

Editorial

The Fascination of Polyoxometalate Chemistry

Pierre-Emmanuel Car * and Greta R. Patzke *

Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland;
E-Mails: pierre-emmanuel.car@chem.uzh.ch (P.-E.C.); greta.patzke@chem.uzh.ch (G.R.P.)

Academic Editor: Duncan H. Gregory

Received: 10 November 2015 / Accepted: 19 November 2015 / Published: 23 November 2015

We are delighted to introduce this special issue of *Inorganics*. This themed issue is dedicated to polyoxometalates (POMs) as an outstanding class of oxo-cluster materials. Polyoxometalates have fascinated generations of researchers since the mid-18th-century, and they continue to attract promising young scientists all over the world. Since the first pioneering studies, the manifold structures and properties of POMs, have been the focus of interdisciplinary research synthetic/structural chemistry, biology, physics and theoretical chemistry. Moreover, polyoxometalates excel through outstanding compositional and structural diversity, which enables fine-tuning of their electronic properties, redox properties, and chemical stability along with robustness for the design of future applied devices. The growing family of polyoxometalates can be divided into two classes: transition-metal-substituted polyoxometalates (TMSPs) and lanthanide-substituted polyoxometalates (LnSPs). They currently attract particular interest due to their strong potential in the most challenging forefront research areas, e.g., water splitting, catalysis, magnetism, electronic materials and bio-medical applications. In the present themed issue, several research domains of polyoxometalate chemistry are covered by internationally renowned research groups in this topical field, ranging from synthesis/characterization and biological properties, through water oxidation catalysis and photochromic properties, to liquid crystal properties.

The present special issue starts with a new report by William H. Casey and co-workers on the synthesis and crystal structure determination of a new polynuclear Ga(III)-oxyhydroxo cluster [1]. This compound extends the hitherto very short list of group 13 clusters (with Al³⁺ and Ga³⁺ cations). The newly discovered oxo-cluster contains 30 Ga(III) centers, and its structure was determined from single crystal X-ray diffraction techniques at the Advanced Light Source.

The contribution of Juan M. Gutierrez-Zorrilla and co-workers [2], sheds light on a fascinating and versatile domain of polyoxometalate chemistry, namely the use of Keggin-type polyoxometalates [XM₁₂O₄₀]ⁿ⁻ (X = Si, Ge) as building-blocks and precursors for the design and synthesis of new

inorganic-metalorganic materials. Juan M. Gutierrez-Zorrilla *et al.* report on three new hybrids that were fully characterized. Single crystal X-ray diffraction techniques revealed the formation of 2D networks for all three compounds, highlighting the structure-directing role of the guanidinium ions.

Next, the up-coming field of lanthanide substituted polyoxometalates is represented by the contributions of Ulrich Kortz and co-workers [3] and of Israël M. Mbomekallé and co-workers [4]. Ulrich Kortz and his team present the synthesis and characterization of a new polynuclear lanthanide-substituted polyoxometalate with the formula $[Y_8(CH_3COO)(H_2O)_{18}(As_2W_{19}O_{68})_4(W_2O_6)_2(WO_4)]^{43-}$. Crystallographic studies revealed that this lanthanide polyoxometalate is formed by four $\{Y_2As_2W_{19}O_{68}\}$ units linked to each other via two $\{W_2O_{10}\}$ groups and one $\{WO_6\}$ fragment. Israël M. Mbomekallé *et al.* synthesized and characterized a mononuclear europium hetero-polyoxometalate. The central europium(III) ion displays a square anti-prismatic coordination environment, and it is surrounded by two monovacant heterometallic W/Mo Keggin moieties $[\alpha-(SiW_9Mo_2O_{39})]^{8-}$. The new compound was fully characterized with a wide range of analytical methods, and it displays promising electro-catalytic activity for O_2 and H_2O_2 reduction.

Among the wide range of properties of POMs, bio-medical applications continue to attract the interest of international research groups. Two chemical approaches are reported in the present themed issue. The first contribution of Tatjana N. Parac-Vogt and co-workers [5] employs Zr(IV)-substituted polyoxometalates for the investigation of the regioselective hydrolysis of human serum albumin. Tryptophan fluorescence spectroscopy studies revealed for the first time a direct correlation between the metal incorporated in the POM and the rate of protein hydrolysis, as well as the strength of their interaction. The second article by Christina Freire and co-workers [6] features a novel hybrid nanocomposite formed from the combination of a vanadium substituted phosphomolybdate $\{PMo_{11}V\}$ and N-doped few layer graphene (N-FLG), which was newly prepared and fully characterized. The efficiency of the novel hybrid material for the electrochemical sensing of biomolecules, as well as for electro-catalytic and sensing properties, was investigated in detail. The polyoxometalate compound was successfully immobilized on N-FLG, and it exhibited excellent electrocatalytic and sensing properties towards acetaminophen and theophylline oxidations.

The present special issue also contains selected contributions focused on polyoxometalates with group 4 (Zr) and 5 (V, Nb, Ta) metal ions: two review articles by Pavel A. Abramov and co-workers on polyoxonobates and polyoxotantalates [7], and by Diego Venegas-Yazigi and co-workers on polyoxovanadates [8]. Pavel A. Abramov *et al.* summarize their contributions to the coordination chemistry of noble metals (Rh, Ir, Ru, Pt(IV)) and polyoxometalates of Nb(V) and Ta(V). In a complementary manner, Diego Venegas-Yazigi *et al.* give an account of the structural and electronic properties of the less explored polyoxovanadoborate system. This review covers the different existing vanadium (V_6 , V_{10} , V_{12}) and borate fragments ($B_{10}O_{22}^{14-}$, ...) as well as the use of the polyoxovanadoborate as building-blocks for the design and the synthesis of extended structures (1D to 3D). This section is rounded off with an article from Yoshihito Hayashi and co-workers [9] who report on the transformation of three different polyoxovanadates and their efficiency as catalysts for the oxidation of thioanisole.

Over the past decade, transition metal substituted polyoxometalates (TMSPs) have been intensely studied as promising catalyst types for water oxidation and water reduction processes. In the present themed issue, two contributions from Simone Piccinin and co-workers [10] and from

José R. Galan-Mascaros and co-workers [11] shed new and interesting light on TMSP compounds as water oxidation catalysts (WOCs). Simone Piccinin *et al.* compared different ruthenium substituted polyoxometalates as WOCs containing one or four ruthenium centers as WOCs by means of density functional theory (DFT). Theoretical studies showed that the oxidation state of the active Ru sites was found to be more important than their nuclearity. José R. Galan-Mascaros *et al.* explore the challenging field of POM-WOCs inspired by the {CaMn₄O₅} cluster of photosystem II. They investigated the activity and the stability of a tetranuclear manganese-substituted polyoxometalate [Mn₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ as an electrocatalyst for the water oxidation reaction, and compared its activity to the well-known {Co₄} analogue. Electrocatalytic studies revealed that the {Mn₄} title POM shows lower efficiency and stability under catalytic conditions in comparison with its {Co₄} analogue, thereby illustrating the challenges associated with bio-inspired POM-WOC design.

Finally, this special issue of *Inorganics* on the most recent advancements of the polyoxometalate chemistry is concluded with several contributions on recent progress in the rewarding field of polyoxomolybdates. The featured articles cover a wide range of investigations, from the synthesis and characterization of hexamolybdate [Mo₆O₁₉]²⁻ functionalized by a heteroaromatic thiophene molecule containing an organoimido group to form the novel polyoxomolybdate [Mo₆O₁₈(L4)]²⁻ (L4 = 4(4-bromo-5-methylthiophen-2-yl)-2,6-dimethylaniline) by Chris Ritchie and co-workers [12], to the investigation of the vanadium(V) substitution reaction in Wells–Dawson type polyoxometalates, by Jun-ichi Nambu and co-workers [13]. In this work, several analytical methods, such as cyclic voltammetry, ³¹P NMR and Raman spectroscopy shed new light on the vanadium(V)-substitution processes in the [X₂M₁₈O₆₂]⁶⁻ to [X₂VM₁₇O₆₂]⁷⁻ (X = P, As; and M = Mo, W) transformation reactions. These two articles are complemented by two contributions on new polyoxomolybdate materials. Emmanuel Cadot and co-workers [14] report on the synthesis and characterization of eight new Keplerates obtained through the combination of [Mo₁₃₂O₃₇₂(CH₃COO)₃₀(H₂O)₇₂]⁴²⁻ polyoxoanions and 1-methyl-3-alkylimidazolium cations. The obtained complexes were fully characterized by a wide range of analytical methods, and the liquid crystal properties of the newly reported materials were investigated. Next, Anne Dolbecq and co-workers [15] synthesized and characterized two new hybrid organic–inorganic Mo(VI) and mixed Mo(V/VI) polyoxomolybdates. The fully oxidized Mo(VI) POM [(Mo^{VI}₃O₈)₂(O₃PC(O)(C₃H₆NH₂CH₂C₅H₄NH)PO₃)₂]⁴⁻ was obtained as sodium salt and as sodium/potassium salt, while the mixed Mo(V/VI) POM [(Mo^V₂O₄)(Mo^{VI}₂O₆)₂{O₃PC(O)(C₃H₆N(CH₂C₅H₄N)₂)PO₃]₂]⁴⁻ was obtained as ammonium salt in the presence of hydrazine. The pH stability domain of the three new hybrids was evaluated by ³¹P NMR spectroscopic studies, and they were found to exhibit solid state photochromic properties with rapid color-change under UV excitation.

Finally, we are very much indebted to all of the authors for their inspirational, exciting and interdisciplinary contributions, which cover a wide range of contemporary POM chemistry. We enjoyed editing this issue, and we hope that our audience will share the fascination of polyoxometalate chemistry.

References

1. Casey, W.H.; Olmstead, M.M.; Hazlett, C.R.; Lamar, C.; Forbes, T.Z. A new nanometer-sized Ga(III)-oxyhydroxide cation. *Inorganics* **2015**, *3*, 21–26.
2. Pache, A.; Reinoso, S.; San Felices, L.; Iturraspe, A.; Lezama, L.; Gutierrez-Zorrilla, J.M. Single-crystal to single-crystal reversible transformations induced by thermal dehydration in Keggin-type polyoxometalates decorated with copper(II)-picolinate complexes: The structure directing role of guanidinium. *Inorganics* **2015**, *3*, 194–218.
3. Ibrahim, M.; Bassil, B.S.; Kortz, U. Synthesis and characterization of 8-yttrium(III)-containing 81-tungsto-8-arsenate(III), $[\text{Y}_8(\text{CH}_3\text{COO})(\text{H}_2\text{O})_{18}(\text{As}_2\text{W}_{19}\text{O}_{68})_4(\text{W}_2\text{O}_6)_2(\text{WO}_4)]^{43-}$. *Inorganics* **2015**, *3*, 267–278.
4. Parent, L.; de Oliveira, P.; Teillout, A.-L.; Dolbecq, A.; Haouas, M.; Cadot, E.; Mbomekallé, I.M. Synthesis and characterisation of the europium (III) dimolybdo-enneatungsto-silicate dimer, $[\text{Eu}(\alpha\text{-SiW}_9\text{Mo}_2\text{O}_{39})_2]^{13-}$. *Inorganics* **2015**, *3*, 341–354.
5. Goovaerts, V.; Stroobants, K.; Absillis, G.; Parac-Vogt, T.N. Understanding the regioselective hydrolysis of human serum albumin by Zr(IV)-substituted polyoxotungstates using tryptophan fluorescence spectroscopy. *Inorganics* **2015**, *3*, 230–245.
6. Fernandes, D.M.; Nunes, M.; Carvalho, R.J.; Bacsa, R.; Mbomekalle, I.-M.; Serp, P.; de Oliveira, P.; Freire, C. Biomolecules electrochemical sensing properties of a $\text{PMo}_{11}\text{V}@N$ -doped few layer graphene nanocomposite. *Inorganics* **2015**, *3*, 178–193.
7. Abramov, P.A.; Sokolov, M.N.; Vicent, C. Polyoxonobates and polyoxotantalates as ligands-revisited. *Inorganics* **2015**, *3*, 160–177.
8. Hermosilla-Ibáñez, P.; Muñoz-Becerra, K.; Paredes-García, V.; Le Fur, E.; Spodine, E.; Venegas-Yazigi, D. Structural and electronic properties of polyoxovanadoborates containing the $[\text{V}_{12}\text{B}_{18}\text{O}_{60}]$ core in different mixed valence states. *Inorganics* **2015**, *3*, 309–331.
9. Kikukawa, Y.; Ogihara, K.; Hayashi, Y. Structure transformation among deca-, dodeca- and tridecavanadates and their properties for thioanisole oxidation. *Inorganics* **2015**, *3*, 295–308.
10. Piccinin, S.; Fabris, S. Water oxidation by Ru-polyoxometalate catalysts: Overpotential dependency on the number and charge of the metal centers. *Inorganics* **2015**, *3*, 374–387.
11. Goberna-Ferrón, S.; Soriano-López, J.; Galán-Mascarós, J.R. Activity and stability of the tetramanganese polyanion $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ during electrocatalytic water oxidation. *Inorganics* **2015**, *3*, 332–340.
12. Healey, M.R.; Best, S.P.; Goerigk, L.; Ritchie, C. A heteroaromatically functionalized hexamolybdate. *Inorganics* **2015**, *3*, 82–100.
13. Ueda, T.; Nishimoto, Y.; Saito, R.; Ohnishi, M.; Nambu, J.-I. Vanadium(V)-substitution reactions of Wells–Dawson-type polyoxometalates: From $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{6-}$ ($\text{X} = \text{P}, \text{As}$; $\text{M} = \text{Mo}, \text{W}$) to $[\text{X}_2\text{VM}_{17}\text{O}_{62}]^{7-}$. *Inorganics* **2015**, *3*, 355–369.
14. Watfa, N.; Floquet, S.; Terazzi, E.; Salomon, W.; Guénée, L.; Buchwalder, K.L.; Hijazi, A.; Naoufal, D.; Piguet, C.; Cadot, E. Synthesis, characterization and study of liquid crystals based on the ionic association of the Keplerate anion $[\text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ and imidazolium cations. *Inorganics* **2015**, *3*, 246–266.

15. Oms, O.; Benali, T.; Marrot, J.; Mialane, P.; Puget, M.; Serier-Brault, H.; Deniard, P.; Dessapt, R.; Dolbecq, A. Fully oxidized and mixed-valent polyoxomolybdates structured by bisphosphonates with pendant pyridine groups: Synthesis, structure and photochromic properties. *Inorganics* **2015**, *3*, 279–294.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).