III-K 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 MRSA and VRE.

III-K-1 Luminescence and Energy Transfer Phenomena in Tb^{3+}/Eu^{3+}-Mixed Polyoxometallolanthanoates $K_{15}H_3[Tb_{1.4}Eu_{1.6}(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$ and $Na_7H_{19}[Tb_{4.3}Eu_{1.7}O_2(OH)_6(H_2O)_6Al_2(Nb_6O_{19})_5]\cdot 47H_2O$

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The energy dissipation of Tb^{3+}/Eu^{3+} cations in both heterolanthanide-multinuclear polyoxometalates, $K_{15}H_3[Tb_{1.4}Eu_{1.6}(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]\cdot 25.5H_2O$ and $Na_7H_{19}[Tb_{4.3}Eu_{1.7}O_2(OH)_6(H_2O)_6Al_2(Nb_6O_{19})_5]\cdot 47H_2O$ is studied by crystal structures, emission and excitation spectra, and emission decay dynamics. The excitation of the Tb^{3+} $^7F_6{}^5 \rightarrow D_4$ 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 lantahanide ions. The mechanism of the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is identified as a Föster-Dexter-type energy transfer from Tb^{3+} (donor) to Eu^{3+} (acceptor). At low temperatures $^5D_4$(Tb) + $^7F_0$(Eu) $\rightarrow$ $^7F_4$(Tb) + $^5D_0$(Eu) governs the transfer process and at high temperatures it is governed by $^5D_4$(Tb) + $^7F_1$(Eu) $\rightarrow$ $^7F_5$(Tb) + $^5D_1$(Eu), $^5D_4$(Tb) + $^7F_1$(Eu) $\rightarrow$ $^7F_4$(Tb) + $^5D_0$(Eu), and $^5D_4$(Tb) + $^7F_2$(Eu) $\rightarrow$ $^7F_5$(Tb) + $^5D_1$(Eu) interactions which involve the thermally populated $^7F_1$ and $^7F_2$ levels. 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 and 4.7×10^5 s^{-1}, and the critical radii at 4.2 K are 10.3 and 10.0 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) and $Na_7H_{19}[Tb_{4.3}Eu_{1.7}O_2(OH)_6(H_2O)_6Al_2(Nb_6O_{19})_5]\cdot 47H_2O$ (with 3.76 Å separation), respectively. The low symmetry (C_s for the former and C_1 for the latter) of the LnO_8 (Ln = Tb and Eu) coordination polyhedra allows the nonvanishing electric-dipole transition probability for the $^7F_J \longleftrightarrow {}^5D_0$ (J = 0, 1) transitions which leads to a faster transfer rate at high temperatures.

III-K-2 Mixed-Valence Ammonium Trivanadate with a Tunnel Structure Prepared by Pyrolysis of Polyoxovanadate

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[*Bull. Chem. Soc. Jpn.* **72**, 2699 (1999)]

The pyrolysis of a polyoxovanadate solid, $(NH_4)_{12}[V_{18}O_{42}(H_2O)]\cdot nH_2O$ ($n \approx 11$), at 300 °C in an Ar + NH_3 atmosphere gave a mixed-valence vanadium oxide, $(NH_4)_xV_3O_7$ ($x \approx 0.6$), isostructural with $Cs_{0.37}V_3O_7$. The crystal structure of $(NH_4)_xV_3O_7$ was refined by the Rietveld method (hexagonal, P63/m, a = 9.8436(6), c = 3.6165(1) Å, V = 303.47(3) Å^3, Z = 2). $(NH_4)_xV_3O_7$ comprises edge- and corner-sharing $V^{IV/V}O_5$ square-pyramids with an approximate ratio of $V^{IV}:V^V \approx 0.49:0.51$, to form a columnar cavity along the c-axis, in which ammonium N atoms are hydrogen-bonded to apical O atoms of the $V^{IV/V}O_5$ square-pyramids. A reflux of the $(NH_4)_xV_3O_7$ powder in a 0.6 M LiOH / 2-methoxyethanol solution brought about Li-insertion into the columnar cavity without any structural change in the $\{V_3O_7\}$ framework.

III-K-3 Photoassisted Dehalogenation of Organo-Chlorine Compounds by Paratungstate A in Aqueous Solutions

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[*Appl. Catal., A* **194-195**, 99 (2000)]

Nearly neutral aqueous solutions of 22 organo-chlorine compounds undergo photodegradation ($\lambda > 250$ nm) catalyzed by paratunstate A anion, $[W_7O_{24}]^{6-}$, which was obtained by adjusting pH levels of the Na_2WO_4 solution to 6–7. In each case the organic substrate was decomposed through dehalogenation. The rate of Cl^- formation strongly depends on substrates. The photochemical redox reaction between paratungstate A and substrates proceeds via precomplexation. The Langmuir-type dependence of the reaction rates on the concentration of substrates provides a promising method for the dechlorination of alkyl- and aromatic-chloride compounds such as $ClCH_2CH_2CH_2Cl$, C_3H_7Cl, and $C_6H_5CH_2Cl$.

III-K-4 A Novel-Type Mixed-ligand Polyoxotungstolanthanoate, $[Ln(W_5O_{18})(BW_{11}O_{39})]^{12-}$ (Ln = Ce^{3+} and Eu^{3+})

NARUKE, Haruo; YAMASE, Toshihiro

(IMS and Tokyo Inst. Tech.) 177 (2000)]

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Two isostructural anions, $[Ln(BW_{11}O_{39})(W_5O_{18})]^{12-}$ (Ln = Ce and Eu), were isolated as K^+ salts from aqueous solutions containing tungstate, Ln^{3+}, and BO_3^{3-}, at pH = 7. An X-ray crystallographic analysis showed that the Ln^{3+} center in the anion is chelated by two kinds of tetradentate polyoxotungstate ligands, $[W_5O_{18}]^{6-}$ and α-$[BW_{11}O_{39}]^{9-}$ with a square antiprismatic LnO_8 configuration, which are monovacant derivatives of $[W_6O_{19}]^{2-}$ and α-$[BW_{12}O_{40}]^{5-}$, respectively. The anion is of approximate C_s symmetry, and the observable asymmetry of K–O bonding between two different K^+ cations and the anion causes the two mirror planes within $[(W_5O_{18})Ln]^{3-}$ and $[(BW_{11}O_{39})Ln]^{6-}$ moieties to be canted to each other by 5.2° for Ln = Ce and 4.1° for Ln = Eu.

III-K-5 Photoreduction Processes of α-Dodecamolybdophosphate, α-$[PMo_{12}O_{40}]^{3-}$: ^{31}P-NMR, Electrical Conductivitiy, and Crystallographic Studies

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The photoreduction processes of α-$[PMo_{12}O_{40}]^{3-}$ (α-PMo_{12}(0)) in aqueous solutions at pH 2.0 are discussed on the basis of the results of the electrical conductivities and ^{31}P NMR spectra of photolytes, and the crystal structures of α-type two-electron and β-type four-electron reduction species isolated from photolytes as α-$[(^iPr)_2NH_2]_4[HPMo_{12}O_{40}]\cdot 4H_2O$ (**1**) (α-PMo_{12}(II)) and β-$[(^iPr)_2NH_2]_3[H_4PMo_{12}O_{40}]\cdot 2H_2O$ (**2**) (β-PMo_{12}(IV)): (i) A one-electron reduction species produced by the photoredox reaction of α-PMo_{12}(0) with methanol is degraded to α-B-$[H_3PMo_9O_{31}(OH)_3]^{3-}$ (α-B-PMo_9(0)) and Mo^V-containing Mo-triad species (Mo_3). (ii) The formation of the α-type monoprotonated two-electron reduction species, α-$[HPMo_{12}O_{40}]^{4-}$ (α-PMo_{12}(II)), results from the isomerization of the β-type two-electron reduction species, β-$[PMo_{12}O_{40}]^{5-}$ (β-PMo_{12}(II)), which is produced by coupling between the one-electron reduced α-B-PMo_9 (α-B-PMo_9(I)) and Mo_3. (iii) The β-type four-protonated four-electron reduction species, β-$[H_4PMo_{12}O_{40}]^{3-}$ (β-PMo_{12}(IV)) as a final product is produced by the disproportionation of α-PMo_{12}(II). The change in the electrical conductivity of the photolytes during photolysis supports the above processes for the photoreduction of α-$[PMo_{12}O_{40}]^{3-}$ to β-$[H_4PMo_{12}O_{40}]^{3-}$ at pH 2.0.

III-K-6 $Na_{10}(glycine)_2[H_2W_{12}O_{42}]\cdot 28H_2O$

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[*Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **56**,

The title compound, decasodium diglycine dihydrogendotetracontaoxododecatungstate(10-) octacosahydrate, consists of a paratungstate $[H_2W_{12}O_{42}]^{10-}$ anion, ten Na^+ cations, two zwitterionoic glycine molecules, and 28 crystallization waters. Two glycine-carboxylate O atoms coordinate three different Na^+ cations and the amino N atom forms hydrogen bonds with both terminal and bridging O atoms, two atoms for each.

III-K-7 Crystal and Electronic Structure and Magnetic Susceptibility of the Photochemically Prepared Layered Vanadyl Phosphate, $Na(VO)_2(PO_4)_2\cdot 4H_2O$

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[*J. Chem. Soc., Dalton Trans.* 1143 (2000)]

Prolonged photolysis of the aqueous solutions containing Na_3VO_4, NaH_2PO_4, and MeOH at pH 1.8 adjusted by use of H_3PO_4 led to the formation of a layered vanadyl phosphate, $Na(VO)_2(PO_4)_2\cdot 4H_2O$ (**1**). A single-crystal X-ray structural analysis of dark green crystal of **1** showed that the structure contains layers of vanadium (randomly with 1:1 ratio of V^{4+} and V^{5+}) phosphorus oxide with the water molecules and sodium cations between the layers. The layer is a 4-connected net in which corner-sharing vanadium oxygen octahedra and phosphate tetrahedra alternate. The molecular structure is identical with that of hydrothermally prepared Na^+-compound but reveals the nonzero dihedral angle (2.61°) between the least-square planes (containing equatorial four-oxygen atoms) of the VO_6 octahedra in contrast to the parallel arrangement of the basal least-square planes for the latter. Magnetic susceptibility measurements for **1** show weak ferromagnetic coupling (J/k = 0.87 K) at $T \leq 100$ K and weak antiferromagnetic behavior at $T > 100$ K. The magneto/structural relationship for the retracted-chair-like $V(OPO)_2V$ rings are compared among other layered vanadyl phosphate compounds. The ferromagnetic property of the d_{xy} orbital at one V^{IV} center in the retracted-chaired $V^{IV}(OPO)_2V^{IV}$ ring can be explained in terms of the interaction with the V=O π* orbital at opposite V^{IV} center, which is possible when both distances of (O=)V··V(=O) and (O=)V··O(=V) are short (~4.55 and ~4.36 Å, respectively). Otherwise, the antiferromagnetic property due to the superexchange interaction between magnetic d_{xy} orbitals at both V^{IV} centers is operative. The results of Extended Hückel (EH) calculations for a fragment model $[V_8P_8O_{40}]^{4-}$ (with V^{IV}/V^V = 1/1) support a variety of the magnetic interaction of the unpaired electron at V^{IV} centers in the V–P–O layer consisting of the retracted-chaired $V(OPO)_2V$ rings.