

Coordination assemblies of polyoxomolybdate cluster framework: From labile building blocks to stable functional materials

Fengyan Li and Lin Xu*

Received 21st June 2010, Accepted 5th January 2011

DOI: 10.1039/c0dt00691b

Polyoxomolybdates, an important branch in polyoxometalates chemistry, present complicated solution chemistry and unmatched physicochemical properties, which endows us with both great opportunities and considerable challenges in creating new functional materials. This perspective highlights the recent development on the coordination assembly of transition-metal-substituted heteropolymolybdates by using labile lacunary heteropolymolybdates as inorganic multidentate ligands. A series of strategies have been used to stabilize the lacunary heteropolymolybdate building blocks. Finally, we introduce some researches on the modification of polymolybdates by organic groups in aqueous media, which may shed light on the green chemistry of the functionalization of polyoxomolybdates.

1. Introduction

Polyoxometalates (POMs), composed of early transition-metals of group V and VI (V, Nb, Ta, Mo, W *etc.*) in their highest oxidation states, are a vast class of metal–oxygen clusters with a variety of chemical composition and definite structures.¹ Generally, there are

two specific families of POMs, namely, the isopolyoxometalates and the heteropolyoxometalates. The former contains a metal–oxide cluster with only the d⁰ metal cations (Mo^{VI}, W^{VI}, V^V *etc.*) and the latter is composed of a metal–oxide framework together with one or more p-, d- or f-block heteroatoms (B, Si, P, Mn, Co, Gd *etc.*)—often in different oxidation state.² Based on the early well-defined pioneering work, polyoxometalate chemistry has become one of the fastest developing regions, in virtue of their fascinating architectures,^{3,4} excellent physicochemical properties, including strong Brønsted acidity, fast reversible multielectron

Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun, 130024, PR China. E-mail: linxu@nenu.edu.cn; Fax: +86-431-85099765; Tel: +86-431-85099668



Fengyan Li

research interests include the synthesis of POM materials and magnetic materials.

Fengyan Li received her B.S. degree in chemistry from Jilin Normal University in 2002, and completed her M.S. & Ph.D. degrees under the direction of Professor Lin Xu from Northeast Normal University (NENU) in 2008. During this time, she worked in Professor Lee Cronin's group (Glasgow, UK) as a Joint-training Ph.D. student in 2007 for one year. After her graduation, she has been working as a Lecturer in NENU. Her current



Lin Xu

*two specific families of POMs, namely, the isopolyoxometalates and the heteropolyoxometalates. The former contains a metal–oxide cluster with only the d⁰ metal cations (Mo^{VI}, W^{VI}, V^V *etc.*) and the latter is composed of a metal–oxide framework together with one or more p-, d- or f-block heteroatoms (B, Si, P, Mn, Co, Gd *etc.*)—often in different oxidation state.² Based on the early well-defined pioneering work, polyoxometalate chemistry has become one of the fastest developing regions, in virtue of their fascinating architectures,^{3,4} excellent physicochemical properties, including strong Brønsted acidity, fast reversible multielectron*

Lin Xu graduated with his first degree in chemistry from Northeast Normal University (NENU) in 1986, and then received his M.S. (1990) and Ph.D. (2001) degrees under the direction of Professor Enbo Wang from NENU. In 1996, he took up an Associate Professorship in chemistry department at NENU, and was promoted to Professor in 2001. After a postdoctoral appointment (2001–2002) at University of Missouri-Kansas City (USA), he returned to China and was appointed to the director of the Institute of Polyoxometalate Chemistry in 2003. His current research interests focus in polyoxometalate-based synthesis chemistry and multifunctional materials, in particular, in the coordination assembly of polyoxomolybdate complexes.

redox transformations, high proton mobility and high solubility in polar solvents and fairly high thermal stability in the solid state,⁵ and the rapid development in various applications such as optics, electronic materials, magnetism, medicine, and catalysis.^{6–16} Since the first polyoxoanion was reported by Berzelius in 1826,¹⁷ actually, most of researches on POMs chemistry focus on the two systems: tungsten-based POMs (polyoxotungstates) and molybdenum-based POMs (polyoxomolybdates).

Despite of the presence of multiple comparability between the two systems of polyoxotungstates and polyoxomolybdates, the inherent characteristic arising from both the difference in chemical bond (W–O and Mo–O) and the difference in electronegativity (tungsten and molybdenum) noticeably affects their behavior in chemical reactivity, reaction mechanism, and structural lability. Typically, the terminal oxygen atom of Mo=O bond in polyoxomolybdates generally manifests high nucleophilicity in coordination linkage to form capped complexes and high activity in chemical reaction to substitute for the terminal oxygen atom,^{18,19} while polyoxotungstates preferably retain the rigid framework with a low nucleophilicity for the terminal oxygen atom. These differences could well be supported by those results of quantum chemistry calculations.²⁰ In aqueous solution, the molybdenum species of POMs reach an equilibration within a matter of minutes, whereas it will take several weeks or even longer for tungsten species of POMs. Unlike polyoxotungstates, the diverse coordination numbers of Mo atom (from 4 to 6) in polyoxomolybdates will increase the linking versatility in coordination assembly of molybdenum–oxide clusters. In addition, the polyoxomolybdates can be reduced more easily than the polyoxotungstates and the reduced Mo species are relatively more stable, e.g., the existence of stable heteropoly blue solids. By the above mentioned properties, the polyoxomolybdates are able to generate a huge variety of structures from small clusters^{21–27} ($\{\text{Mo}_6\}$, $\{\text{Mo}_7\}$, $\{\text{Mo}_8\}$, $\{\text{Mo}_{16}\}$, $\{\text{Mo}_{36}\}$) to mixed-valence nanosized species^{28–32} ($\{\text{Mo}_{132}\}$, $\{\text{Mo}_{150}\}$, $\{\text{Mo}_{154}\}$, $\{\text{Mo}_{176}\}$, $\{\text{Mo}_{248}\}$, $\{\text{Mo}_{368}\}$). Most recently, cryospray mass spectrometry (CSI-MS) has been used to probe the mechanism of self-assembly of the polyoxomolybdate clusters in solution by Cronin's group.³³ In this report, the Lindqvist $\{\text{Mo}_6\}$ rearranges into the silver-linked β - $\{\text{Mo}_8\}$ when Ag^+ ion exists in solution. Using CSI-MS in conjunction with electronic absorbance spectroscopy, a real-time decrease in $\{\text{Mo}_6\}$ and associated increase in $\{\text{Mo}_8\}$ have been observed. Also, the rate of $\{\text{Mo}_6\}$ interconversion to $\{\text{Mo}_8\}$ was found to decrease on increasing the size of the counter-cation. Meanwhile, a novel 'flow system' was explored to study the steps assembly of the big molybdenum oxide wheel by this group.²⁹ They observed the crystallization of an intermediate structure $\{\text{Mo}_{36}\} \subset \{\text{Mo}_{150}\}$, in which a central $\{\text{Mo}_{36}\}$ cluster appears to template the assembly of the surrounding $\{\text{Mo}_{150}\}$ wheel. The increasing size and the complexity of polyanions are expected to generate multifunctionality of interest in materials science. The structures of some basic isopolymolybdate ions are shown in Fig. 1.

Compared with the isopolyoxometalates, heteropolyoxometalates are more numerous with more than 50 different kinds of heteroatoms, including many non-metals and most transition metals, and their structural and electronic properties are easier to modify by forming defect (lacunary) structures through the loss of one or more MO_6 octahedra and enclosing transition-metal (TM) cations in the vacancies. Consequentially, the lacunary

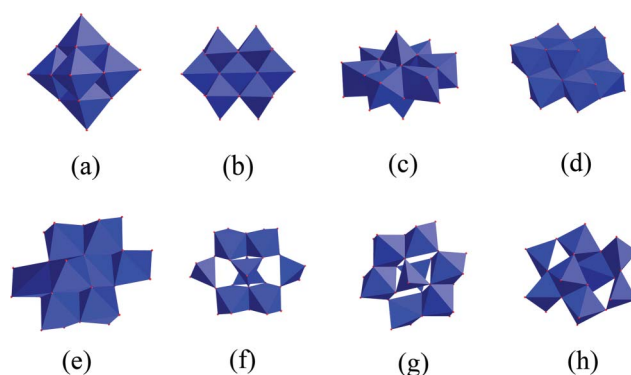


Fig. 1 Some basic structure types of isopolymolybdates in polyhedral representation: (a) $[\text{Mo}_6\text{O}_{19}]^{2-}$, (b) $[\text{Mo}_7\text{O}_{24}]^{6-}$, (c) $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$, (d) $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$, (e) $[\gamma\text{-Mo}_8\text{O}_{26}]^{4-}$, (f) $[\delta\text{-Mo}_8\text{O}_{26}]^{4-}$, (g) $[\varepsilon\text{-Mo}_8\text{O}_{26}]^{4-}$, (h) $[\xi\text{-Mo}_8\text{O}_{26}]^{4-}$.

POMs, obtained by removing one or more octahedral metal atoms from the plenary POMs, act as inorganic multidentate ligands to enclose transition-metal (or lanthanide) cations for further coordination assembly; this type of complexes constitute a special region in both coordination chemistry and magnetism. Thus, more attention has recently been paid to the exploration of transition-metal substituted heteropolytungstates^{34–51} by the reaction of transition-metal cations with the lacunary POM precursors, especially for the Keggin and Dawson type heteropolyanions (e.g. $\text{XW}_{11}\text{O}_{39}^{n-}$, $\text{X} = \text{P}, \text{Si}$; $\text{XW}_9\text{O}_{34}^{n-}$, $\text{X} = \text{Si}, \text{Ge}, \text{Se}, \text{P}, \text{As}, \text{Sb}, \text{Bi}, \text{Ni}, \text{Co}, \text{Zn}$ etc.; $\text{X}_2\text{W}_{17}\text{O}_{61}^{10-}$, $\text{X} = \text{P}, \text{As}$; $\text{X}_2\text{W}_{15}\text{O}_{56}^{12-}$, $\text{X} = \text{P}, \text{As}$; $\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}^{12-}$; $\text{SiW}_{10}\text{O}_{36}^{8-}$). In comparison with the most intensively studied heteropolytungstates, the investigation on the modification of heteropolymolybdates is relatively less explored, and a few reported results are mainly the modification of plenary heteropolymolybdates linking with metal cations *via* terminal or bridging oxygen atoms.^{52–56} The structures of some basic heteropolymolybdate ions are shown in Fig. 2.

Taking account of the practical applications, especially the catalysis aspect, polyoxomolybdates have played an important role in catalytic oxidation and epoxidation because of their higher oxidation potential than polyoxotungstates. The Keggin-type mixed-addenda heteropolyanion $\text{PMo}_{12-n}\text{V}_n\text{O}_{40}^{(3+n)-}$, discovered by Matveev *et al.*,⁶² is proved to be the most efficient and versatile catalyst in the POM series for oxidation reaction by O_2 , which have been used in industry for the gas-phase oxidation of methacrolein to methacrylic acid.^{63,64} The $[\text{H}_4\text{PMo}_{10}\text{V}_2\text{O}_{40}]^-$ anion with a crown-ether complex cation $[\text{Pd}^{\text{II}}\{(\text{H}_2\text{O})[15]\text{crown-5-phen}\}\text{Cl}_2]^+$ can catalyze Wacker alkene oxidation with N_2O instead of O_2 as oxidant.⁶⁵ In 2004, Dumesic *et al.* found that the reducible polyoxometalate $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ could serve as a strong oxidizing agent to remove CO gas by oxidizing it into CO_2 and as an energy-storage agent in fuel cells.⁶⁶

A noteworthy situation is that the current researches on the coordination assemblies based on the lacunary POMs only focus on the facile utilization of the lacunary heteropolytungstate anions, so that the coordination assembly based on the lacunary heteropolymolybdate anions is nearly a "deserted field". Such a situation should be attributed to the fact that the lacunary heteropolymolybdate anions are generally kinetically labile in aqueous solution, while the lacunary heteropolytungstate anions

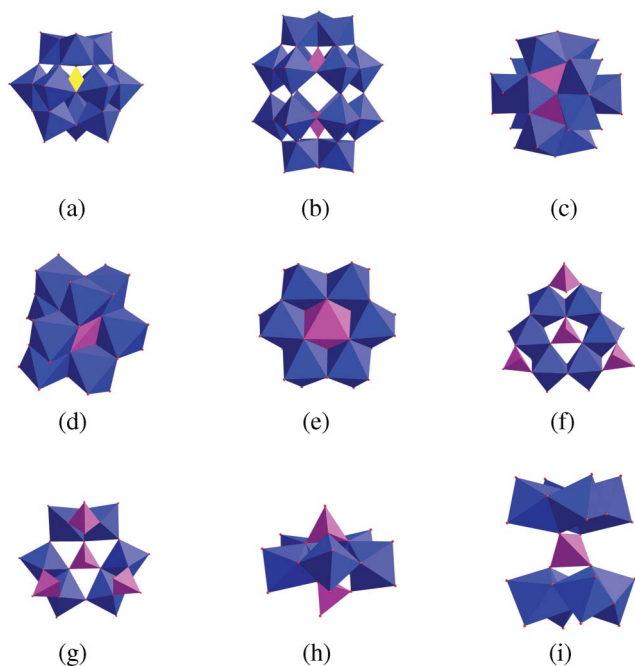


Fig. 2 Some basic structure types of heteropolymolybdates in polyhedral representation: (a) Keggin type $[\text{XMo}_{12}\text{O}_{40}]^{n-}$ ($\text{X} = \text{Si}^{\text{IV}}, \text{Ge}^{\text{IV}}, \text{P}^{\text{V}}, \text{As}^{\text{V}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$ etc.), (b) Wells–Dawson type $[\text{X}_2\text{Mo}_{18}\text{O}_{62}]^{n-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}$, etc.), (c) Silverton type $[\text{XMo}_{12}\text{O}_{42}]^{9-}$ ($\text{X} = \text{Ce}^{\text{III}}, \text{Gd}^{\text{III}}$ etc.), (d) Waugh type $[\text{XMo}_9\text{O}_{32}]^{6-}$ ($\text{X} = \text{Mn}^{\text{IV}}, \text{Ni}^{\text{IV}}$ etc.),⁵⁷ (e) Anderson type $[\text{H}_m\text{XMo}_6\text{O}_{24}]^{n-}$ ($\text{X} = \text{Al}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}, \text{Co}^{\text{III}}$ etc.), (f) $[\text{P}_4\text{Mo}_6\text{O}_{31}]^{12-}$,⁵⁸ (g) $[\text{P}_4\text{Mo}_6\text{O}_{34}]^{12-}$,⁵⁹ (h) Standberg type $[\text{X}_2\text{Mo}_5\text{O}_{23}]^{6-}$ ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}$, etc.),⁶⁰ (i) $[\text{PMo}_6\text{O}_{30}]^{7-}$.⁶¹

could be controllable to retain their vacant structures in aqueous solution. The kinetic lability of the lacunary heteropolymolybdate anions in aqueous solution severely obstructs both the formation of stable species and the crystal growth; this makes the isolation of their stable products considerably difficult. Furthermore, the lacunary heteropolymolybdate anions, even in an equilibrated solution, are prone to crystallize into full structures like Keggin or Wells–Dawson type polyanions.⁶⁷ Therefore, the exploration and development of the coordination assembly based on the lacunary heteropolymolybdates anions undoubtedly become a great challenge, and both the risks and the opportunities should be of coexistence in exploitation of the “deserted field”. Thus, several strategies, including the reduction from Mo^{6+} to Mo^{5+} for some of the Mo atoms on the framework; the incorporation of low-valence heteroatoms with lone pair electrons, such as As^{III} , Sb^{III} , into polymolybdate framework; and the use of hydrothermal synthesis etc., have been tried to separate the lacunary heteropolymolybdate anions.^{68–70} Müller and co-workers reported the existence of an $\{\text{As}^{\text{III}}\text{Mo}_9\text{O}_{33}\}$ fragment in the complexes $\text{K}_7[(\text{AsOH})_3(\text{MoO}_3)_3(\text{AsMo}_9\text{O}_{33})] \cdot 15\text{H}_2\text{O}$, $\text{K}_{10}[(\text{AsOH})_6(\text{MoO}_3)_2(\text{O}_2\text{Mo}-\text{O}-\text{MoO}_2)_2(\text{AsMo}_9\text{O}_{33})_2] \cdot 12\text{H}_2\text{O}$ ⁶⁸ and the mixed-valence heteropolymolybdate $(\text{HNMe}_3)_8[\text{H}_6\text{As}_{10}\text{Mo}_8\text{Mo}^{\text{V}}_{16}\text{O}_{90}] \cdot 9\text{H}_2\text{O}$, but the $\{\text{As}^{\text{III}}\text{Mo}_9\text{O}_{33}\}$ fragment will rearrange into a Keggin-type cluster of $\{\text{As}^{\text{V}}\text{Mo}_9\text{O}_{33}\}$ by the oxidation of O_2 when exposed to air.⁶⁹ It should be noted that filling transition-metal ions into the vacant sites could enhance the stability of lacunary heteropolymolybdate anions. The first sandwich-like heteropolymolybdate $[\text{Cu}_2(\text{SiMo}_9\text{O}_{33})_2]^{12-}$, based on the lacunary heteropolymolybdate anion of $[\text{SiMo}_9\text{O}_{33}]^{8-}$, was reported by

Fukushima *et al.* in 1981.⁷¹ Later, several heteropolymolybdates $[\text{Dy}(\text{SiMo}_{11}\text{O}_{39})_2]^{13-}$,^{72,73} $[\text{Nd}(\text{GeMo}_{11}\text{O}_{39})_2]^{13-}$,⁷⁴ $[\text{Ln}(\text{PMo}_{11}\text{O}_{39})_2]^{11-}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Lu}$),^{75,76} based on monovacant Keggin polyoxoanions were reported. Recently, we attempted to research on the coordination assemblies of polyoxomolybdate cluster frameworks based on the lacunary heteropolymolybdate building blocks, aiming at the difficult task to obtain stable crystal products suitable to the structural determination by single-crystal X-ray diffraction.^{77–84} Soon afterwards several other groups also made an important contributions to this area.^{85–87} In this perspective, after a brief overview of the noticeable differences between polytungstates and polyoxomolybdate, we will focus on the coordination assemblies of polyoxomolybdate clusters into stable functional complexes by using the lacunary heteropolymolybdates as inorganic multidentate ligands, and we will also report on some coordination assemblies of new polyoxomolybdates by organic components in aqueous solution. This present perspective may arouse more attention to the fascinating challenge of polyoxomolybdates which awaits exploitation to transform the labile building blocks into stable functional materials; such chemical transformation should be of current frontiers in polyoxometalate chemistry.

2. Using lacunary heteropolymolybdates as ligands

Since the first sandwich-like heteropolymolybdate $[\text{Cu}_2(\text{SiMo}_9\text{O}_{33})_2]^{12-}$ was discovered, only a few examples of metal complexes based on lacunary heteropolymolybdate anions have been reported so far. We have been trying to find feasible rational reaction conditions to obtain stable sandwich-type TM-substituted heteropolymolybdates and then to achieve their crystal structure determination. On the basis of our research results, we consider that both the solution pH value and a suitable counter-cation are the key factor for the successful synthesis. The favorable pH value of the aqueous solution is a critical factor to stabilize the formation of sandwich-type complexes, and the suitable counter-cation could facilitate the crystal growth, which determines whether the crystal structure can be obtained. The reaction of Mn^{2+} ions and $[\alpha\text{-AsMo}_{12}\text{O}_{40}]^{3-}$ in the presence of $(\text{CH}_3)_4\text{N}^+$ at pH 4.2 could lead to the isolation of two new sandwich-type heteropolymolybdates $[(\text{CH}_3)_4\text{N}]_8[\text{M}(\text{H}_2\text{O})_5]_2(\text{H}_3\text{O})_2[\text{M}_2(\text{H}_2\text{O})_{10}(\text{MA}^{\text{V}}\text{Mo}_9\text{O}_{33})_2][\text{M}(\text{H}_2\text{O})_4(\text{MA}^{\text{V}}\text{Mo}_9\text{O}_{33})_2] \cdot 20\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{2+}$, **1**; Co^{2+} , **2**),⁷⁷ see Fig. 3. The basic building block in these complexes is an unusual trivacant arsenomolybdate anion $[\text{As}^{\text{V}}\text{Mo}_9\text{O}_{33}]^{7-}$ (**1c**), which derives from the well-known $[\text{B-}\beta\text{-AsMo}_9\text{O}_{33}]^{7-}$ by moving one MoO_6 octahedron from the $\{\text{B-}\beta\text{-AsMo}_9\text{O}_{33}\}$ unit to the other side, and the MoO_6 octahedron covers the cavity between the other two Mo_3O_{13} units. Such a structural transformation indicated in Scheme 1 really reflects the lability of lacunary heteropolymolybdate building blocks, and the structural transformation also makes the transferred MoO_6 octahedron possess two terminal oxygen atoms, which can coordinate to additional M^{2+} ions.

The versatile $[\text{As}^{\text{V}}\text{Mo}_9\text{O}_{33}]^{7-}$ ligands could not only sandwich two M^{2+} ions, but also bind with one or two M^{2+} ions, forming an interesting one-dimensional chain structure. These two compounds represent the first examples of the sandwich-type

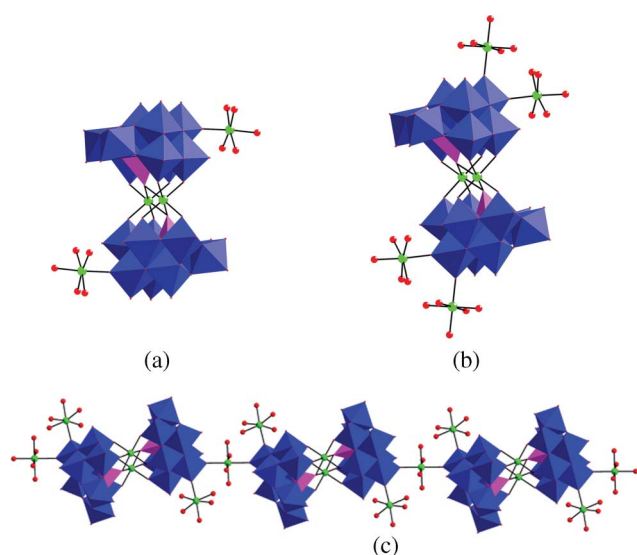
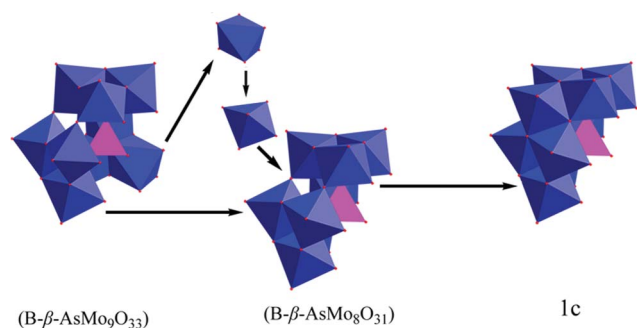


Fig. 3 (a) Combined polyhedral/ball-and-stick representation of the $[\{\text{Mn}(\text{H}_2\text{O})_5\}_2(\text{MnAs}^{\text{V}}\text{Mo}_9\text{O}_{33})_2]^{6-}$ fragment. (b) A part of the one-dimensional chain-like $[\text{Mn}(\text{H}_2\text{O})_4(\text{MnAs}^{\text{V}}\text{Mo}_9\text{O}_{33})_2]^{8n-}$ fragment in **1**. (c) The one-dimensional chain structure in **1**. Color code: MoO_6 (blue), AsO_4 (pink), Mn (green), O (red).



Scheme 1 The unusual $\{\text{AsMo}_9\text{O}_{33}\}$ unit in **1c** derives from the well-known $(\text{B-}\beta\text{-AsMo}_9\text{O}_{33})$ structure by moving one MoO_6 octahedron from the $\text{B-}\beta\text{-AsMo}_9\text{O}_{33}$ unit to the other side, and the MoO_6 octahedron covers the cavity between the other two Mo_3O_{13} units.

complexes with extended structure based on the lacunary heteropolymolybdates ligands.

The solution stability of these complexes was investigated by a control measurement for the cyclic voltammograms and UV/Vis spectra in both solid state and aqueous solutions. These experimental results demonstrate that they are instable in aqueous solution and disintegrate into some small fragments once they are dissolved. The magnetic properties of the two sandwich-type complexes were investigated to indicate typical antiferromagnetic interactions through the $\text{Mn}(\text{II})\text{--O--Mn}(\text{II})$ bridge unit for complex **1** and the $\text{Co}(\text{II})\text{--O--Co}(\text{II})$ bridge unit for complex **2**.

This above work was further extended owing to the discovery of a new sandwich-like vanadium molybdate⁷⁸ $[\text{HN}(\text{CH}_3)_3]_{10}[\text{Mn}_2(\text{V}^{\text{V}}\text{Mo}_9\text{O}_{33})_2]\cdot 10\text{H}_2\text{O} **3**, as shown in Fig. 4, which has a similar structure to $[\text{Cu}_2(\text{SiMo}_9\text{O}_{33})_2]^{12-}$,⁷¹ and the $\{\text{MAS}^{\text{V}}\text{Mo}_9\text{O}_{33}\}_2$ fragment in **1** and **2**. The most interesting feature of **3** is the occurrence of ferromagnetic interactions between the Mn^{2+} ions bridged by the oxygen atoms from the two $\text{V}^{\text{O}}\text{O}_4$ tetrahedra, different from the usual antiferromagnetic coupling$

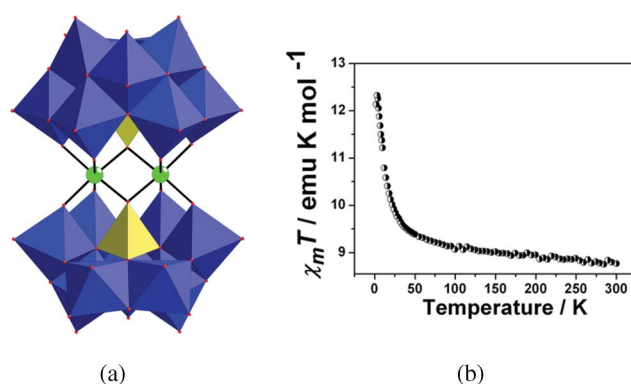


Fig. 4 (a) Representation of the $[\text{Mn}_2([\text{V}^{\text{V}}\text{Mo}_9\text{O}_{33})_2]^{10-}$ anion in **3**. The $[\text{V}^{\text{V}}\text{Mo}_9\text{O}_{33}]^{7-}$ anions are shown as polyhedra, and the central $\{\text{Mn}_2\text{O}_{10}\}$ cluster and the connecting heteroatoms are shown as ball-and-stick. Color code: MoO_6 (blue), VO_4 (yellow) and Mn (green). (b) Plot of $\chi_m T$ vs. T of **3**.

in the dinuclear $\text{Mn}(\text{II})$ unit bridged by oxygen atoms, though some $\text{Mn}(\text{II})$ complexes bridged by alkoxo or phenoxo oxygen atoms show ferromagnetic interactions.^{88–90} The reason for the occurrence of ferromagnetic interactions in complex **3** remains uncertain, but the ferromagnetic interactions may directly depend on the different bond lengths and angle of Mn--O--Mn related with the oxygen atoms of the VO_4 tetrahedron in the complex. According to the structural data, the central $\text{Mn}_2(\mu\text{-O})_2$ moiety in complex **3** has smaller Mn--O--Mn angles and longer Mn--O bonds than those of the $\{\text{Mn}_2(\text{As}^{\text{V}}\text{Mo}_9\text{O}_{33})_2\}$ unit, which may be responsible for the ferromagnetic interaction.

Most recently a new member of lacunary heteropolymolybdate building blocks $[\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27}]^{9-}$ was discovered by Xue *et al.*^{85,86} The reaction of an As_2O_3 solution with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ at pH 6.5–7.0 in the presence of Cu^{2+} , Fe^{3+} , Cr^{3+} and $\text{Fe}^{3+}/\text{Cr}^{3+}$ mixture, respectively, enables the isolation of homometallic and heterometallic sandwich arsenatomolybdates $(\text{NH}_4)_{14}[\text{M}_2\text{--}(\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27})_2]\cdot 13\text{H}_2\text{O} **4**, $(\text{NH}_4)_{12}[\text{M}_2(\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27})_2]\cdot 11\text{H}_2\text{O}$ ($\text{M} = \text{Cr}$, **5**; Fe , **6**), $(\text{NH}_4)_{12}[\text{FeCr}(\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27})_2]\cdot 13\text{H}_2\text{O} **7**, see Fig. 5. The $[\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27}]^{9-}$ fragment here can also be derived from the trivacant Keggin ion $[\text{B-}\alpha\text{-AsMo}_9\text{O}_{33}]^{9-}$ by moving one Mo_3O_{13} group and inserting one MoO_6 octahedron to the cavity between$$

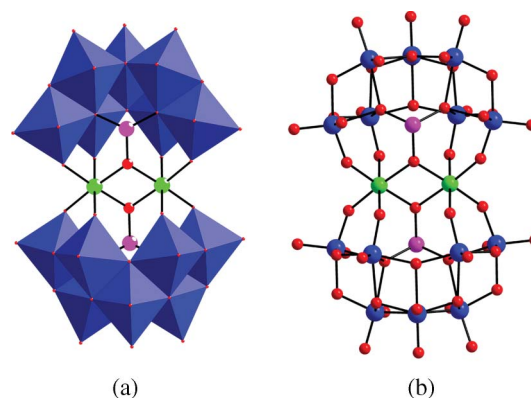


Fig. 5 (a) Combined polyhedral/ball-and-stick representation of the polyanion $[\text{M}_2(\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27})_2]^{n-}$ ($\text{M} = \text{Cu}$, Cr , Fe). (b) ORTEP representation of the polyanion $[\text{M}_2(\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27})_2]^{n-}$. Color code: MoO_6 (blue), As (pink), transition metals (green), O (red).

the two Mo_3O_{13} units. The position of the removed Mo_3O_{13} group is partly occupied by the lone pair electrons of the As^{III} atom. Two TM ions can be sandwiched between two $[\text{As}^{\text{III}}\text{Mo}_7\text{O}_{27}]^{9-}$ ligands and the distance between the two metal ions is shorter (about 3.1 Å) than that in oxalato-bridged dinuclear complexes and singly $\mu\text{-O}$ bridged dinuclear complexes. Magnetic studies indicate a significant antiferromagnetic exchange between the magnetic centers with $J = -6.26$, -2.09 and -4.09 cm^{-1} in **5**, **6** and **7**, respectively.

The first tetra-TM substituted sandwich-type polyoxometalate was reported by Weakley *et al.* in 1973,⁹¹ and is the most familiar one in TM-substituted heteropolytungstates. However, no Weakley-type TM-substituted heteropolymolybdate analogues have been reported in the long history of POMs chemistry. In 2009, the first tetra-TM substituted sandwich-type heteropolymolybdates $[\text{Na}_{11}(\text{H}_2\text{O})_{25}]\text{H}[\text{M}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeMo}_9\text{O}_{34})_2]\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Ni}$, **8**; Mn , **9**; Co , **10**), see Fig. 6, based on the trivacant Keggin ion $[\text{B-}\alpha\text{-GeMo}_9\text{O}_{34}]^{10-}$, which is well-known but first present itself, was reported by Niu *et al.*⁸⁷ A one-pot synthetic strategy was used instead of the lacunary precursor anion of $[\text{GeMo}_9\text{O}_{34}]^{8-}$, via the decomposition of $[\text{GeMo}_{12}\text{O}_{40}]^{4-}$, suggesting that a synergic self-assembly beginning from the raw materials should have a higher reactivity than that from the lacunary precursor anion of $[\text{GeMo}_9\text{O}_{34}]^{8-}$. However, a sodium acetate buffer solution (pH 4.5–5.0) must be selected to favor the formation of lacunary germanomolybdate units in aqueous solution. A diffusion method was also used in preparing **9** and **10**. In addition, the nature of the TM ions can influence the final structural architecture. When Cu^{2+} or Cr^{3+} ion was introduced in the system, a dinuclear TM-substituted germanomolybdate $[\text{M}_2(\text{GeMo}_9\text{O}_{33})_2]^{n-}$, which has the

same structure as $[\text{Cu}_2(\text{SiMo}_9\text{O}_{33})_2]^{12-}$ and $[\text{M}_2(\text{As}^{\text{V}}\text{Mo}_9\text{O}_{33})_2]^{10-}$, was isolated instead. *In situ* UV spectroscopic measurements show that the aqueous solution of **8** could be stable at pH 3.0–10. Surface photovoltage spectroscopy and electric field induced surface photovoltage spectroscopy measurements indicate n-type semiconductor behavior for complex **8**. Magnetic interaction between neighboring Ni^{2+} ions in the rhombic Ni_4O_{16} cluster was proved to be ferromagnetic, similar to that of heteropolytungstate analogues.

As an extension of this work, the first 1D chain-like germanomolybdate $(\text{Him})_8\text{Na}_7\text{H}_7[\text{Cu}(\text{im})_4(\text{CuGeMo}_9\text{O}_{33})_2][(\text{CuGeMo}_9\text{O}_{33})_2]$ ($\text{im} = \text{imidazole}$) **11**, based on a di-TM-substituted sandwich-type germanomolybdate, was reported by our group in 2010.⁸⁰ As well as the inorganic polyanion ligand $[\text{GeMo}_9\text{O}_{33}]^{8-}$, a second organic ligand imidazole (im) was introduced in the synthesis. Two Cu^{2+} ions are first sandwiched between two polyanion ligands, forming a sandwich-type germanomolybdate unit $[(\text{CuGeMo}_9\text{O}_{33})_2]^{12-}$, then the basic sandwich units are further connected by $[\text{Cu}(\text{im})_4]^{2+}$ cations into a one-dimensional chain structure, see Fig. 7. From an electrochemical investigation, compound **11** displays excellent electrocatalytic activity toward the reduction of nitrite. Moreover, the result of a magnetic investigation suggests the existence of antiferromagnetic interactions in **11**.

In worldwide concern, carbon dioxide has been well-recognized as one of the green-house gases causing global warming. The development of environmentally friendly and economic methods for CO_2 fixation remains a long-standing challenge. Our recent research has revealed that the monovacant heteropolymolybdate ions can capture CO_2 gas by means of the mono-TM substituted heteropolymolybdates coordinating to CO_2 through the TM ions.⁸¹ Two CO_2 -ligated compounds $(\text{C}_3\text{H}_5\text{N}_2)_3(\text{C}_3\text{H}_4\text{N}_2)[\text{PMo}_{11}\text{CoO}_{38}(\text{CO}_2)]\cdot 4\text{H}_2\text{O}$ **12**, $(\text{C}_3\text{H}_5\text{N}_2)_4[\text{SiMo}_{11}\text{CoO}_{38}(\text{CO}_2)]\cdot 4\text{H}_2\text{O}$ **13** were isolated from an aqueous solution in which $[\text{H}_2\text{XMo}_{11}\text{CoO}_{40}]^{n-}$ polyoxoanion reacts with bubbled CO_2 under mechanical stirring without heating. Of note, the $\mu\text{-}\eta^1, \eta^1\text{-OCO}$ linear coordination mode (see Fig. 8) in **12** and **13** is shown for the first time among the known CO_2 complexes. The C–O distances obtained from single-crystal structure data are 1.287(9) Å for **12** and 1.304(13) Å for **13**, similar to the values observed in other CO_2 -ligated compounds.^{92,93} The coordination binding of the two O atoms from CO_2 with electropositive Mo^{VI} and Co^{II} ions should reduce the electron density of O atoms in **12** and **13**, resulting in increased C–O bond lengths. A large number of researches on the TM-coordinated CO_2 complexes in organic solvents are well documented, but the formation of TM-coordinative CO_2 complexes in aqueous solution has not been reported before. The successful syntheses of these two

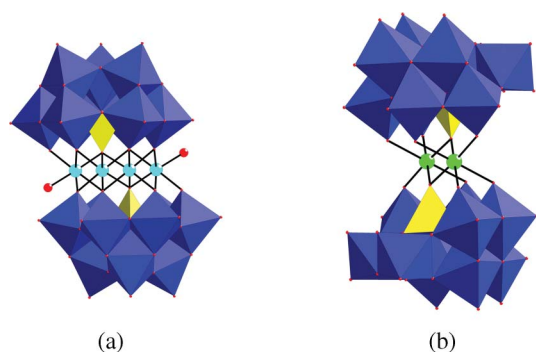


Fig. 6 (a) Combined polyhedral/ball-and-stick representation of the polyanion $[\text{M}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-GeMo}_9\text{O}_{34})_2]^{12-}$ ($\text{M} = \text{Ni}$, Mn , Co). (b) Combined polyhedral/ball-and-stick representation of the polyanion $[\text{M}_2(\text{GeMo}_9\text{O}_{33})_2]^{n-}$ ($\text{M} = \text{Cu}$, Cr). Color code: MoO_6 (blue), GeO_4 (yellow), transition metals (turquoise for Ni , Mn , Co ; green for Cu , Cr), O (red).

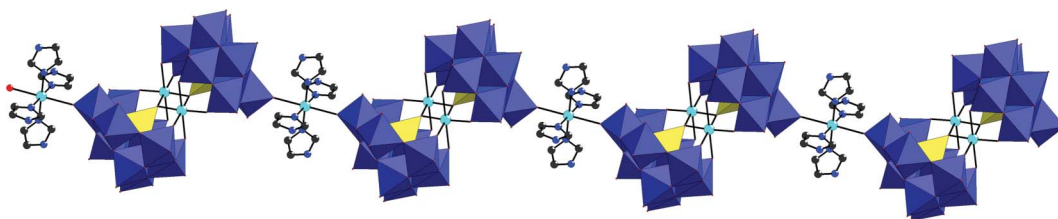


Fig. 7 Combined polyhedral/ball-and-stick representation of one-dimensional chain structure in **11**. Color code: MoO_6 (blue octahedra), GeO_4 (yellow), Cu (turquoise), O (red), C (black), N (blue balls).

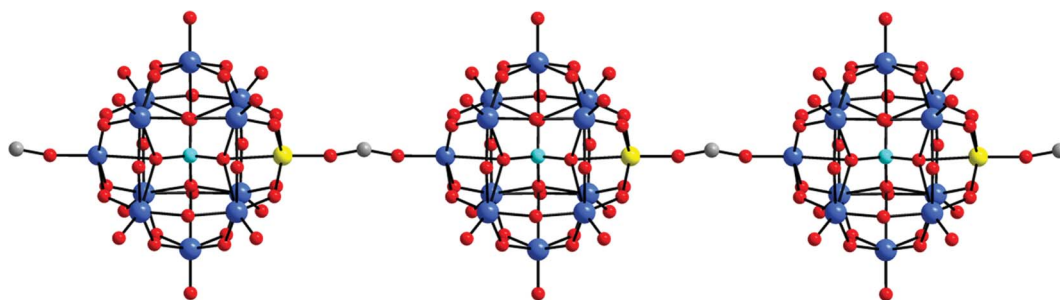


Fig. 8 Ball-stick representation of polymeric chain structure of complex **12**. All imidazole and water molecules are omitted. Color code: Mo (blue), P (turquoise), Co (yellow), O (red), C (grey).

complexes in aqueous medium provides a green chemical approach in CO_2 coordination chemistry. And this could also be related with the high reactive activity and chemical flexibility for the polyoxomolybdate framework.

Besides the coordination assembly of POM-based complexes by using the conventional heteropolymolybdates as ligands, we are also interested in creating new members of the heteropolymolybdates family. To date most of the heteropolymolybdates are of nonmetal-centered polyoxoanions, while the transition-metal-centered Keggin-type POMs are rarely explored.⁹⁴ We devoted ourselves to isolate transition-metal-centered Keggin-type heteropolymolybdates, and finally two new Keggin-type species, $(\text{C}_3\text{H}_5\text{N}_2)_6[\text{Co}^{\text{II}}\text{Mo}_{12}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ **14** and $(\text{NH}_4)_3(\text{C}_4\text{H}_5\text{N}_2\text{O}_2)_3[\text{Ni}^{\text{II}}\text{Mo}_{12}\text{O}_{40}]$ **15**, were successfully synthesized under conventional and hydrothermal conditions, respectively (see Fig. 9).⁸² The pH value, suitable organic cation (imidazole), and use of an excess of $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ play key roles in the preparation of **14**. Without addition of imidazole

(at pH = 3.0), only a crystalline complex **Mo₈Co** formed. After removing of solid products in the mother-liquor of complex **14**, another polymolybdate **Mo₇Co** was obtained. The formation of complexes of **Mo₈Co** and **Mo₇Co** with higher yield is in agreement with the fact that the $[\text{Mo}_7\text{O}_{24}]^{6-}$ anion is the predominant species in a pH range 4.0–7.0 and only small amounts of MoO_4^{2-} anions form the dodecamolybdate framework by self-assembly.⁹⁵

3. Modifying polymolybdate frameworks by organic groups in aqueous solution

So far, the most effective approach to the functionalization of POMs is the modification of Lindqvist-type POMs by organoimido ligands, which strongly depends on the use of an anhydrous organic solvent and usually results in a mixtures of multiple-functionalized products.⁹⁶ Driven by the development of green chemistry, we are interested in the functionalization

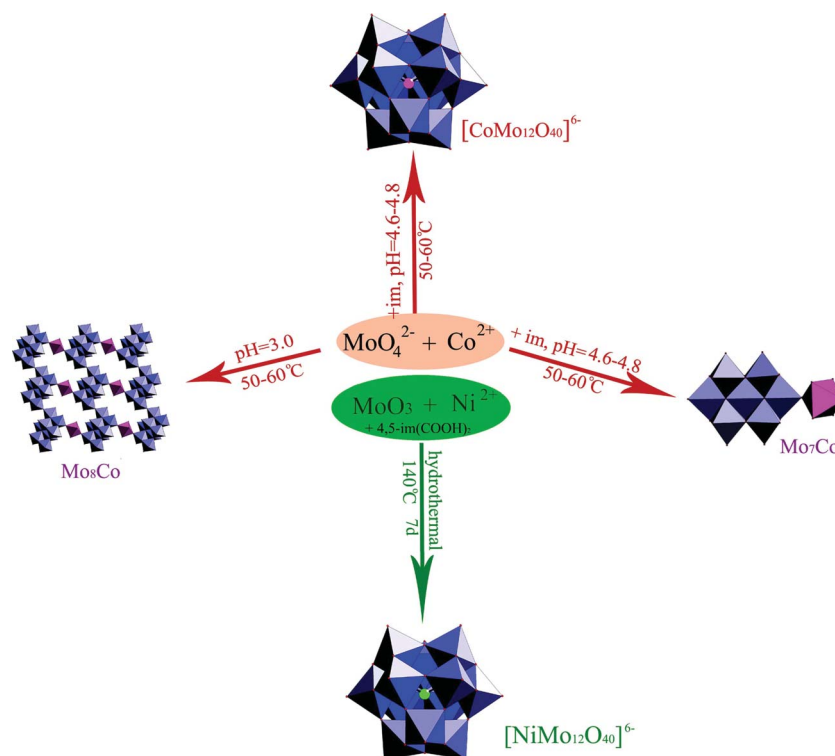


Fig. 9 Summary of pH effect on the system of molybdate and transition metals.

of polyoxomolybdates in aqueous media. Recently, we tried to synthesize organopolymolybdate polymers with covalently linked multicarboxylic ligands in aqueous solution. Two decamolybdate polymers, $[\text{Na}_8(\text{Mo}_{10}\text{O}_{32}\text{EDTA})(\text{H}_2\text{O})_{35}]_n$ **16** and $[(\text{NH}_4)_8(\text{Mo}_{10}\text{O}_{32}\text{PDTA})(\text{H}_2\text{O})_{30}]_n$ **17** could be isolated from the self-assembly reaction of molybdate with organic groups of 1,2-diaminoethanetetraacetate (EDTA) or 1,3-diaminoporpanetetraacetate (PDTA),⁸³ which display unusual *meso*-helical structures, see Fig. 10. This is the first time that an organopolymolybdate polymer with covalently linked multicarboxylic ligands is realized in aqueous solution. In addition, we found that other carboxylic acids (aminoacetate, 4-diaminoethanetetraacetate) or a pyridine derivative (nicotinic amide) could also be grafted to the framework of γ -type octamolybdate in aqueous phase.

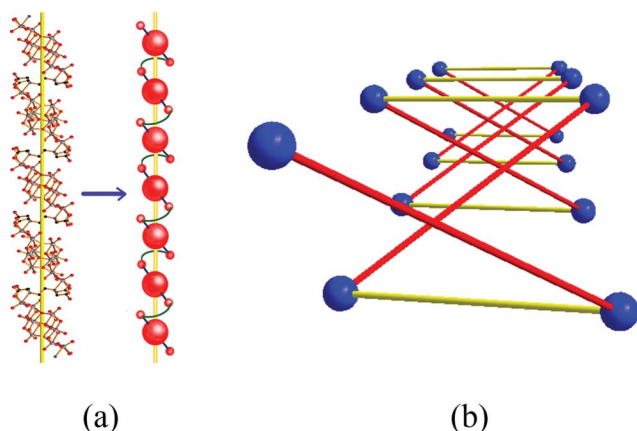


Fig. 10 (a) Left: Detail of the *meso*-helical chain structure of **16** (all H atoms are omitted). Color code: Mo (lavender), O (red), N (blue), C (black). Right: Schematic illustration of the *meso*-helical chain. (b) Perspective view of the *meso*-helical structure of **16** along the chain direction (only the capped Mo atoms are drawn as blue balls, while the octamolybdate subunits and organic ligands are omitted for clarity).

As is well known, the bridging oxygens of POMs (Lindqvist-, Anderson-, Wells–Dawson-type) can be substituted with some tridentate ligands, such as tri(hydroxymethyl)aminomethane, 2-acetamido-2-ethyl-1,3-propanediol, *etc.*, in organic solvents.^{97,98} Since triethanolamine has a similar geometry with those tridentate ligands and water-solubility, we attempted to use it to functionalize heteropolymolybdates in aqueous solution. As expected, a triethanolamine functionalized hexamolybdoarsen-

ate **18** was isolated, in which a new type of heteropolyanion $[\text{HN}(\text{CH}_2\text{CH}_2\text{O})_3\text{AsMo}_6\text{O}_{22}]^{5-}$ is linked by Mn^{2+} ions to form a zigzag chain (see Fig. 11).⁹⁹ In the heteropolyanion $[\text{HN}(\text{CH}_2\text{CH}_2\text{O})_3\text{AsMo}_6\text{O}_{22}]^{5-}$, six MoO_6 octahedra link together with edge sharing mode to form a planar structure, which is further capped with a triethanolamine ligand and an AsO_4 tetrahedron on both sides. Then the $[\text{HN}(\text{CH}_2\text{CH}_2\text{O})_3\text{AsMo}_6\text{O}_{22}]^{5-}$ units are connected by Mn^{2+} ions through the oxygen atoms from the heteropolyanions. This provides a special example of both organic and inorganic group grafted polyanion.

Since Kwak *et al.* reported on the heteropolymolybdate family $[(\text{RP})_2\text{Mo}_5\text{O}_{21}]^+$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{C}_2\text{H}_4\text{NH}_3^+, p\text{-CH}_2\text{C}_6\text{H}_4\text{NH}_3^+$) in 1975,¹⁰⁰ much effort has been made on the modifying the surface of the Standberg type polyanion $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}$. In 2001, Finn and Zubieta introduced a secondary metal–ligand component, as a charge-compensating unit and a structure-directing component, to synthesise bimetallic organophosphonate oxide phases of the $\text{Mo}/\text{Cu}/\text{O}/\text{RPO}_3^{2-}$ family.^{101,102} Later, they studied the synergistic influence of diphosphonate tether lengths and the metal–organic component on the structures of the hybrid oxide materials.^{103–105} In 2003, Kortz *et al.* reported on the first examples of polyoxomolybdates functionalized with phosphonocarboxylates, $\text{Rb}_4\text{KNa}[(\text{O}_2\text{CCH}_2\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]\cdot\text{H}_2\text{O}$ and $\text{Rb}_4\text{KNa}[(\text{O}_2\text{CC}_2\text{H}_4\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]$.¹⁰⁶ Recently, they obtained a unique POM-based soft material, constructed from chiral aminophosphonate pentamolybdate units $[(\text{R}^*\text{PO}_3)_2\text{Mo}_5\text{O}_{15}]^{2-}$ ($\text{R}^* = \text{CH}_3\text{CH}(\text{NH}_3) \text{19}, \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_3) \text{20}$).¹⁰⁷ The pentamolybdate core is assembled in solution with two phosphonate ligands attached on opposite, external sides of the Mo_5O_{15} ring through three oxygen atoms in a trigonal pyramidal fashion (see Fig. 12).

4. Modifying heteropolymolybdate frameworks by coordination assembly

It was well known that the Keggin-type family comprises five structural isomers denoted as α -, β -, γ -, δ - and ϵ -species, among which only α - and β -Keggin-type anions are the most familiar. Recently, several polyoxomolybdates of ϵ -Keggin-type polyanions were used as efficient heterogeneous catalysts for the aerobic oxidation of aldehydes to carboxylic acids.¹⁰⁸ Compared with α -Keggin-type and β -Keggin-type polyoxomolybdates, the ϵ -Keggin-type polyoxomolybdates naturally contain more Mo^{V} centers except for Mo^{VI} , which could increase the nucleophilicity of the oxygen atoms on the anionic surface, so that the

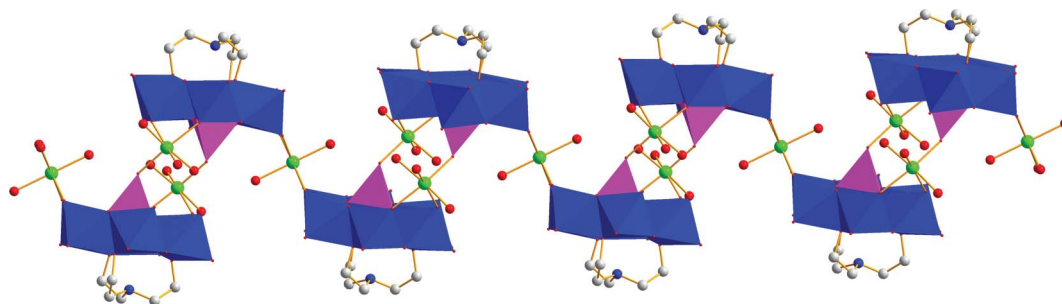


Fig. 11 Combined polyhedra/ball-and-stick of the 1D zig-zag chain in **18**. Color code: MoO_6 (blue octahedra), AsO_4 (pink), Mn (green), O (red), N (blue), C (grey).

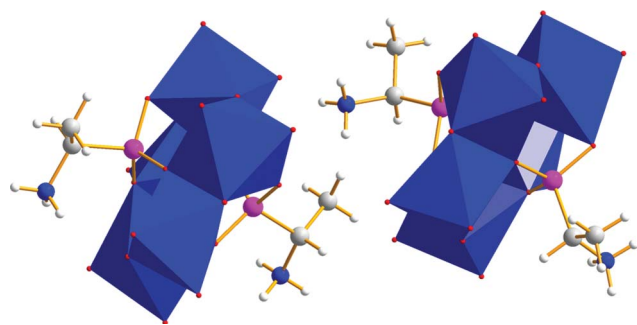


Fig. 12 Polyhedral/ball-and-stick representation of the two diastereomeric forms of (R,R) -**19**. Color code: MoO_6 (blue octahedra), P (pink), O (red), N (blue ball), C (grey), H (white).

coordination linkage with electrophilic metal cations may become more favorable.¹⁰⁹ By using the bidentate organic ligands as linker units, 1D, 2D and 3D organic–inorganic hybrids based on ϵ -Keggin polyanions $[\epsilon\text{-H}_m\text{PMo}_{12}\text{O}_{40}\text{M}_4]^{n-}$, have been reported by Dolbecq *et al.*,^{110,111} proving that the inorganic building blocks

of the ϵ -Keggin anions are efficient monomers to assemble new extended hybrid frameworks. We recently reported the first ϵ -Keggin type molybdogermanates⁸⁴ $[\text{GeMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{36}(\mu_2\text{-OH})_4\{\text{Ni}(\text{pda})(\text{H}_2\text{O})\}_2\{\text{Ni}(\text{pda})\}\{\text{Ni}(\text{pda})(\text{bpe})\}(\text{bpe})_{0.5}]_n$ **21** and $[\text{GeMo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{36}(\mu_2\text{-OH})_4\{\text{Ni}(\text{pda})(\text{H}_2\text{O})\}_2\{\text{Ni}(\text{pda})(\text{bpy})_{0.5}\}]_n \cdot 5n\text{H}_2\text{O}$ **22** (pda = 1,2-propanediamine, bpe = 1,2-bis(4-pyridine)ethane, bpy = 4,4'-bipyridine), with flexible organic N-donor ligands. These two compounds appeared in 1D chain and 2D layered structures, see Fig. 13, respectively. Interestingly, dual Ni–O–Mo linkages on the same side of the ϵ -Keggin core in **22** could be observed, a rare case to date.

Antimony-containing Keggin type heteropolyoxometalates have been investigated to play an important role in heterogeneous oxidation catalysis and the antimony cations have been proved to have a stabilizing effect on POMs at high temperature.^{112,113} Therefore, the main group element Sb was used as capping atoms to modify the Keggin type clusters. In 2006, J. Q. Xu *et al.* reported the first Sb bicapped pseudo-Keggin polyoxoanion $[\text{PMo}^{\text{V}}_5\text{Mo}^{\text{VI}}_7\text{O}_{40}\text{Sb}^{\text{III}}_2]^{2-}$.¹¹⁴ Later, they isolated another highly reduced Keggin polyoxoanion $[\text{PMo}^{\text{V}}_7\text{Mo}^{\text{VI}}_5\text{O}_{40}\text{Sb}^{\text{III}}_2]^{4-}$ under

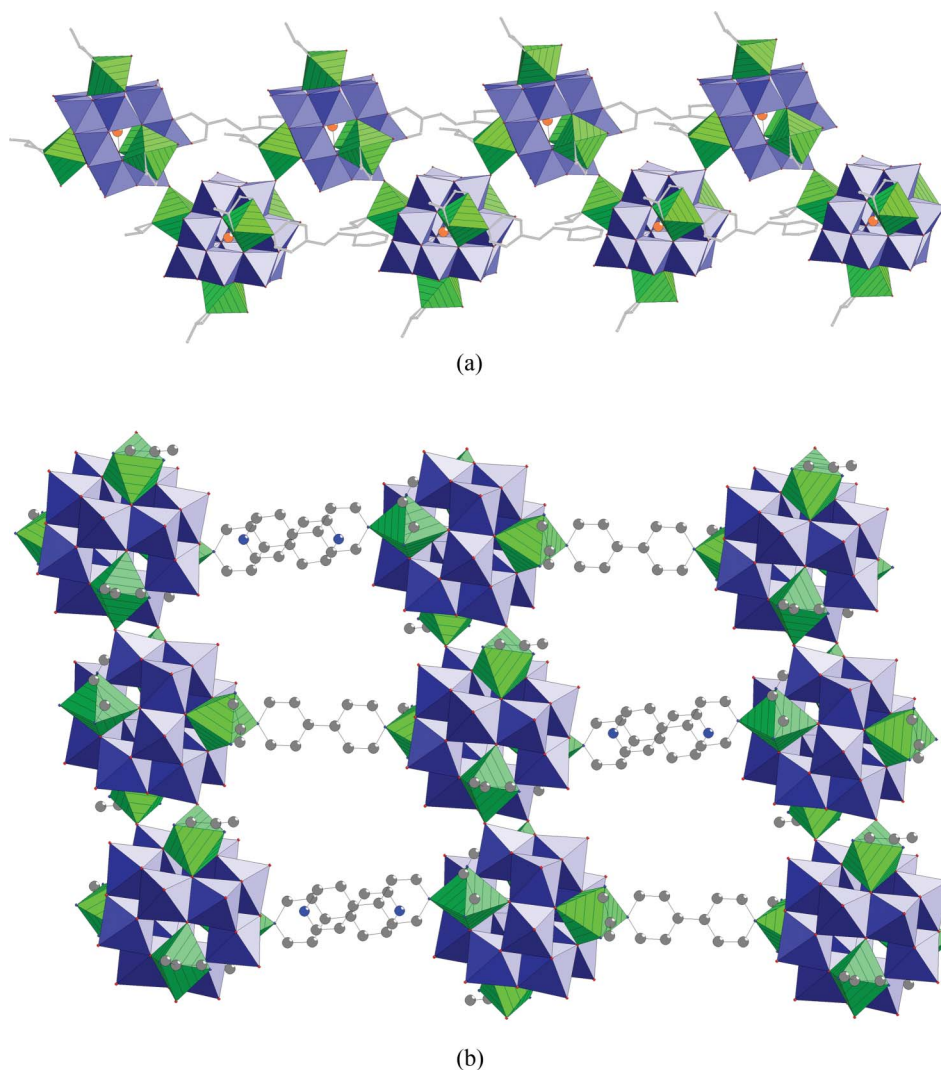


Fig. 13 (a) Ball-and-stick and polyhedra view of the zigzag chain structure in **21**. (b) 2D layer structure in **22** (blue octahedra, MoO_6 ; green octahedra, NiO_6 ; the organic ligands in **21** are drawn as grey).

strong reducing agents.¹⁸ With the bi-antimony capped Keggin polyoxoanion as building blocks, the first examples of extended structures based on $[\text{PMo}_{12}\text{Sb}_2\text{O}_{40}]^{2-}$ were structurally characterized through the linkage of different transition metal coordination complexes.¹¹⁵ In order to supplement the members in the bi-antimony capped Keggin family, we recently extended this work to other heteropolyanions and isolated three heteropolymolybdate ions $[\text{BMo}_{12}\text{Sb}_2\text{O}_{40}]^{4-}$, $[\text{SiMo}_{12}\text{Sb}_2\text{O}_{40}]^{3-}$ and $[\text{AsMo}_{12}\text{O}_{40}\text{Sb}_2]^{2-}$ with a mixed-solvothermal method.¹¹⁶ The modification of heteropolymolybdates makes them possess multidimensional structures and tunable redox properties, offering possible candidates in the development of functional materials.

5. Conclusions and outlook

In this perspective, we have mainly described recent advances in the coordination assembly of polymolybdate cluster frameworks with lacunary heteropolymolybdate ligands, followed by discussion of related research on the modification of polymolybdate frameworks by organic groups or TM coordination assembly. Two synthetic routes have been applied in order to obtain lacunary heteropolymolybdate precursors: one is from the decomposition of saturated heteropolymolybdates by raising the pH of the solution; the other is one-pot syntheses from simple starting materials, such as MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$, in a buffer solution. The optimal pH value to obtain trivacant heteropolymolybdate ions is 4.2–5.0. With the pH increasing to 6.5–7.0, pentavacant heteropolymolybdate ligands will be obtained. Besides the pH, many other synthetic variables, such as type of counter-cation, ionic strength and temperature *etc.*, also have a significant impact on the results of a synthetic reaction. However, no matter what kind of lacunary heteropolymolybdate precursor is used, as yet lacunary heteropolymolybdates can not be isolated as free solid products. Only with the substitution of TMs into the lacunary sites, the lacunary heteropolymolybdate anions could be stabilized and were generally crystallized as sandwich-type heteropolymolybdates either in an separated clusters or in extended chain-like structures. Although major progress has been achieved in this area, there have been limited reports on this topic, so it is still a great challenge to develop new strategies for discovering novel lacunary building blocks in the labile heteropolymolybdate system.

Apart from the designable syntheses and the structural characterization, interesting physicochemical properties of the assembled heteropolymolybdate anions should also be demonstrated, including reversible redox properties, magnetic and electrical properties, *etc.* The efficient operation of modification and functionalization can stabilize some labile polyoxomolybdate systems, which allows adjusting their acid–base property and solubility in different solvents. As outlined, organic groups and coordination assemblies could be introduced to modify the polymolybdate frameworks for the sake of tuning their properties, which might improve the efficiency and the selectivity in some important catalytic reactions, especially some oxidation and epoxidation reactions.

Finally, perspectives of the research with functional polymolybdates that remain to be addressed include the following questions: (i) what is the key factor in controlling the formation of lacunary heteropolymolybdate ions and how does it affect the formation? (ii) Can other types of vacant heteropolymolybdate ions, such as XMo_{10} , XMo_8 , XMo_6 , XMo_5 , ..., be obtained through rational

control reaction parameters? (iii) How to make labile building blocks stable in solution and active in reaction? (iv) How to select suitable chemical groups to functionalize the polymolybdate frameworks? (v) How to create new functional materials by coordination assembly of the labile polymolybdate with TM or lanthanide ions? Overall, although it is still difficult to develop the complex polymolybdate system, there are many attractive opportunities to be explored by the researchers. Depending on both the interdisciplinary research and the advanced analysis techniques, an exciting progress in synthesis chemistry and functional materials will arrive in the near future for the polyoxomolybdate system of polyoxometalate chemistry.

Acknowledgements

This project is financially supported by the Natural Science Foundation of China (Grant No. 20731002, 20971019, and 21001021) and Science Foundation for Young Teachers of Northeast Normal University (Grant No. 20090403).

References

- 1 M. T. Pope and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
- 2 J. T. Rhule, C. L. Hill and D. A. Judd, *Chem. Rev.*, 1998, **98**, 327.
- 3 M. T. Pope, *Isopolyanions and Heteropolyanions, Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 3, pp. 1023–1058.
- 4 D. L. Long, R. Tsunashima and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1736.
- 5 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983.
- 6 S. Q. Liu, D. G. Kurth, H. Mohwald and D. Volkmer, *Adv. Mater.*, 2002, **14**, 225.
- 7 Y. B. Xie, *Adv. Funct. Mater.*, 2006, **16**, 1823.
- 8 M. A. Al-Damen, J. M. Clemente-Juan, E. Coronado, C. Marti-Gastaldo and A. Gaita-Ariño, *J. Am. Chem. Soc.*, 2008, **130**, 8874.
- 9 H. Yanagie, A. Ogata, S. Mitsui, T. Hisa, T. Yamase and M. Eriguchi, *Biomed. Pharmacother.*, 2006, **60**, 349.
- 10 A. Ogata, H. Yanagie, E. Ishikawa, Y. Morishita, S. Mitsui, A. Yamashita, K. Hasumi, S. Takamoto, T. Yamase and M. Eriguchi, *Br. J. Cancer*, 2008, **98**, 399.
- 11 I. V. Kozhevnikov, *Chem. Rev.*, 1998, 171–198.
- 12 N. M. Okun, T. Anderson and C. L. Hill, *J. Mol. Catal.*, 2003, **197**, 283.
- 13 K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi and N. Mizuno, *Science*, 2003, **300**, 964.
- 14 A. M. Khenkin and R. Neumann, *J. Am. Chem. Soc.*, 2002, **124**, 4198.
- 15 E. F. Kozhevnikova and I. V. Kozhevnikov, *J. Catal.*, 2004, **224**, 164.
- 16 P. Kögerler, B. Tsukerblat and A. Müller, *Dalton Trans.*, 2010, **39**, 21.
- 17 J. Berzelius, *Poggendorff's Ann. Phys.*, 1826, **6**, 369.
- 18 Y. K. Lu, J. N. Xu, X. B. Cui, J. Jin, S. Y. Shi and J. Q. Xu, *Inorg. Chem. Commun.*, 2010, **13**, 46.
- 19 A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, 1837.
- 20 L. K. Yan, X. Lopez, J. J. Carbo, R. Sniatynsky, D. C. Duncan and J. M. Poblet, *J. Am. Chem. Soc.*, 2008, **130**, 8223.
- 21 A. F. Masters, S. F. Ghellu, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem.*, 1980, **19**, 3866.
- 22 W. B. Yang, C. Z. Lu and H. H. Zhuang, *J. Chem. Soc., Dalton Trans.*, 2002, 2879.
- 23 M. L. Niven, J. J. Cruywagen and J. B. Heyns, *J. Chem. Soc., Dalton Trans.*, 1991, 2007.
- 24 D. Hargman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 873.
- 25 J. Q. Xu, R. Z. Wang, G. Y. Yang, Y. H. Xing, D. M. Li, W. M. Bu, L. Ye, Y. G. Fan, G. D. Yang, Y. Xing, Y. H. Lin and H. Q. Jia, *Chem. Commun.*, 1999, 983.
- 26 D. R. Xiao, Y. Hou, E. B. Wang, S. T. Wang, Y. G. Li, L. Xu and C. W. Hu, *Inorg. Chim. Acta.*, 2004, **357**, 2525.

- 27 D. L. Long, P. Kögerler, L. J. Farrugia and L. Cronin, *Angew. Chem., Int. Ed.*, 2003, **42**, 4180.
- 28 A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Peters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath and C. Menke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2122.
- 29 H. N. Miras, G. J. T. Cooper, D. L. Long, H. Bögge, A. Müller, C. Stred and L. Cronin, *Science*, 2009, **327**, 72.
- 30 A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, C. Beuholt, P. Kögerler and C. Z. Lu, *Angew. Chem., Int. Ed.*, 1998, **37**, 1220.
- 31 A. Müller, E. Beckmann, H. Bögge, M. Schmidtman and A. Dress, *Angew. Chem., Int. Ed.*, 2002, **41**, 1162.
- 32 A. Müller, S. Q. N. Shah, H. Bögge and M. Schmidtman, *Nature*, 1999, **397**, 48.
- 33 E. F. Wilson, H. Abbas, B. J. Duncombe, C. Streb, D. L. Long and L. Cronin, *J. Am. Chem. Soc.*, 2009, **130**, 13876.
- 34 S. S. Mal and U. Kortz, *Angew. Chem., Int. Ed.*, 2005, **44**, 2.
- 35 B. S. Bassil, S. Nellutla, U. Kortz, A. C. Stowe, J. van Tol, N. S. Dalal, B. Keita and L. Nadjo, *Inorg. Chem.*, 2005, **44**, 2659.
- 36 S. Nellutla, J. van Tol, N. S. Dalal, L. H. Bi, U. Kortz, B. Keita, L. Nadjo, G. A. Khitrov and A. G. Marshall, *Inorg. Chem.*, 2005, **44**, 9795.
- 37 M. Sadakane, D. Tsukuma, M. H. Dickman, B. S. Bassil, U. Kortz, M. Capron and W. Ueda, *Dalton Trans.*, 2007, 2833.
- 38 B. Botar, P. Kogerler and C. L. Hill, *Inorg. Chem.*, 2007, **46**, 5398.
- 39 S. S. Mal, M. H. Dickman, U. Kortz, A. M. Todea, A. Merca, H. Bogge, T. Glaser, A. Muller, S. Nellutla, N. Kaur, J. van Tol, N. S. Dalal, B. Keita and L. Nadjo, *Chem.-Eur. J.*, 2008, **14**, 1186.
- 40 C. Pichon, A. Dollbecq, P. Mialane, J. Marrot, E. Rivière, M. Goral, M. Zynek, T. McCormac, S. A. Borshch, E. Zueva and F. Sécheresse, *Chem.-Eur. J.*, 2008, **14**, 3189.
- 41 S. T. Zheng, D. Q. Yuan, H. P. Jia, J. Zhang and G. Y. Yang, *Chem. Commun.*, 2007, 1858.
- 42 J. W. Zhao, H. P. Jia, J. Zhang, S. T. Zheng and G. Y. Yang, *Chem.-Eur. J.*, 2007, **13**, 10030.
- 43 S. T. Zheng, D. Q. Yuan, J. Zhang and G. Y. Yang, *Inorg. Chem.*, 2007, **46**, 4569.
- 44 C. M. Wang, S. T. Zheng and G. Y. Yang, *Inorg. Chem.*, 2007, **46**, 616.
- 45 J. W. Zhao, J. Zhang, S. T. Zheng and G. Y. Yang, *Inorg. Chem.*, 2007, **46**, 10944.
- 46 S. T. Zheng, J. Zhang and G. Y. Yang, *Angew. Chem., Int. Ed.*, 2008, **47**, 3909.
- 47 S. T. Zheng, J. Zhang, J. M. Clemente-Juan, D. Q. Yuan and G. Y. Yang, *Angew. Chem., Int. Ed.*, 2009, **48**, 7176.
- 48 Z. M. Zhang, Y. F. Qi, C. Qin, Y. G. Li, E. B. Wang, X. L. Wang, Z. M. Su and L. Xu, *Inorg. Chem.*, 2007, **46**, 8162.
- 49 Z. M. Zhang, S. Yao, Y. G. Li, Y. H. Wang, Y. F. Qi and E. B. Wang, *Chem. Commun.*, 2008, 1650.
- 50 C. P. Pradeep, D. L. Long, P. Kogerler and L. Cronin, *Chem. Commun.*, 2007, 4254.
- 51 L. Ruhlmann, J. Canny, J. Vaissermann and R. Thouvenot, *Dalton Trans.*, 2004, 794.
- 52 A. X. Tian, J. Ying, J. Peng, J. Q. Sha, Z. G. Han, J. F. Ma, Z. M. Su, N. H. Hu and H. Q. Jia, *Inorg. Chem.*, 2008, **47**, 3274.
- 53 P. Q. Zheng, Y. P. Ren, L. S. Long, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2005, **44**, 1190.
- 54 X. J. Kong, Y. P. Ren, P. Q. Zheng, Y. X. Long, L. S. Long, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2006, **45**, 10702.
- 55 Y. P. Ren, X. J. Kong, X. Y. Hu, M. Sun, L. S. Long, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2006, **45**, 4016.
- 56 J. Q. Sha, J. Peng, Y. Q. Lan, Z. M. Su, H. J. Pang, A. X. Tian, P. P. Zhang and M. Zhu, *Inorg. Chem.*, 2008, **47**, 5145.
- 57 L. C. W. Baker and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, 1966, **28**, 447.
- 58 R. C. Haushalter and F. W. Lai, *Inorg. Chem.*, 1989, **28**, 2904.
- 59 J. P. Wang, J. W. Zhao, P. T. Ma, J. C. Ma, L. P. Yang, Y. Bai, M. X. Li and J. Y. Niu, *Chem. Commun.*, 2009, 2362.
- 60 R. Strandberg, *Acta Chem. Scand.*, 1973, **27**, 1004.
- 61 Y. C. Bai, L. P. Liu, X. J. Yan, W. Chu, Y. Y. Zhu, Y. T. Song and R. D. Huang, *J. Solid State Chem.*, 2009, **182**, 89.
- 62 K. I. Matveev, E. G. Zhizhina, N. B. Shitova and L. I. Kuznetsova, *Kinet. Katal.*, 1977, **18**, 380.
- 63 I. V. Kozhevnikov, *J. Mol. Catal. A*, 1997, **117**, 151.
- 64 M. Misono and N. Nojiri, *Appl. Catal.*, 1990, **64**, 1.
- 65 J. Etdedgui and R. Neumann, *J. Am. Chem. Soc.*, 2009, **131**, 4.
- 66 W. B. Kim, T. Voigt, G. J. Rodriguez-Rivera and J. A. Dumesic, *Science*, 2004, **305**, 1280.
- 67 L. A. Combs-Walker and C. L. Hill, *Inorg. Chem.*, 1991, **30**, 4016.
- 68 A. Müller, E. Krickemeyer, S. Dillinger, J. Meyer, H. Bögge and A. Stammler, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 171.
- 69 A. Müller, E. Krickemeyer, M. Penk, V. Wittneben and J. Döring, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 88.
- 70 E. G. Fidalgo, A. Neels, H. Stoeckli-Evans and G. Süss-Fink, *Polyhedron*, 2002, **21**, 1921.
- 71 H. F. Fukushima, A. Kobayashi and Y. Sasaki, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1981, **37**, 1613.
- 72 Y. K. Shan, Z. X. Liu, B. E. Wang, Z. S. Jin, G. C. Wei and Y. S. Liu, *Jiegou Huaxue*, 1990, **9**, 159.
- 73 E. B. Wang, Y. K. Shan, Z. X. Zu, J. F. Liu and B. G. Zhang, *Acta Chim Sin.*, 1991, **49**, 774.
- 74 Y. K. Shan, Z. X. Liu, Z. S. Jin and G. C. Wei, *Acta Chim Sin.*, 1992, **50**, 357.
- 75 A. J. Gaunt, I. May, M. J. Sarsfield, D. Collison, M. Helliwell and I. S. Denniss, *Dalton Trans.*, 2003, 2767.
- 76 R. Copping, A. J. Gaunt, I. May, M. J. Sarsfield, D. Collison, M. Helliwell, I. S. Denniss and D. C. Apperley, *Dalton Trans.*, 2005, 1256.
- 77 Y. Y. Yang, L. Xu, G. G. Gao, F. Y. Li, Y. F. Qiu, X. S. Qu and H. Liu, *Eur. J. Inorg. Chem.*, 2007, 3405.
- 78 Y. Y. Yang, L. Xu, G. G. Gao, F. Y. Li, X. Z. Liu and W. H. Guo, *Eur. J. Inorg. Chem.*, 2009, 1460.
- 79 Y. Y. Yang, L. Xu, G. G. Gao, F. Y. Li, X. S. Qu and W. H. Guo, *J. Mol. Struct.*, 2008, **886**, 85.
- 80 L. L. Zhao, X. Z. Luo, L. Xu, N. Jiang, F. Y. Li and Y. G. Li, *Inorg. Chem. Commun.*, 2010, **13**, 554.
- 81 G. G. Gao, F. Y. Li, L. Xu, X. Z. Liu and Y. Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 10838.
- 82 G. G. Gao, L. Xu, W. J. Wang, X. S. Qu, H. Liu and Y. Y. Yang, *Inorg. Chem.*, 2008, **47**, 2325.
- 83 G. G. Gao, L. Xu, X. S. Qu, H. Liu and Y. Y. Yang, *Inorg. Chem.*, 2008, **47**, 3402.
- 84 W. J. Wang, L. Xu, G. G. Gao, L. Liu and X. Z. Liu, *CrystEngComm*, 2009, **11**, 2488.
- 85 L. L. Li, Q. Sheng, G. L. Xue, H. S. Xu, H. M. Hu, F. Fu and J. W. Wang, *Dalton Trans.*, 2008, 5698.
- 86 H. S. Xu, L. L. Li, B. Liu, G. L. Xue, H. M. Hu, F. Fu and J. W. Wang, *Inorg. Chem.*, 2009, **48**, 10275.
- 87 S. Z. Li, J. W. Zhao, P. T. Ma, J. Du, J. Y. Niu and J. P. Wang, *Inorg. Chem.*, 2009, **48**, 9819.
- 88 J. C. Jeffery, P. Thornton and M. D. Ward, *Inorg. Chem.*, 1994, **33**, 3612.
- 89 H. R. Chang, S. K. Larsen, P. D. W. Boyd, C. G. Pierpont and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1988, **110**, 4546.
- 90 M. Wesolek, D. Meyer, J. A. Osborn, A. Cian, J. Fischer, A. Derory, P. Legoll and M. Drillon, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1592.
- 91 T. J. R. Weakley, H. T. Evans Jr., J. S. Showell, G. F. Tourné and C. M. Tourné, *J. Chem. Soc., Chem. Commun.*, 1973, 139.
- 92 I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold and K. Meyer, *Science*, 2004, **305**, 1757.
- 93 C. H. Lee, D. S. Laiter, P. Mueller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2007, **129**, 13802.
- 94 J. Y. Niu, Z. L. Wang and J. P. Wang, *Inorg. Chem. Commun.*, 2003, **6**, 1272.
- 95 V. Coué, R. Desapt, M. Bujoli-Doeuff, M. Evain and S. Jobic, *Inorg. Chem.*, 2007, **46**, 2824.
- 96 A. Proust, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2008, 1837.
- 97 C. P. Pradeep, M. F. Misdrabi, F. Y. Li, J. Zhang, L. Xu, D. L. Long, T. B. Liu and L. Cronin, *Angew. Chem., Int. Ed.*, 2009, **48**, 8309.
- 98 J. Li, I. Huth, L. M. Chamoreau, B. Hasenknopf, E. Lacôte, S. Thorimbert and M. Malacria, *Angew. Chem., Int. Ed.*, 2009, **48**, 2035.
- 99 This work will be published elsewhere in the near future.
- 100 W. Kwak, M. T. Pope and T. F. Scully, *J. Am. Chem. Soc.*, 1975, **97**, 5753.
- 101 R. C. Finn and J. Zubieta, *Inorg. Chem.*, 2001, **40**, 2466.
- 102 R. C. Finn, E. Burkholder and J. Zubieta, *Chem. Commun.*, 2001, 1852.
- 103 R. C. Finn, R. S. Raring Jr. and J. Zubieta, *Inorg. Chem.*, 2002, **41**, 2109.

- 104 E. Burkholder, V. Golub, C. J. O'Connor and Zubieta, *Inorg. Chem.*, 2004, **43**, 7014.
- 105 N. G. armadas, D. G. Allis, A. Prosvirin, G. Carnutu, C. J. O'Connor, K. Dunbar and J. Zubieta, *Inorg. Chem.*, 2008, **47**, 832.
- 106 U. Kortz, C. Marquer, R. Thouvenot and M. Nierlich, *Inorg. Chem.*, 2003, **42**, 1158.
- 107 M. Carraro, A. Sartorel, G. Scorrano, C. Maccato, M. H. Dickman, U. Kortz and M. Bonchio, *Angew. Chem., Int. Ed.*, 2008, **47**, 7275.
- 108 D. Slobada-Rozner, K. Neimann and R. Neumann, *J. Mol. Catal. A*, 2007, **262**, 109.
- 109 P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2002, **41**, 2398.
- 110 A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot and F. Sécheresse, *Chem.–Eur. J.*, 2003, **9**, 2914.
- 111 A. Dolbecq, C. Mellot-Draznieks, P. Mialane, J. Marrot, G. Férey and F. Sécheresse, *Eur. J. Inorg. Chem.*, 2005, 3009.
- 112 F. Cavani, M. Koutyrev and F. Trifiro, *Catal. Today*, 1995, **24**, 365.
- 113 F. Cavani, M. Koutyrev and F. Trifiro, *Catal. Today*, 1996, **28**, 319.
- 114 Q. B. Zhang, Y. K. Lu, Y. B. Liu, J. Lu, M. H. Bi, J. H. Yu, T. G. Wang, J. Q. Xu and J. Liu, *Inorg. Chem. Commun.*, 2006, **9**, 544.
- 115 S. Y. Shi, Y. H. Sun, Y. Chen, J. N. Xu, X. B. Cui, Y. Wang, G. W. Wang, G. D. Yang and J. Q. Xu, *Dalton Trans.*, 2010, **39**, 1389.
- 116 This work will be published elsewhere in the near future.