

## III-I Structure and Properties of Polyoxometalates with a Magnetic, Electronic, or Biological Significance

Polyoxometalates constitute model systems for the study of the electron and energy transfer in the infinite metal-oxide lattice and their simplicity allows to treat at the molecular scale the coupling of electronic and nuclear movements, which is an inherent problem for the mixed-valence systems. As is clear from such a variety of both structure and reactivity of polyoxometalates, our current works on polyoxometalates are 1) structure/reactivity relationships with particular regard to the mechanism of electron transfer reactions, 2) magnetic interaction and molecular magnetic device, 3) energy-transfer mechanism and luminescence device (including nonlinear optical device), 4) encapsulation of templates in the photo-induced self-assembly process, 5) template-exchange reaction and topology, and 6) antibacterial effects on methicillin-resistant *Staphylococcus aureus* (MRSA) and human gastric pathogen of *Helicobacter pylori*.

### III-I-1 Synthesis and Crystal Structure of a Novel Vanadium-Containing Tungstobismutate(III) $K_{12}[(VO)_3(BiW_9O_{33})_2] \cdot 30H_2O$

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The tris(vanadyl)-substituted tungstobismutate(III)  $[(VO)_3(BiW_9O_{33})_2]^{12-}$  anion has been synthesized by reaction of  $\alpha-B[BiW_9O_{33}]^{9-}$  with  $VOSO_4$  in aqueous solution. The anion is made of two  $\alpha-B[BiW_9O_{33}]^{9-}$  unit linked by a belt of three exterior  $VO^{2+}$  groups into an assembly of virtual  $D_{3h}$  symmetry. The three vanadium centers are well separated by  $V \cdots V$  distance of 5.375(4)–5.474(4) Å.

### III-I-2 Crystallization and Structural Characterization of Two Europium Molybdates, $Eu_4Mo_7O_{27}$ and $Eu_6Mo_{10}O_{39}$

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Crystals of two new europium molybdates,  $Eu_4Mo_7O_{27}$  and  $Eu_6Mo_{10}O_{39}$ , were grown in a melt of  $Eu_2O_3 \cdot 6.1\text{--}6.5MoO_3$  obtained by thermal decomposition of  $[Eu_2(H_2O)_{12}Mo_8O_{27}] \cdot 6H_2O$  or firing of the  $Eu_2O_3 + 8MoO_3$  mixture at 800 °C for 2 h in air. Repeated uses of reaction containers are effective in the crystallization.  $Eu_4Mo_7O_{27}$  crystallized in monoclinic,  $C2/c$  (No. 15),  $a = 23.031(1)$ ,  $b = 14.720(1)$ ,  $c = 14.4097(7)$  Å,  $\beta = 105.174(2)^\circ$ ,  $V = 4714.8(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_I = 0.035$ , and  $wR_2 = 0.064$ .  $Eu_4Mo_7O_{27}$  is a layer compound consisting of  $\{MoO_4\}$ - and  $\{Mo_3O_{11}\}$ -containing layers parallel to the  $bc$  plane and interstitial Eu atoms.  $Eu_6Mo_{10}O_{39}$  crystallized in monoclinic,  $C2/c$  (No. 15),  $a = 12.3008(5)$ ,  $b = 19.6596(9)$ ,  $c = 13.7691(47)$  Å,  $\beta = 100.8934(9)^\circ$ ,  $V = 3269.8(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_I = 0.036$ , and  $wR_2 = 0.101$ . The structure of  $Eu_6Mo_{10}O_{39}$  is constructed of three-dimensionally arranged  $\{MoO_4\}$  and  $\{Mo_2O_7\}$  groups and Eu atoms, being closely related to the structure of  $Ce_6Mo_{10}O_{39}$ . In both compounds, Eu

atoms achieve seven- or eight-fold coordination by O atoms ( $< 2.7$  Å), and two  $EuO_n$  polyhedra share their edges or faces with a short  $Eu \cdots Eu$  separation ranging from 3.6297(8) to 3.7168(6) Å.

### III-I-3 Nanocluster Crystals of Lacunary Polyoxometalates as Structure-Design-Flexible, Inorganic Nonlinear Materials

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Lacunary polyoxometalates, large inorganic, structure-design-flexible, nanocluster crystals are found to have optical nonlinearity than  $KH_2PO_4$  by the powder second-harmonic-generation method. Moreover, the capability of generating ultraviolet radiation down to around 300 nm is found. The basic criteria to design the high nonlinearity are also discovered by the reduction of the molecular symmetry.

### III-I-4 A Three-Dimensional Inorganic/Organic Hybrid Vanadium Oxide Complex with Pentacoordinate $Co^{II}$ , $[CoV_2O_6(4,4'-bipy)]$

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The title compound, poly{[cobalt(II)- $\mu$ -(hexaaxodivandium- $O:O'$ )]- $\mu$ -bipyridine- $N:N'$ },  $[CoV_2O_6(C_{10}H_8N_2)]$ , has been prepared hydrothermally and characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. The structure consists of bimetallic oxide layers,  $[Co_2V_4O_{12}]$ , linked through 4,4'-bipyridine ligands into a three-dimensional network.

**III-I-5 Tb<sub>2</sub>Mo<sub>4</sub>O<sub>15</sub>**

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The title compound, tetramolybdenum(VI) dterbate (III), was prepared by pyrolysis of Tb<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>Mo<sub>8</sub>O<sub>27</sub>·6H<sub>2</sub>O at 1023 K for 2 h in air. The structure consists of trigonal bipyramidal MoO<sub>5</sub>, tetrahedral MoO<sub>4</sub>, and monocapped trigonal prismatic TbO<sub>7</sub> units. The two MoO<sub>5</sub> and two MoO<sub>4</sub> units are corner-shared, to form a Mo<sub>4</sub>O<sub>15</sub> group.

**III-I-6 H<sub>2</sub>O<sub>2</sub>-Based Epoxidation of Bridged Cyclic Alkenes with [P{Ti(O<sub>2</sub>)<sub>2</sub>W<sub>10</sub>O<sub>38</sub>}]<sup>7-</sup> in Monophasic Systems: Active Site and Kinetics**

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The H<sub>2</sub>O<sub>2</sub>-based epoxidation of bridged cyclic alkenes in a monophasic system containing low concentrations (< 2 mM) of [Bu<sup>n</sup><sub>4</sub>N]<sub>4</sub>[Pr<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>H[P{Ti(O<sub>2</sub>)<sub>2</sub>W<sub>10</sub>O<sub>38</sub>}]<sub>2</sub>·H<sub>2</sub>O (**1**) (with two η<sup>2</sup>-peroxotitanium sites in the anion) has been studied in search of the catalytically active species involved. <sup>31</sup>P-NMR spectra of **1**, measured under a variety of conditions, revealed that the active species was not hydroperoxotitanium complex [P{Ti(OOH)}<sub>2</sub>W<sub>10</sub>O<sub>38</sub>]<sup>7-</sup> or [P{Ti(OOH)}Ti(O<sub>2</sub>)W<sub>10</sub>O<sub>38</sub>]<sup>7-</sup>. The reaction pathways for the alkene epoxidation are discussed to understand the kinetics (especially the initial [H<sub>2</sub>O<sub>2</sub>] dependence). It was concluded that the net catalytic reaction for the epoxidation occurred through the two-electron oxidation at the hydroperoxotitanium site in the catalyst.

**III-I-7 Photochemical Formation of a Lacunary Tire-Shaped Anion, [Mo<sub>142</sub>O<sub>432</sub>H<sub>26</sub>(H<sub>2</sub>O)<sub>58</sub>]<sup>14-</sup>, through Degradative Self-Assembly of [Mo<sub>36</sub>O<sub>112</sub>(H<sub>2</sub>O)<sub>16</sub>]<sup>8-</sup>: Topology of Ring-Structural Molybdenum Blues**

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A diamagnetic blue 28-electron reduced species [Mo<sup>V</sup><sub>28</sub>Mo<sup>VI</sup><sub>114</sub>O<sub>432</sub>H<sub>26</sub>(H<sub>2</sub>O)<sub>58</sub>]<sup>12-</sup> ({Mo<sub>142</sub>}) was produced photochemically through the degradative self-assembly of [Mo<sub>36</sub>O<sub>112</sub>(H<sub>2</sub>O)<sub>16</sub>]<sup>8-</sup> ({Mo<sub>36</sub>}). The molybdenum blue photochemistry favors not only the mechanistic investigation of the degradation self-assembly processes but also provides a basis for the molecular design of nano-sized ring clusters.

**III-I-8 Size-dependent Population of Trivalent Rare Earth Cations (RE<sup>3+</sup>) in [(RE)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(SbW<sub>9</sub>O<sub>33</sub>)(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>15-</sup>, and Structural Characterization of a Lutetium-Polyoxotungstate Complex [Lu<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>21-</sup>**

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The effect of ionic radius of trivalent rare earth cations (RE<sup>3+</sup>) on the population at two square-antiprismatic sites (*Site I* and *Site II*) in [(RE)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(SbW<sub>9</sub>O<sub>33</sub>)(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>15-</sup> was studied by luminescence spectroscopic and X-ray crystallographic measurements in the Eu/Y- and Eu/Lu-mixed systems. The results indicated that a small RE<sup>3+</sup> cation favorably occupies *Site II* where RE<sup>3+</sup> is coordinated by four bridging O atoms of [SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> and four terminal O atoms of [W<sub>5</sub>O<sub>18</sub>]<sup>6-</sup>. With the help of a structural characterization of pure [(RE)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(SbW<sub>9</sub>O<sub>33</sub>)(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>15-</sup> (RE = Er, Y, Dy, Eu, Sm), the large occupancy of small RE<sup>3+</sup> at *Site II* was explained by a favorable coordination of [SbW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> for small RE<sup>3+</sup>. A trial of the isostructural Lu complex unexpectedly showed formation of a novel [Lu<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>(SbW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>21-</sup> complex which consists of two [Lu(SbW<sub>9</sub>O<sub>33</sub>)(W<sub>5</sub>O<sub>18</sub>)]<sup>12-</sup> groups linked by [Lu(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup> with C<sub>2</sub> configuration.

**III-I-9 Gd<sub>4</sub>Mo<sub>7</sub>O<sub>27</sub>, a Novel Phase in the Gd<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> System**

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The title compound, heptamolybdenum(VI) tetragadolinate(III), a novel phase in the Gd<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> system, has been prepared by pyrolysis of [Gd<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>·Mo<sub>8</sub>O<sub>27</sub>]<sub>2</sub>·6H<sub>2</sub>O at 1023 K for 2 h in air. The compound can be described as a layer structure consisting of [MoO<sub>4</sub>]-, [Mo<sub>3</sub>O<sub>11</sub>]-, and [Gds]-containing layers, which are stacked along the *a* direction. The coordination polyhedra of square-antiprismatic GdO<sub>8</sub> and monocapped trigonal prismatic GdO<sub>7</sub> are dimerized to give [Gd<sub>2</sub>O<sub>*n*</sub>] (*n* = 12 and 13) groups which possess short Gd···Gd separation [3.6345(4)–3.6404(4) Å].

**III-I-10 Time-Resolved ESR-Spectroscopic Investigation of Polyoxometalate Photochemistry**

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The time-resolved ESR spectroscopy is based on the detection of electron spin polarization (ESP) which let us enable to investigate the dynamics of the photochemically produced radicals. After a brief qualitative

and conceptual review of time-resolved ESR spectroscopy, exemplar photoredox reactions of polyoxometalates are discussed based on the observable chemically-induced-dynamic-electron -polarization (CIDEP) spectra which can be explained by the triplet mechanism.