III-J 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-J-1 A Highly Nuclear Vanadium-Containing Tungstobismutate: Synthesis and Crystal Structure of $K_{11}H[(BiW_9O_{33})_3Bi_6(OH)_3(H_2O)_3V_4O_{10}]\cdot 28H_2O$

BOTAR, Bogdan; YAMASE, Toshihiro; ISHIKAWA, Eri
(IMS and Tokyo Inst. Tech.)

[*Inorg. Chem. Commun.* **3**, 578 (2000)]

A novel and large heteropolyanion $[(BiW_9O_{33})_3Bi_6(OH)_3(H_2O)_3V_4O_{10}]^{12-}$ has been synthesized by reaction of sodium metavanadate with $Na_9[BiW_9O_{33}]\cdot 16H_2O$ in acetate buffer solutions (at pH 4.8). The present anion has a trilobal structure in which three α-B $[BiW_9O_{33}]$ units are connected to each other by an unique core $[Bi_6(OH)_3(H_2O)_3V_4O_{10}]^{15+}$. A central bismutate/vanadate-mixed core comprises three sets of two types of the BiO_6 pentagonal pyramid, the edge-sharing VO_5 square-pyramidal triad, and a VO_4 tetrahedron.

III-J-2 Photochemical Self-Assembly Reaction of β-$[Mo_8O_{26}]^{4-}$ to Mixed-Valence Cluster $[Mo_{37}O_{112}]^{26-}$ in Aqueous Media

YAMASE, Toshihiro; ISHIKAWA, Eri
(IMS and Tokyo Inst. Tech.)

[*Langmuir* **16**, 9023 (2000)]

Prolonged photolysis of β-$[Mo_8O_{26}]^{4-}$ in the presence of electron-donative MeOH in aqueous solutions at pH 3.3 provides stepwise self-organization to paramagnetic reddish-brown mixed-valence species $[H_{14}Mo^{V}{}_{24}Mo^{VI}{}_{13}O_{112}]^{12-}$. The X-ray structural analysis of the reddish brown crystals, isolated as $[NMe_4]^+$ salt, shows that $[H_{14}Mo^{V}{}_{24}Mo^{VI}{}_{13}O_{112}]^{12-}$ anion consists of a central T_d $[H_{10}(Mo^{V}{}_{12}O_{40})(Mo^{VI}O_2)_3]^{4-}$ core sandwiched by two $[H_2Mo^{V}{}_6Mo^{VI}{}_5O_{33}]^{4-}$ ligands, with overall symmetry of D_{2d}. The central $\{Mo^{V}{}_{12}O_{40}\}$ subcore (with six short Mo^V–Mo^V contacts, 2.56(1) and 2.625(7) Å) is a tetrahedral ε-Keggin structure with a cavity (in the size of ~3.3 Å) accommodating four protons, and is stabilized by capture of four $\{Mo^{VI}O_2\}$ groups with 3/4 occupancy. The $\{Mo^{V}{}_6Mo^{VI}{}_5O_{33}\}$ framework as the ligand consists of two sets of a dinuclear $\{Mo^{V}{}_2O_4\}$ pair with a $Mo^V\cdots Mo^V$ distance of 2.567(7) Å, two sets of the edge-shared $\{Mo^{VI}{}_2O_{10}\}$ octahedra, and three mononuclear groups of one $Mo^{VI}O$ and two Mo^VO_2. The Mo^V atoms in the two Mo^VO_2 groups in the ligand are separated with distance of 6.31(1) Å, being ESR-active ($\langle g \rangle = 1.909$, $g_\perp = 1.894$, and $g_{||} = 1.939$ at 77 K). The structure of the $[H_{14}Mo^{V}{}_{24}Mo^{VI}{}_{13}O_{114}]^{12-}$ anion is slightly different from the diamagnetic species $\{[H_6Mo^{VI}{}_2O_{40}(Mo^VO_3)_4]$-$[H_3Mo^{V}{}_4Mo^{VI}{}_6O_{29}][H_5Mo^{V}{}_6Mo^{VI}{}_5O_{31}]\}^{14-}$ prepared by thermal reduction of $[Mo_7O_{24}]^{6-}$ with $N_2H_4\cdot H_2SO_4$, in both structure and mixed-valency of the ligand. The stepwise self-assembly processes from β-$[Mo_8O_{26}]^{4-}$ to $[H_{14}Mo^{V}{}_{24}Mo^{VI}{}_{13}O_{114}]^{12-}$ are discussed in terms of the photochemical multi (six- and four-) electron reduction of β-$[Mo_8O_{26}]^{4-}$ which results in the splitting into $\{Mo_4\}$, $\{Mo_2\}$, and $\{Mo_1\}$ fragments.

III-J-3 A Spherical Potassium-Capped Vanadium Methylphosphonate as Another ε-Keggin Fragment, $[H_6KV_{12}O_{27}(VO_4)(PO_3CH_3)_3]^{5-}$

YAMASE, Toshihiro; MAKINO, Haruyo; NARUKE, Haruo; SAN JOSÉ WÉRY, Ana Maria
(IMS and Tokyo Inst. Tech.)

[*Chem. Lett.* 1350 (2000)]

An $[H_3KV_{12}O_{27}(AsO_4)_4]^{6-}$-isostructural ε-Keggin fragment anion, $[H_6KV_{12}O_{27}(VO_4)(PO_3CH_3)_3]^{5-}$, was photochemically prepared. This K^+-capped anion is formally built of nine $V^{IV}O_6$ octahedra, three PO_3C tetrahedra, and four V^VO_4 tetrahedra, one of the latter being a central $VO_4{}^{3-}$ group. The capping K^+ cation lies on the C_3 axis and links two adjacent anion, to form a linear chain of the anions along c-axis.

III-J-4 Chemical Structure and Intramolecular Spin-Exchange Interaction of $[(VO)_3(SbW_9O_{33})_2]^{12-}$

YAMASE, Toshihiro; BOTAR, Bogdan; ISHIKAWA, Eri; FUKAYA, Keisuke
(IMS and Tokyo Inst. Tech.)

[*Chem. Lett.* 56 (2001)]

The crystal structure determination of tris(vanadyl)-substituted tungstoantimonate(III) $K_{11}H[(VO)_3(SbW_9$-

$O_{33})_2]\cdot 27H_2O$ reveals that the $[(VO)_3(SbW_9O_{33})_2]^{12-}$ anion contains three exterior VO^{2+} groups sandwiched by two α-B $[SbW_9O_{33}]^{9-}$ ligands in $V^{IV}\cdots V^{IV}$ separation of 5.411(8)–5.464(8) Å and is stabilized by equatorial three K^+ ions triangle with virtual D_{3h} symmetry. An observable spin-exchange interaction between V^{IV} centers within the vanadyl coplanar triangle is demonstrated in terms of $S = 1/2$ and $S = 3/2$ states.

III-J-5 Synthesis and Structure of $Ln(W_5O_{18})$-Capped Mixed-Ligand Polyoxotungstolanthanoate $[Ln(W_5O_{18})\{Ln(H_2O)_2(SbW_9O_{33})(W_5O_{18})\}]^{15-}$ (Ln = Sm and Er)

NARUKE, Haruo; YAMASE, Toshihiro
(IMS and Tokyo Inst. Tech.)

[*Bull. Chem. Soc. Jpn.* **74**, 1289 (2001)]

Polyoxotungstolanthanoate, $[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (Ln = Sm and Er), possessing Ln^{3+}, trivacant α-B-Keggin $[SbW_9O_{33}]^{9-}$, and monovacant Lindqvist $[W_5O_{18}]^{6-}$ groups with a ratio of 2:1:2, was prepared and structurally characterized. In the anion the α-B-$[SbW_9O_{33}]^{9-}$ group coordinates to two $[Ln(W_5O_{18})]^{3-}$ moieties through terminal- and bridging-O atoms at vacant and non-vacant sites, respectively. A ^{183}W-NMR spectrum for Y^{3+}-analog in aqueous solution was consistent with this anion structure.

III-J-6 Three-Dimensional Inorganic/Organic Hybrid Material, $[Ni_2(4,4'\text{-}bipy)_3(H_2O)_2V_4O_{12}]\cdot 2.5H_2O$

YANG, Lan; HU, Changwen; NARUKE, Haruo; YAMASE, Toshihiro
(IMS and Tokyo Inst. Tech.)

[*Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **57**, 799 (2001)]

The title compound has been prepared by hydrothermal method and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The structure consists of $\{V_2O_6\}$, $\{Ni(1)(4,4'\text{-}bipy)_4O_2\}$ and $\{Ni(2)(H_2O)_2(4,4'\text{-}bipy)_2O_2\}$ polyhedra, and water molecules of crystallization. The Ni atoms and one bipyridyl group lie on centers of symmetry.

III-J-7 Molecular Aspect of Energy Transfer from Tb^{3+} to Eu^{3+} in Polyoxometalate Lattices: An Approach for Molecular Design of Rare-Earth Metal-Oxide Phosphors

YAMASE, Toshihiro
(IMS and Tokyo Inst. Tech.)

[*Polyoxometallates: From Topology to Industrial Applications* M. T. Pope and A. Müller, Eds., Kluwer Academic Publishers, pp. 187–203 (2001)]

The exploitation of mixed heteronuclear rare-earth-element-containing polyoxometalates to probe the multipolar nature of heteronuclear rare-earth interactions is imaginative. It appears that polyoxometallolanthanoates are ideal for this type of investigation. Three structural types of Tb^{3+}/Eu^{3+} heterolanthanide-multinuclear polyoxometalates, $K_{15}H_3[Tb_{1.4}Eu_{1.6}(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$, $Na_7H_{19}[Tb_{4.3}Eu_{1.7}O_2(OH)_6(H_2O)_6Al_2(Nb_6O_{19})_5]\cdot 47H_2O$, and $[NH_4]_{12}H_2[Tb_{3.1}Eu_{0.9}(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 13H_2O$ are studied by crystal structures, emission and excitation spectra, and emission decay dynamics. The excitation of the Tb^{3+} $^7F_6 \to {}^5D_4$ transitions produces not only the emission lines of Tb^{3+}, but also those of Eu^{3+}, accompanied by nonexponential rise and decay curves of the emission from Tb^{3+} and Eu^{3+}. There is no significant exchange interaction between the lanthanide ions, as a result of the coordination of aqua and/or hydroxo ligands to the lanthanide ions. The mechanism of the $Tb^{3+} \to Eu^{3+}$ energy transfer is identified as a Förster-Dexter-type energy transfer from Tb^{3+} (donor) to Eu^{3+} (acceptor). The nearest-neighbor energy-transfer rates by electric dipole-dipole interactions between a Tb-Eu pair at 4.2 K are estimated to be 4.5×10^4, 4.7×10^5, and 4.9×10^3 s^{-1} and the critical radii at 4.2 K are 10.3, 10.0, and 6.17 Å for $K_{15}H_3[Tb_{1.4}Eu_{1.6}(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$ (with Tb-Eu separation of 5.05 Å), $Na_7H_{19}[Tb_{4.3}Eu_{1.7}O_2(OH)_6(H_2O)_6Al_2(Nb_6O_{19})_5]\cdot 47H_2O$ (with 3.76 Å separation), and $[NH_4]_{12}H_2[Tb_{3.1}Eu_{0.9}(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 13H_2O$ (with 6.17 Å separation), respectively. The low symmetry (C_s or C_1) of the LnO_8 (Ln = Tb and Eu) coordination polyhedra allows the nonvanishing electric-dipole transition probability for the $^7F_J \leftrightarrow {}^5D_0$ (J = 0, 1) transitions which leads to a faster transfer rate at high temperatures. The photoexcitation of the host lattices (tungstate, niobate, and molybdate) induced the energy transfer from the oxygen-to-metal charge-transfer {O → M (= Nb, Mo, W) lmct} triplet states to Tb^{3+} ($^7F_6 \to {}^5D_4$) and Eu^{3+} ($^7F_{0,1,2} \to {}^5D_{0,1}$). In the case of $[NH_4]_{12}H_2[Tb_{3.1}Eu_{0.9}(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 13H_2O$ this transfer is not complete and the O → Mo lmct triplet emission of molybdates is observed to provide the rate constant for the energy transfer to Tb^{3+}/Eu^{3+} sites with 4.4×10^6 s^{-1}.