons in proline has been delivered to the whole compound. This work opens the door to chiral POM-based structures that may be useful in asymmetric catalysis resolution and even medicine [16].

Yamase reported chiral γ-type octamolybdates coordinated by chiral lysines $Na_2[Mo_8O_{26}(D/L\text{-}lysH_2)_2]\cdot 8H_2O$ ($lysH_2 = $lysine), crystallized in the chiral space group $P1$ (figure 13) [17a]. In 2001, the stereoselective interaction of amino acids with the enantiomers of $[Ce^{III}(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_4]^{7-}$ was reported by Pope [17b]. The polyoxoanions are composed of two $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_4]^{7-}$ units; when the chiral amino acid L-proline was added into aqueous solutions of $[Ce_2(H_2O)_8(P_2W_{17}O_{61})_2]^{14-}$, formation of chiral POMs results in splitting of the ^{31}P NMR signals, but the crystalline products were not obtained [17b]. Interaction of large Ce cations and chiral L-proline

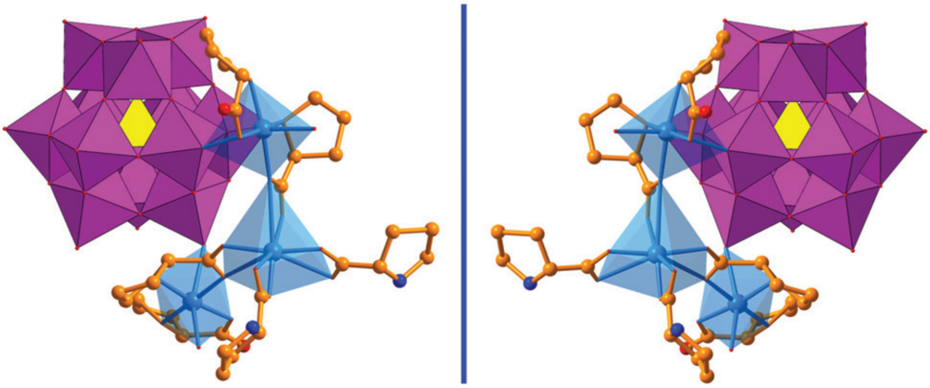

Figure 12. The structural unit of $KH_2[(L/D\text{-}C_5H_8NO_2)(H_2O)Cu_3][BW_{12}O_{40}] \cdot 5H_2O$.

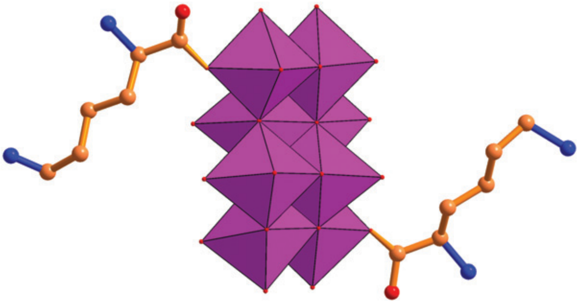

Figure 13. The structure of $[Mo_8O_{26}(D/L\text{-}lysH_2)_2]^{2-}$.

leads to distortion of two $[Ce(\alpha_1\text{-}P_2W_{17}O_{61})(H_2O)_4]^{7-}$ units to lose its symmetry centers, resulting in chirality of the whole polyoxoanion. Kortz synthesized a series of similar chiral POMs consisting of octamolybdates coordinated by L-alanine or L-lysine, $[Se^{IV}Mo_6O_{21}(L\text{-}O_2CCHCH_3NH_3)_3]^{2-}$ (figure 14), $[Sb^{III}Mo_6O_{21}(L\text{-}O_2CCHCH_3NH_3)_3]^{3-}$ and $[Bi^{III}Mo_6O_{21}\{L\text{-}O_2CCH[(CH_2)_4NH_2]NH_3\}_3]^{3-}$. The chirality of the chiral amino acids in these compounds is transferred to the polyoxoanions to break their high asymmetry. The crystal crystallized in $P2_12_12_1$ [17c].

Furthermore, Wang reported the first pure inorganic 3-D chiral interpenetrating structures $L/D\text{-}Zn_3[MnMo_9O_{32}] \cdot 9H_2O$ (figure 15) [6a], which were synthesized by reactions of racemic $[MnMo_9O_{32}]^{6-}$ and $ZnCl_2$ in solution. With crystal differences of the left- and right-hand compounds, the enantiomers were artificially separated. The polyoxoanions are constructed from $[MnMo_9O_{32}]^{6-}$ units and Zn^{2+} to be a 3-D framework, finally giving a 2-fold interpenetrating net. The chirality of the compounds are due to chirality of $[MnMo_9O_{32}]^{6-}$. It may offer a new synthetic route for the chiral frameworks based on chiral POMs [6a].

In 2009, Wang synthesized two enantiomerically pure chiral ferric aggregates $K_2Na_{18}[Fe_{28}(\mu_3\text{-}O)_8(L\text{-}(-)\text{-}tart)_{16}(CH_3COO)_{24}] \cdot 29H_2O$ and $K_2Na_{18}[Fe_{28}(\mu_3\text{-}O)_8(D\text{-}(+)\text{-}tart)_{16}(CH_3COO)_{24}] \cdot 29H_2O$ (tart = tartaric acid) crystallized in the orthorhombic chiral space group $I222$, composed of four $\{Fe_7\}$ units each linked by five chiral tartrates, also coordinating to four acetates to form the $\{Fe_{28}\}$ clusters (figure 16) [18a].

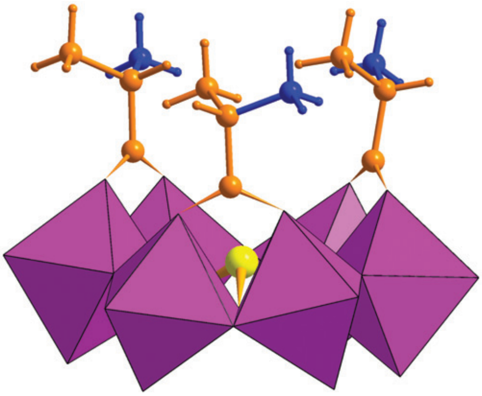

Figure 14. The structure of $[Se^{IV}Mo_6O_{21}(L\text{-}O_2CCHCH_3NH_3)_3]^{2-}$.

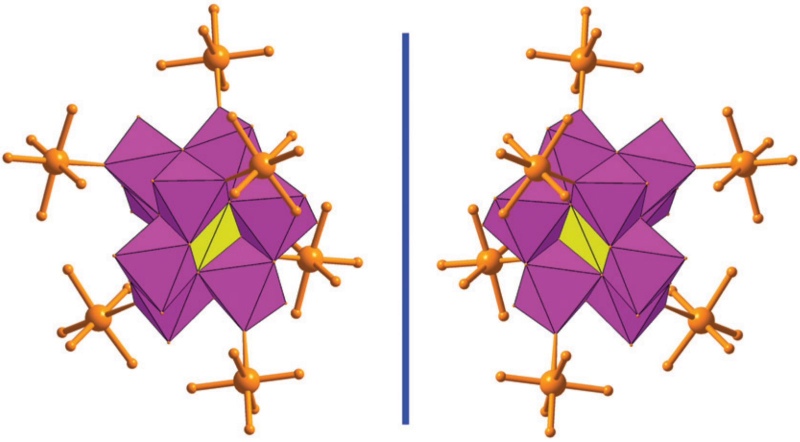

Figure 15. The structural unit of L/D-$Zn_3[MnMo_9O_{32}] \cdot 9H_2O$.

Other protein-sized chiral Fe_{168} cages $Na_{96}[Na_{24}Fe_{168}(L\text{-tart})_{96}(\mu_3\text{-}O)_{48}(HCOO)_{144}] \cdot 310H_2O$ and $Na_{96}[Na_{24}Fe_{168}(D\text{-tart})_{96}(\mu_3\text{-}O)_{48}(HCOO)_{144}] \cdot 310H_2O$ (tart = tartaric acid) have been synthesized, which present NbO-type topology. The $\{Fe_{28}\}$ wheels are connected by $\{Na_4\}$ linkers *via* eight carboxyl ligands to a 3-D open framework [18b]; the chirality of the tartrate is delivered to the clusters.

3.2. *Resolution of chiral POMs*

Chiral compounds mostly exist as racemic mixtures in solutions. In the 1960s, a chiral drug named "thalidomide" was a sedative for pregnant women, but when it came into the market, it led to 12,000 babies with physical defects, because one of its enantiomers possesses teratogenicity, so only one enantiomer is needed. Thus it is extremely important to independently obtain the different enantiomers of chiral molecules [1]. There are two main methods for resolution of chiral POMs, including spontaneous

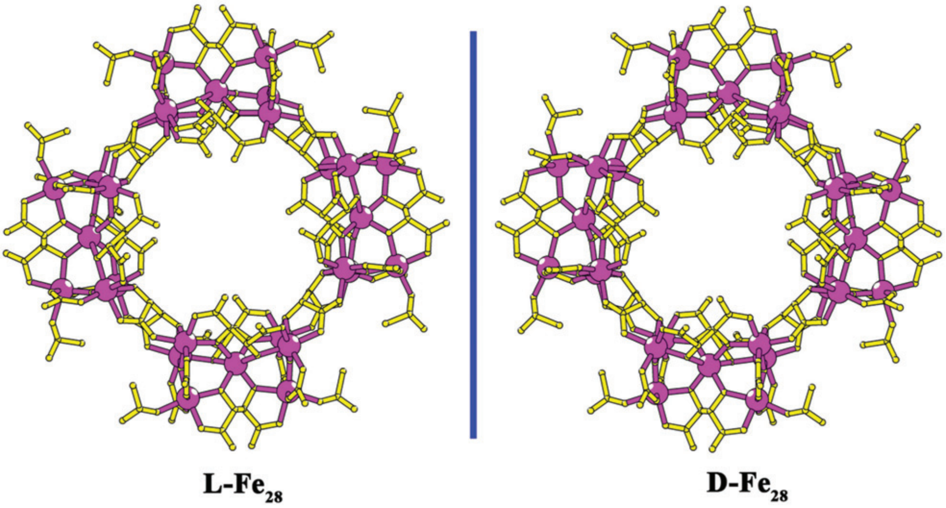

Figure 16. The enantiomers of chiral $\{Fe_{28}\}$ clusters.

resolution and the chiral ligand induced resolution [19]. It is still a challenge to separate the racemic mixtures using new methods including enzyme splitting, high-performance liquid chromatography, and the capillary electrophoresis split method.

Spontaneous resolution is that chiral polyoxoanions are naturally separated in solution, and then the racemic mixtures are separated artificially. In 2007, Hill synthesized the chiral sandwiching polyanion $[Hf(PW_{11}O_{39})_2]^{10-}$, which crystallized in the chiral space group $P2_12_12$; crystal products have been obtained by spontaneous resolution in the absence of any chiral source [19a]. Su reported the 3-D chiral POMs $[Ni_2(bbi)_2(H_2O)_4V_4O_{12}] \cdot 2H_2O$ and $[Co(bbi)(H_2O)V_2O_6]$ (bbi = 1,1′-(1,4-butanediyl)bisimidazole), which were obtained by spontaneous resolution in the absence of any chiral sources [19b]. Two enantiomerically chiral POMs $[(CH_3)_2NH_2]_{10}[Zr(PW_{11}O_{39})_2] \cdot 10H_2O$ were reported by Liu by means of spontaneous resolution without a chiral auxiliary [19c]. In 2009, Wang found that the chiral polyoxoanion $[MnMo_9O_{32}]^{6-}$ realized from the racemic compounds to spontaneous resolution by changing the linkers from imidazole molecules and Na^+ to Mn^{2+} in the structures. The enantiomers $L/D\text{-}NH_4Mn_{2.5}[MnMo_9O_{32}] \cdot 11H_2O$ were obtained by spontaneous resolution [19d]. Meanwhile, Wang also realized the spontaneous resolution of new diphosphonate-functionalized POMs $L/D\text{-}(NH_4)_6\{Mo_2^VO_4[(Mo_2^{VI}O_6)NH_3CH_2CH_2CH_2C(O)(PO_3)_2]_2\} \cdot 10H_2O$ (figure 17) [19e].

On the other hand, Shimura successfully separated $(NH_4)_6[Co_2Mo_{10}O_{34}(OH)_4] \cdot 7H_2O$ with chiral ligand $(+)\text{-}[Co(en)_3]Br_3 \cdot H_2O$ (en = ethylenediamine) in 1970 [20a] and Miwa used L-sulfate dimethyl strychnine to split the chiral polyanion $[MnMo_9O_{32}]^{6-}$ in 1983 [20b]. $[S_2Mo_5O_{23}]^{4-}$ was separated with arabinose by Das [20c]. Recently, Wang obtained the enantiomerically pure compound, $H_3(L/D\text{-}HC_6H_9N_3O_2)_3[P_2Mo_{18}O_{62}] \cdot 20H_2O$, which realized the resolution of the Dawson-type racemic polyoxoanions $[P_2Mo_{18}O_{62}]^{6-}$ with chiral histidine [20d]. In addition, Lacôte reported chiral recognition of α_1-substituted Dawson polyoxotungstate by peptides [20e].

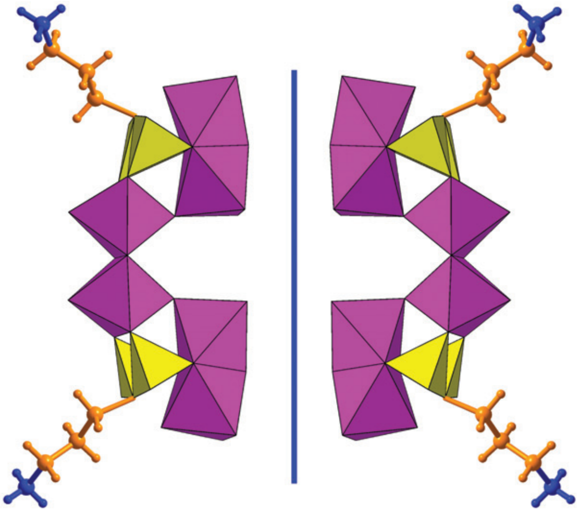

Figure 17. Structures of L/D-$(NH_4)_6\{Mo^V_2O_4[(Mo^{VI}_2O_6)NH_3CH_2CH_2CH_2C(O)(PO_3)_2]_2\} \cdot 10H_2O$.

3.3. *Theoretical calculations of chiral POMs*

Calculations of chiral POMs may resolve many questions such as the generation of chirality, and the transfer direction of chirality, which may be the theoretical basis for synthesis of chiral POMs. Theoretical studies of chiral POMs are still a challenge. Recently, Poblet discovered that alternating short and long bond length distortions exist in POMs. Four POM structural types, $[M_6O_{19}]^{q-}$ ($M = Mo^{VI}$ or W^{VI}, $q = 2$), α-$[XM_{12}O_{40}]^{q-}$ ($X = Si^{IV}$ or Ge^{IV}, $M = Mo^{VI}$ or W^{VI}, $q = 4$; $X = P^V$ or As^V, $M = Mo^{VI}$ or W^{VI}, $q = 3$; $X = S^{VI}$ or Se^{VI}, $M = Mo^{VI}$ or W^{VI}, $q = 2$), α-$[X_2M_{18}O_{62}]^{q-}$ ($X = Si^{IV}$ or Ge^{IV}, $M = Mo^{VI}$ or W^{VI}, $q = 8$; $X = P^V$ or As^V, $M = Mo^{VI}$ or W^{VI}, $q = 6$; $X = S^{VI}$ or Se^{VI}, $M = Mo^{VI}$ or W^{VI}, $q = 4$), and $[(Na)P_5W_{30}O_{110}]^{14-}$, are investigated by DFT methods; the chirality is induced by alternating bond lengths, finally resulting in the distortion [21].

4. The bionic investigations of POMs

4.1. *The studies of chiral helix structures*

Helices possess the chirality since the left- and right-hand helices cannot be overlapped. Their structures are similar to polysaccharides, nucleic acids, and some peptide compounds [22c], providing an impetus for chemists to simulate the relevant biological structures with helices, and develop their applications in asymmetric catalysis, nonlinear optics, and biomimetic chemistry. POMs with helices enrich structural chemistry and bionic research of chiral POMs [5b, 7, 22].

Polyoxovanadates usually are easier to form helical structures because of various coordination modes of the vanadium cations. The inorganic helical chains of polyoxovanadates $M(VO_2)_2(HPO_4)_4$(4,4′-bipy) (M = Ni, Co) (4,4′-bipy = 4,4′-bipyridine) were synthesized by Feng [23a]. Furthermore, Yu reported polyoxovanadates with helical chains $[Co(en)_3][V_3O_9] \cdot H_2O$ (en = ethylenediamine) using the chiral $[Co(en)_3]^{3+}$ cations as the templates [23b].

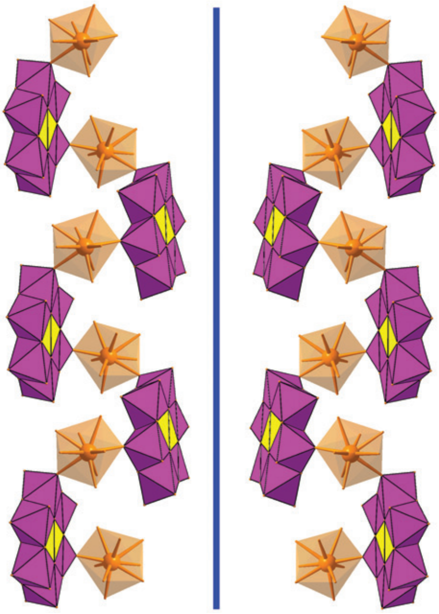

Figure 18. Chains of $(C_6H_5NO_2)[(H_2O)_4(C_6H_5NO_2)Ce(CrMo_6H_6O_{24})]\cdot 4H_2O$.

Lu reported a double-helix compound with 3-D microporous structure, $[CuMo_2O_8(4,4'\text{-bpy})]_n\cdot 3nH_2O$, which consists of left- and right-hand helices forming the double helix $[CuMo_2O_8\text{-N}]_n$ [24a]. They then synthesized a series of chiral double-helix structures $\{A[Mo_2^{VI}\text{-}O_4Ln^{III}(H_2O)_6(C_4H_2O_6)_2]\cdot 4H_2O\}_n$ (Ln = Sm, Eu, Gd, Ho, Yb, Y; $C_4H_2O_6$ = L- or D-tartaric acid; A = NH_4^+ or H_3O^+), which are composed of two chiral helical chains linked by eight-coordinate rare-earth ions [24b]. Xu synthesized the 1-D helical chains $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]_2[Mo_9O_{30}]$ constructed from $[Mo_9O_{30}]^{6-}$ units, the first helical chain structure composed of only molybdenum-oxide building blocks [25]. In 2005, Wang reported a series of POM-based helical structures $(C_6NO_2H_5)[(H_2O)_4(C_6NO_2H_5)Ln(CrMo_6H_6O_{24})]\cdot 4H_2O$ (Ln = Ce, Pr, La, Nd), which consists of Anderson-type polyoxoanions and rare earth-isonicotinic acid complexes (figure 18); adjacent chains are connected with isonicotinic molecules to form a 2-D chiral layer structure [26a]. In 2008, Wang reported a pair of enantiomers $(C_4NH_7O_4)[Na_2(L/D\text{-}C_4H_8N_2O_3)_2(H_2O)_9Zn]_2[CrMo_6H_6O_{24}]_2\cdot 7H_2O$, which are composed of $[CrMo_6H_6O_{24}]^{3-}$ and chiral Zn-asparagine complexes linked by Na^+ to form 1-D chains [26b]. Luo also obtained 1-D helical chains based on $[Ce(H_2O)(DMF)_6]^{4+}$ fragments and $[W_{10}O_{32}]^{4-}$ anions [27a]. Another 1-D helical chain $[H_2en]_2[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]\cdot 4H_2O$ was reported by Xu, which are constructed from $[Mo_5P_2O_{23}]^{n-}$ building blocks and $\{Cu(en)\}^{2+}$ [27b]. Das obtained 1-D helical chains $[Cu(2,2'\text{-bipy})(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$ (2,2′-bipy = 2,2′-bipyridine) consisting of $[Al(OH)_6Mo_6O_{18}]^{3-}$ polyanions and $\{Cu(2,2'\text{-bipy})(H_2O)_2\}^{2+}$ fragments [27c].

4.2. *The bionic studies of simulated biological molecules*

Synthesis of the simulated biological molecules is useful for design and synthesis of new nanomaterials to apply in materials science and physics [28]. Müller synthesized a series of high-nuclear clusters, from $Mo_{57}M_6$ [28a], $Mo_{75}V_{20}$ [28b], Mo_{148} [28b], Mo_{132} [28c], Mo_{154} [28d], Mo_{176} [28e, 28f], Mo_{248} [28g], to the largest aggregates Mo_{368} [28h], which have been applied in bionic studies [28]; the most striking cluster is $\{(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(CH_3COO)\}_{30}$ ($\equiv\{Mo_{132}\}$) [28c]. Müller *et al.* have concluded six unique advantages of the large cage [28b, 28i]; first, $\{Mo_{132}\}$ is a hollow cluster with tunnels and the cluster is independent and unconnected, different from previous 3-D open frameworks with tunnels; second, the near-spherical cluster is composed of 20 $\{Mo_9O_9\}$ circular tunnels interconnected with the cage cavity; third, the $\{Mo_9O_9\}$ ring tunnel windows of the cluster possess the function of ion recognition, similar to crown ether molecules. Opening or closing of the window depends on the passing in or out of the transition metal cations; fourth, the cage-type compound can make water and small metal ions freely enter or leave, demonstrating the functional characteristics of inorganic semi-permeable membranes; fifth, the charge of cluster is adjusted by changing the different types of ligands; finally, the cage-type structure is stable in water and anaerobic organic phases. On the basis of the advantages, $\{Mo_{132}\}$ is the closest cell model of inorganic compounds now. Additionally, Müller found that various counter cations might react with $\{Mo_{132}\}$, being found freely around $\{Mo_{132}\}$ by means of hydrogen bonds on the top of the $\{Mo_9O_9\}$ circular tunnels, also imbedded into the $\{Mo_9O_9\}$ circular tunnels and there may be some small-sized ions entering into the internal cavities of $\{Mo_{132}\}$ [29a, 29b]. All the investigations prove the nature of inorganic semi-permeable membrane, which is very similar to the functionality of the membrane. Furthermore, Müller discovered that entering or leaving abilities of cations to $\{Mo_{132}\}$ cluster were influenced by ion concentrations around the cage, which indicated the essence of the penetration phenomenon of cell membranes [29c, 29d]. The water content in the largest lemon-type aggregates, Mo_{368}, is about 10,000 water molecules, similar to jellyfish in the ocean, whose water content is 99% [28h].

5. The outlook for chirality in POMs chemistry

The ultimate objective of chiral POMs is their applications, especially of chiral catalysis [3, 30] and biomedical studies. Luo developed new chiral amine-based POMs as asymmetric catalysts in asymmetric direct aldol reactions, which are efficient, with excellent stereoselectivity and highly active (figure 19) [3]. It can also be reused for six times with unchanged enantioselectivity, while the activity is slightly decreased. The effective catalysis in the reactions is less than 1 mol % of chiral amine loading [3]. The investigations indicate that chiral POMs show excellent catalytic activity in chiral catalysis. Zhang showed that the sandwich polyanion $[ZnW(VO)_2(ZnW_9O_{34})_2]^{12-}$ was an excellent asymmetric oxidant for epoxidation of allylic alcohols, which is a highly chemoselective and stereoselective catalyst [30a].

6. Conclusion

The synthetic strategy of chiral POMs, the structures of chiral POMs, chiral resolution, theoretical calculations of chiral polyoxoanions, chiral catalysis, and bionic

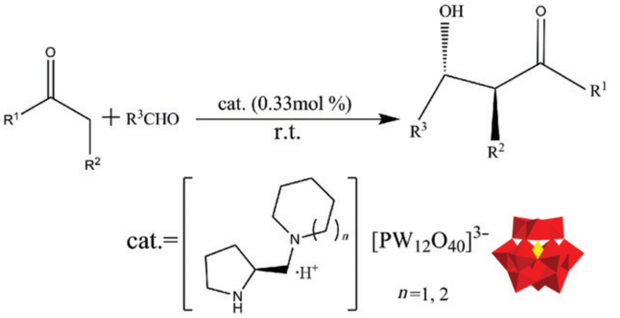

Figure 19. Chiral amine-based POMs catalyzed aldol reactions [3].

investigations have been summarized in the review. Some reported chiral polyoxoanions are unstable in solutions, existing as racemic mixtures in solutions or solid state. From the solution instability and structural similarities of racemization, the complex chirality directly affects their catalytic and biological activities. So syntheses of chiral POMs still need further investigations. Synthesis methods of pure chiral POMs both stabilized in solution and solid state still need to be explored. Furthermore, strategy to inhibit fast racemization of their structures needs to be developed. The important research directions of chiral POMs will be their applications in the fields of chiral catalysis, bionics, and biomedicine.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 91027002/21001022/21131001); the Science and Technology Development Project Foundation of Jilin Province (No. 20100169); the Postdoctoral station Foundation of Ministry of Education (No. 20060200002); the Analysis and Testing Foundation of Northeast Normal University (NENU), and the Program for Changjiang Scholars and Innovative Research Team in University.

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