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Essay

Keggin POMs

Isopoly and Heteropoly Compounds of Molybdenum, Tungsten, and Vanadium

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Abstract: Migration from early photochemical and photoelectrochemical studies to pharmacochemotherapy and magnetochemistry very often involves Keggin structures –deficient ones as well. Their significance is presented in this recollection of my career.

This essay is an opportunity for me to recount aspects of my career beginning with research in the Toshihiro Yamase laboratory on polyoxometalate photochemistry focusing on biological activities and molecular magnets, because the structure, properties, and reactions of polyoxometalates very often involve Keggin compounds (including deficient ones) and their derivatives. Overall, we cover a span of nearly 40 years.

A study on the photochromism (white ↔ brown) of alkylammonium polyoxomolybdate solids[1] demonstrated that UV-induced coloration corresponds to the formation of the localized $Mo^{V}O_5(OH)$ site resulting from the proton-coupled electron transfer through the oxygen-to-metal charge-transfer (O→M LMCT) state of the polyoxometalate lattice.[2] The degree of localization of the d^1 electron in the lattice was strongly associated with the disparity between the excited- and ground-state electronic configurations, which was reflected by the bond angle of the M–O–M linkage (due to especially significant dπ–pπ–dπ orbital mixing at the corner-sharing MO_6 octahedra). The intra- and intermolecular electron transfer occurred through the electronic triplet state of the O→M LMCT excited state, which was also involved in both the energy transfer for the sensitized Ln^{3+} emission of polyoxometallolanthanoates and O→M LMCT luminescence.[3]

A variety of photoredox reactions of polyoxometalates with proton/electron donors such as alcohols, carboxylates, alkenes, alkynes, and alkylammonium compounds in homogeneous solutions was investigated, and a high negativity of the electrochemical oxidation potential of photoreduced polyoxometalates (especially tungstates) led to the generation of a hydrogen molecule.[4] The energetic conversion of photoinduced H_2 gas to both electric and motive powers by homogeneous photocatalysis was demonstrated in the $Na_2WO_4{\cdot}2H_2O/[NH_3iPr]^+$/Pt system (at pH 7) under UV exposure (with a 20 W low-pressure mercury lamp together with both a wind-wheel propeller and a H_2/O_2 fuel cell), as shown in Figure 1 (see the Supporting Information for a video), where the quantum yield of H_2 generation though UV photolysis of $[W_7O_{24}]^{6-}$ was 0.02 at 254 nm.

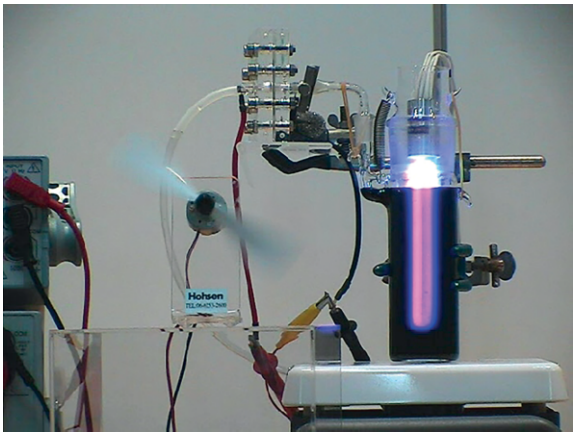

Figure 1. The energetic conversion of UV-generated H_2 gas to both electric and motive powers by use of the $Na_2WO_4{\cdot}2H_2O/[NH_3iPr]^+$/Pt system (at pH 7).

A prolonged photoredox reaction of aqueous solutions containing isopolyoxomolybdates (at pH ≤ 6) led to the formation of Mo blues and browns through multielectron reduction: UV photolysis of $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ (={Mo^{VI}_{36}}), β-$[Mo_8O_{26}]^{4-}$

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(={Mo^{VI}_8}), and $[Mo_7O_{24}]^{6-}$ (={Mo^{VI}_7}) generated 32- and 28-electron (e^-) reduced wheel-shaped Mo-blue rings of {Mo_{176}}, {Mo_{154}}, and {Mo_{142}}, the 24-e^- reduced Mo-brown of {Mo_{37}}, and the 12-e^- reduced Mo-brown of {Mo_{16}}, the latter two of which constitute the ε-Keggin core.[5–9] Also, the 60-e^- reduced Mo-brown {Mo_{132}} Keplerate was generated at pH 4 through the 20-e^- reduced open-ring Mo-blue intermediate.[10] Assuming that the construction of the outer and inner rings for all the Mo-blue rings proceeds in a mode similar to that of the two-e^- reductive condensation of {Mo^{VI}_7} to $[(Mo^{V}Mo^{VI}_6O_{23})_2]^{10-}$ (={Mo_{14}}), the self-assembly mechanism of the wheel-shaped rings was discussed on the basis of the dehydrative condensation among the formally four-e^- reduced {Mo_{20-22}} building units.

The potent antitumor activity of $[NH_3iPr]_6[Mo_7O_{24}]\cdot 3H_2O$ (PM-8) opened an application of polyoxometalates in the biomedical fields.[11] They reacted with nucleotides and protein polypeptides to yield d^0 complexes, as exemplified by $Na_2(Hamp)_2Mo_5O_{15}]\cdot 6H_2O$ and Mo_4O_{12}(glycylglycylglycine)$_2\cdot 9H_2O$.[12,13] Molecular interactions with biomolecules (such as ATP, FMN, and siaryl/sulfotransferases), strongly dependent on environmental parameters of solution pH, concentration, and the coexistence of foreign inorganic and/or organic substances, assist the antitumor, antiviral, and/or antibacterial activities of polyoxometalates,[14–18] and this is important to consider for the realization of an inorganic medicinal chemistry showing biologically excellent activity that cannot be replaced by other approved medicines. The high cytotoxicity of {Mo_{16}}, $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(MoO_3)_4]^{6-}$ (PM-17 anion) (as a photochemically 12-e^- reduced species of the PM-8 $[Mo_7O_{24}]^{6-}$ anion), might be a clue to the antitumor activity of PM-8, if PM-17 is one of the metabolites produced by the metabolism of PM-8. Several candidates for clinical use have been licensed for the chemotherapy of solid tumors (such as human breast cancer MX-1, human colon cancer CO-4, human gastric cancer MKN-45, and human pancreatic cancer AsPC-1), DNA and RNA viruses (such as HSV, HIV, influenza, and SARS), and drug-resistant bacteria (such as MRSA and VRSA): $[NH_3iPr]_6[Mo_7O_{24}]\cdot 3H_2O$ (PM-8) and $[Me_3NH]_6[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]\cdot 2H_2O$ (PM-17) for solid tumors; $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ (PM-19), $K_9H_5[(GeTi_3W_9O_{37})_2O_3]\cdot 16H_2O$ (PM-504), $[iPrNH_3]_6H[PTi_2W_{10}O_{38}(O_2)_2]\cdot H_2O$ (PM-523), and $K_{11}H[(VO)_3(SbW_9O_{33})_2]\cdot 27H_2O$ (PM-1002) for viruses; and $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ (PM-27), $K_4[SiMo_{12}O_{40}]\cdot 3H_2O$ ($SiMo_{12}$), and PM-19 for MRSA and VRSA.[19,20] It should also be mentioned that a variety of these compounds enhance the nerve growth factor (NGF)-induced neurite outgrowth of PC-12 cells with expression of the axonal growth associated protein 43 (GAP-43); these may be candidates for a drug against neurodegenerative disorders like Alzheimer's disease.[21]

A series of quantum hysteresis has been investigated by using PM-1002 as a spin-frustrated $(VO)_3^{6+}$ triangle, $(n\text{-}BuNH_3)_{12}[Cu_4(GeW_9O_{34})_2]\cdot 14H_2O$ as a rhomblike Cu_4^{8+} tetragon through α-Keggin linkage, and $[n\text{-}BuNH_3]_{12}[(CuCl)_6(XW_9O_{33})_2]\cdot 6H_2O$ (X = Sb^{3+}, As^{3+}) as a D_{3d}-symmetric Cu_6^{12+} hexagon.[22–25] The magnetostructural correlation among analogues for each spin ring, based on the results of crystal structure, dc and ac magnetic susceptibilities, in-depth magnetization (under pulsed fields), and high-frequency/high-field ESR measurements, indicated that polyoxometalates provide model systems for a better understanding of the exchange interaction of magnetic clusters, which is very important in the research areas of molecular magnetism and bioinorganic chemistry. The origin of the zero-field splitting parameter (D) of the ground states and the primary contribution thereto were discussed in terms of the magnetic dipole–dipole interaction between electrons located on the magnetic sites. The suitability as models is based on the following points: (1) polyoxometalates can coordinate moieties of paramagnetic ions with unusual geometries and highly symmetrical topologies at specific sites of their structures; (2) such magnetic centers embedded in the polyoxometalate structures are isolated from neighboring molecules with different sizes and high stability resulting from the diamagnetic frameworks of the polyoxometalate ligands; (3) modification of the magnetic centers is possible by modifying the structure, symmetry, and size of the polyoxometalate ligands.

It should be noted that the O→M LMCT excited state can also be generated by application of high electric fields to polyoxometalate solids, as demonstrated by the observation of the electroluminescence of $[Eu(W_5O_{18})_2]^{9-}$: the alkaline-earth metal salt of $[Eu(W_5O_{18})_2]^{9-}$ was deposited on the transparent SnO_2/In_2O_3 (ITO) electrode with a thickness of about 40–80 μm, the layer of which after drying was covered by both Mylar film (with a thickness of about 4–12 μm) and counter ITO electrode.[26,27] The application of a dc-pulsed electric field (about –0.8 to –1.0 kV) between the ITO electrodes resulted in an observation of red electroluminescence. To improve this type of high-field electroluminescence, the electroluminescent paper cell of the simple ITO-film/luminescent layer/ITO-film system was proposed, in which the alkaline-earth metal salt of $[Ln(W_5O_{18})_2]^{9-}$ (Ln = Eu^{3+}, Tb^{3+}, Dy^{3+}) was embedded in the pulp fiber and functioned by a reduced applied voltage of –0.2 to –0.5 kV. Such a flexible electroluminescent paper cell was also feasible for conventional ZnS phosphor systems. A multicolor (red from $[Eu(W_5O_{18})_2]^{9-}$, green from ZnS:Cu, and blue from ZnS:Ag) high-field electroluminescent paper display is shown in Figure 2, where the technical uniformity of the luminescent layer in the test paper is not attained yet. The work on maintaining bright luminescence with long-term stability is in progress after my retirement (in 2008) at the Tokyo Institute of Technology (TIT), partially to find real commercial applications in the flat-panel display market, together with a trial to compile unpublished

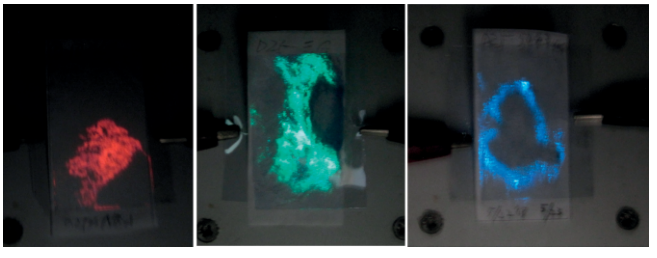

Figure 2. The multicolored (red, green, and blue) display sample by the electroluminescence paper sandwiched between the transparent ITO film electrodes.

data obtained on other projects mentioned above for publication.

Keywords: Polyoxometalates · Photochemistry · Pharmacochemotherapy · Magnetochemistry

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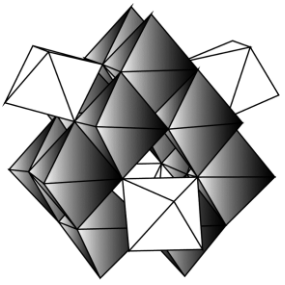

Toshihiro Yamase presents instances of his research in polyoxometalate photochemistry, focusing on biological activities and molecular magnets, often involving Keggin compounds, as the one shown in the picture.

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