Reactivity of 12-tungstophosphoric acid and its inhibitor potency toward Na^+/K^+-ATPase: a combined ^{31}P *NMR* study, *ab initio* calculations and crystallographic analysis

Nada Bošnjaković-Pavlović[a*], Danica Bajuk-Bogdanović[a], Joanna Zakrzewska[b], Zeyin Yan[c,d], Ivanka Holclajtner-Antunović[a], Jean-Michel Gillet[c,d] and Anne Spasojević-de Biré[c,d*]

[a] Faculty of Physical Chemistry, University of Belgrade, P.O. Box 47, 11001 Belgrade, Serbia

[b] Institute of General and Physical Chemistry, Belgrade, Serbia

[c] Université Paris-Saclay, CentraleSupélec, Campus de Gif, Plateau du Moulon, 3 rue Joliot Curie, 91192 Gif-sur-Yvette, France

[d] CNRS, UMR 8580, Laboratory "Structures Propriétés et Modélisation des Solides" (SPMS), Campus de Gif, Plateau du Moulon, 3 rue Joliot Curie, 91192 Gif-sur-Yvette, France

Supporting information

S1. a) Y.Z. Han, C.L. Zhang, Q. Cai, Y. Cheng, S.X. Ai, Q. Deng, Syntheses, Crystal Structure, Characterization and Properties of Two Novel Superamolecular Phosphotungstate - Pyridine Complexes, *Synth. React. Inorg. Met. Org. Chem.* 46 (**2016**) 351-364.

b) D. Meziani, K. Abdmeziem, S. Bouacida, M. Trari, Photo-electrochemical and physical characterizations of a new single crystal POM-based material. Application in photocatalysis, *J. Mol. Struct*. 1125 (**2016**) 540-545.

c) C.L. Teng, H.X. Xiao, Q. Cai, J.T. Tang, T.J. Cai, Q. Deng, Two multifunctional organic-inorganic hybrid complexes based on polyoxometalates, Bi EDTA and sodium linker: crystal structures, photochromic, and catalytic performances, *J. Coord. Chem*. 69 (14) (**2016**) 2148-2163.

d) X. Wang, C.Y. Kong, J.J. Lai, M.L. Wei, Synthesis, Structure and Proton Conductivity of a Complex Based on Decorated Keggin-Type Cluster: $\{[Cu(dmbipy)(H_2O)_2Cl_{0.5}]_2[PW_{12}O_{40}]\}.7H_2O$ (dmbipy = 4,4'-dimethyl-2,2'-bipyridine), *J. Clust. Sci.* 27 (**2016**) 645-656.

e) D. Chen, Z. Deng, Q. Li, X. Wang, X. Liu, Synthesis, crystal structure and catalytic behavior of a novel polyoxometalate-based complex, *Inorg. Chim. Acta* 438 (**2015**) 208-211.

f) H. Hu, W. Zhang, J. Gong, H. Dong, F. Zhao, H.Huang, Y.Liu, G. Zhang, Z. Kang, Can tetrazole-functionalized ligands realize the role-control of Keggin-type POMs in hybridframeworks?, *Cryst. Eng. Comm.* 16 (**2014**) 5642-5649.

g) A.X. Tian, Y. Yang, N. Sun, J.C. Li, J. Ying, J.W. Zhang, X.L.Wang, Three 2-(4-thiazolyl)benzimidazole-based supramolecular assemblies oriented by Keggin and Wells–Dawson anions, *J. Coord. Chem*. 67 (9) (**2014**) 1550-1561.

h) H. Zhang, K. Yu, S. Gao, C. Wang, C. Wang, H. Wang, B. Zhou, Assembly of two-fold interpenetrated silver supramolecular coordination polymer using Keggin phosphotungstate template, *Inorg. Chem. Commun*. 44 (**2014**) 91-95.

i) D. Chen, A. Sahasrabudhe, P. Wang, A. Dasgupta, R. Yuan, S. Roy, Synthesis and properties of a novel quarternerized imidazolium $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ salt as a recoverable photo-polymerization catalyst, *Dalton Trans.* 42(29) (**2013**) 10587-96.

j) X. Li, L. Cheng, W. Fang, G. Yang, A Series of Open-Frameworks Constructed From Polyoxoanion Clusters and Copper-tetrazolate Complexes: Synthesis, Structure and Properties, *Acta Chim. Sinica* 71 (**2013**) 179-185.

k) L. Liu, X.Z. Xu, X. Zhang, N.X. Zhang, S.G. Fan, Y.P. Huang, Synthesis, Crystal structure and Luminescent Property of a New 3D Supramolecular Compound $(C_6H_6NO_2)_3(C_6H_5NO_2)(PW_{12}O_{40})\cdot 2H_2O$, *Chin. J. Struct. Chem*. 32 (**2013**) 1813-1820.

l) X. Wang, J. Peng, K. Alimaje, Z. Zhang, Z. Shi, Two Keggin polyoxoanion-based hybrids composed of CuI/tbz segments: Syntheses, structures and electrochemical properties, *Inorg. Chem. Commun*. 36 (**2013**) 141-145.

m) M. Wei, X. Wang, J. Sun, X. Duan, A 3D POM–MOF composite based on Ni(II) ion and 2,2′-bipyridyl-3,3′-dicarboxylicacid: Crystal structure and proton conductivity, *J. Solid State Chem.* 202 (**2013**) 200-206.

n) X. Zhao, X. Sun, Z. Han, C. Zhao, H. Yu, X. Zhai, Two new polyoxometalate-based hybrids consisting of Keggin-type cluster modified by $\{Ag_4\}$ group, *J. Solid State Chem*. 207 (**2013**) 178-183.

o) M.G. Liu, P.P. Zhang, J. Peng, H.X. Meng, X. Wang, M. Zhu, D.D. Wang, C.L. Meng, K. Alimaje, Organic-Inorganic Hybrids Constructed from Mixed-Valence Multinuclear,

Copper Complexes and Templated by Keggin Polyoxometalates, *Cryst. Growth Des.* 12(3) (**2012**) 1273-1281.

p) C.J. Zhang, H.J. Pang, Q. Tang, Y.G. Chen, A feasible route to approach 3D POM-based hybrids: utilizing substituted or reduced Keggin anions with high charge density, *Dalton Trans.* 41 (**2012**) 9365-9372.

q) Y. Jiang, S. Liu, J. Miao, J. Zhang, L. Wu, Anisotropic ionic liquids built from nonmesogenic cation surfactants and Keggin-type polyoxoanions, *Chem.Commun.* 47 (**2011**) 10287-10289.

r) C. Pichon, P. Mialane, J. Marrot, C. Binet, A. Vimont, A. Travert, J.-C. Lavalley, Combined XRD and infrared studies of pyridinium species in (PyH) 3[$PW_{12}O_{40}$] single crystals, *Phys. Chem. Chem. Phys.* 13 (**2011**) 322–327.

s) L.N. Xiao, Y. Wang, C.L. Pan, J. N. Xu, T.G. Wang, H. Ding, Z.M. Gao, D.F. Zheng, X.B. Cui, J.Q. Xu, Three novel supramolecular hybrid compounds based on kegging polytungstates, *Cryst. Eng. Comm.* 13 (**2011**) 4878-4885.

t) Y.P. Ren, X.J. Kong, X.Y. Hu, M. Sun, L.S. Long, R.B. Huang, L.S. Zheng, Influence of Steric Hindrance of Organic Ligand on the Structure of Keggin-Based Coordination Polymer, *Inorg Chem.* 45(10) (**2006**) 4016-4023.

u) M. Schulz-Dobrick, M. Jansen, Supramolecular Intercluster Compounds Consisting of Gold Clusters and Keggin Anions, *Eur. J. Inorg. Chem.* (**2006**) 4498-4502.

v) X. Lu, B. Liu, Sarula, J. Wang, C. Ye, Synthesis, crystal structure and NMR of [$Na(DB_{18}C_6)(CH_3CN)]_3[\alpha$-$PW_{12}O_{40}$], *Polyhedron* 24 (**2005**) 2889-2893

w) Z. Han, Y. Zhao, J. Peng, H. Ma, Q. Liu, E. Wang, N. Hu, Supramolecular assembly of organic bicapped Keggin Polyoxometalate, *J. Solid State Chem*. 177 (**2004**) 4325-4331.

x) J. Wang, X. Duan, J. Niu, Synthesis and crystal structure of a 1D double-chain polyoxometalate based complex $\{[Ba(DMSO)_3(H_2O)_3]\ [C_5H_6N]\ PW_{12}O_{40}\cdot DMSO\cdot 2H_2O\}_n$, *J. Mol. Struct*. 692 (**2004**) 17-21.

y) W. Huang, T. Louis, P.A. Glenn, R.B. Yap, L.C. Francesconi. T. Polenova, ^{51}V Magic Angle Spinning NMR Spectroscopy of Keggin Anions $[PV_nW_{12-n}O_{40}]^{(3+n)-}$: Effect of Countercation and Vanadium Substitution on Fine Structure Constants, *J. Am. Chem. Soc.* 126 (**2004**) 11564-11573.

z) C. Inman, J.M. Knaust, S. W. Keller, A polyoxometallate-templated coordination polymer: synthesisand crystal structure of $[Cu_3(4,4'\text{-bipy})_5(MeCN)_2]PW_{12}O_{40}\cdot 2C_6H_5CN$, *Chem. Commun.* (**2002**) 156-157.

α) Y. Xu, K.L. Zhang, Y. Zhang, X.Z. You, J.Q. Xu, Keggin unit supported transition metal complexes: hydrothermal synthesis and characterization of $[Ni(2,2'\text{-bipy})_3]_{1.5}$ $[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$ and $[Co(1,10'\text{-phen})_3]_{1.5}[PMo_{12}O_{40}Co(1,10'\text{-phen})_2(H_2O)]\cdot 0.5H_2O$, *Chem. Commun.* (**2000**) 153-154.

S2. M.H. Alizadeh, I.M. Zonoz, 12-Tungstophosphoric acid-1,1'-methylenebis(imidazolidine-2,4-dione)-imidazolidine-2,4-dione-water, *Acta Crystallogr.* E66 (**2010**) m839.

S3. a) F. Gschwind, M. Jansen, Crystal structure of hexakis (dimethylsulfoxide-κ-*O*) iron(III) dodecatungstophosphate, $C_{12}H_{36}FeO_{46}PS_6W_{12}$, *Z. Krist.-New Cryst. Struct.* 229 (**2014**) 5-6.

b) S. Busbongthong, T. Ozeki, Structural Relationships among Methyl-, Dimethyl-, and Trimethylammonium Phosphododecatungstates, *Bull. Chem. Soc. Jpn.* 82 (**2009**) 1393-1397.

c) Q.X. Han, C.Z. Wang, J.R. Ma, J.Y. Niu, J.P. Wang, Synthesis, Crystal Structure and Electrochemistry of Two Complexes $(YL_n)^{3+}[PW_{12}O_{40}]^{3-}$ (L=Me_2SO, Me_2NCHO), *Chem. Res. Chinese Univ.* 24 (**2008**) 255-259.

d) A. Kremenović, D. Poleti, N.E. Ghermani, Lj. Karanović, U.B. Mioč, Z. Nedić, A. Spasojević-de Biré, Synthesis and crystal structure of hexaaquamagnesium hydrogen phosphododecatungstate tetrahydrate $(Mg(H_2O)_6)$ $(HPW_{12}O_{40})$ * $4(H_2O)$, *Cryst. Res. Technol.* 42 (**2007**) 98-104.

e) A. Kremenović, A. Spasojević-de Biré, F. Bourée, P. Colomban, R. Dimitrijević, M. Davidović, U.B. Mioč, Structural modifications of dodecatungstophosphoric acid hexahydrate induced by temperature in the 10–358 K range. In situ high-resolution neutron powder diffraction investigation, *Solid State Ion.* 150 (**2002**) 431-442.

f) M.R. Spirlet, W.R. Busing, Dodecatungstophosphoric acid-21-water by neutron diffraction, *Acta Crystallogr.* B34 (**1978**) 907-910,

g) G.M. Brown, M.R. Noe-Spirlet, W.R. Busing, H.A. Levy, Dodecatungstophosphoric acid hexahydrate, $(H_5O_2)_3$ $(PW_{12}O_{40})$, the true structure of Keggin's 'pentahydrate' from single crystal X-ray and neutron diffraction data, *Acta Crystallogr.* B33 (**1977**) 1038-1046.

S4. a) S.C. Almo, J. Bonanno, J.M Sauder, S. Emtage, T.P. Dilorenzo, V. Malashkevich, S.R. Wasserman, S. Swaminathan, S. Eswaramoorthy, R Agarwal, D. Kumaran, M. Madegowda, S. Ragumani, Y. Patskovsky, J. Alvarado, U.A. Ramagopal, J. Faber-Barata, MR. Chance, A. Sali, A. Fiser, Z-Y. Zhang, D.S. Lawrence, S.K. Burley, Structural Genomics of Protein Phosphatases, *J. Struct. Funct. Genom.* 8 (**2007**) 121-140.

b). G. Rudenko, L. Henry, K. Henderson, K. Ichtchenko, M.S. Brown, J.L. Goldstein, J. Deisenhofer, Structure of the LDL receptor extracellular domain at endosomal, *Science* 298 (**2002**) 2353-2358.

c). Y. Ren, P. Schmiege, G. Blobel, Structural and biochemical analyses of the DEAD-box ATPase Sub2 in association with THO or Yra1, *eLife* 6 e20070 (**2017**) 1-17