Three Organic-Inorganic Polyoxoniobate-Based Compounds Modified With Cu(II) Amine Complexes: Synthesis, Characterization, And Catalytic Studies For Oxidation of Styrene

Zhi-cheng duan and Guahua Li, Ke-Chang Li, Xiao-Bing Cui,*

College of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, Jilin, 130023, P. R. China. Email: cuixb@mail.jlu.edu.cn.

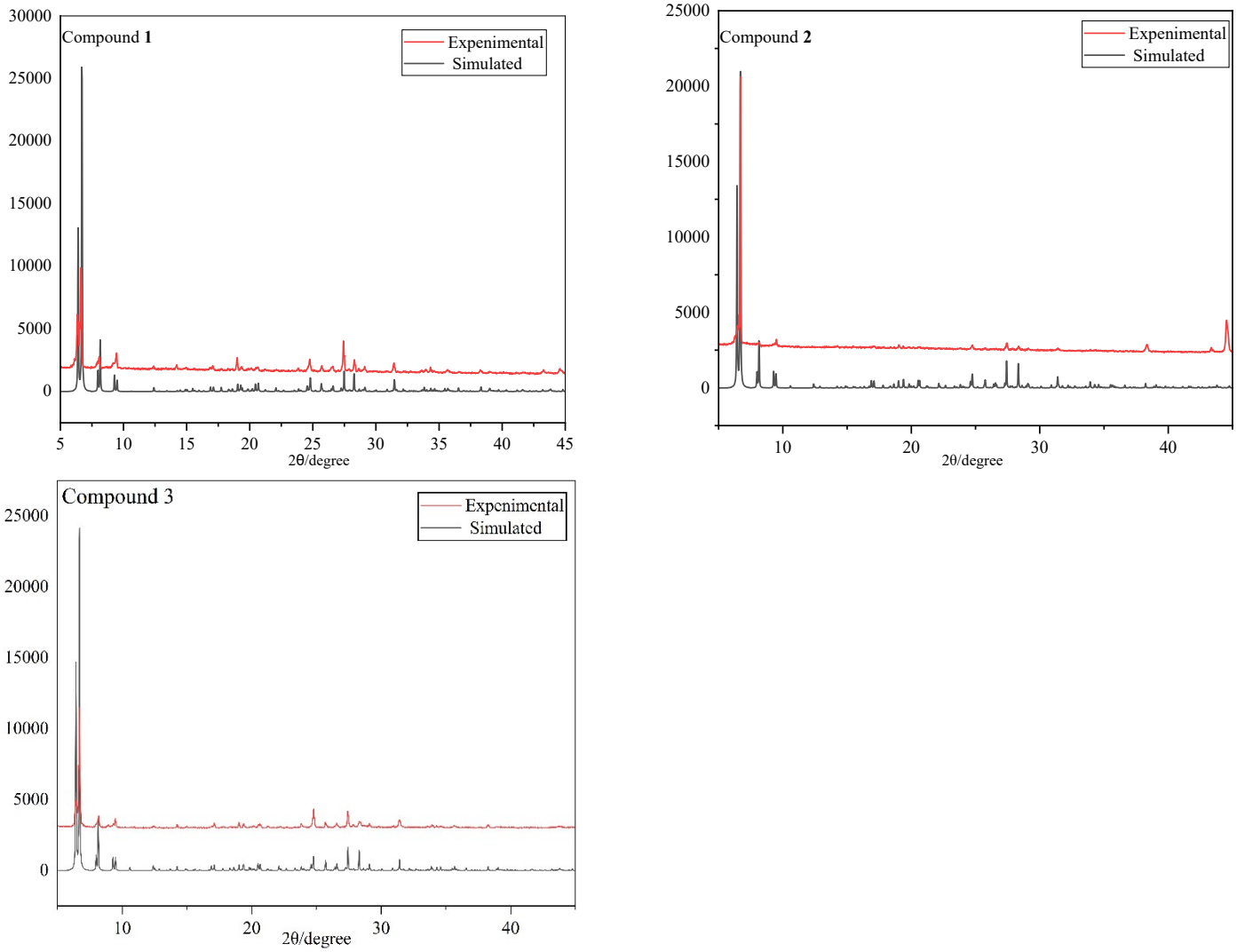

Fig. s1. The simulated and experimental patterns of compounds **1-3**.

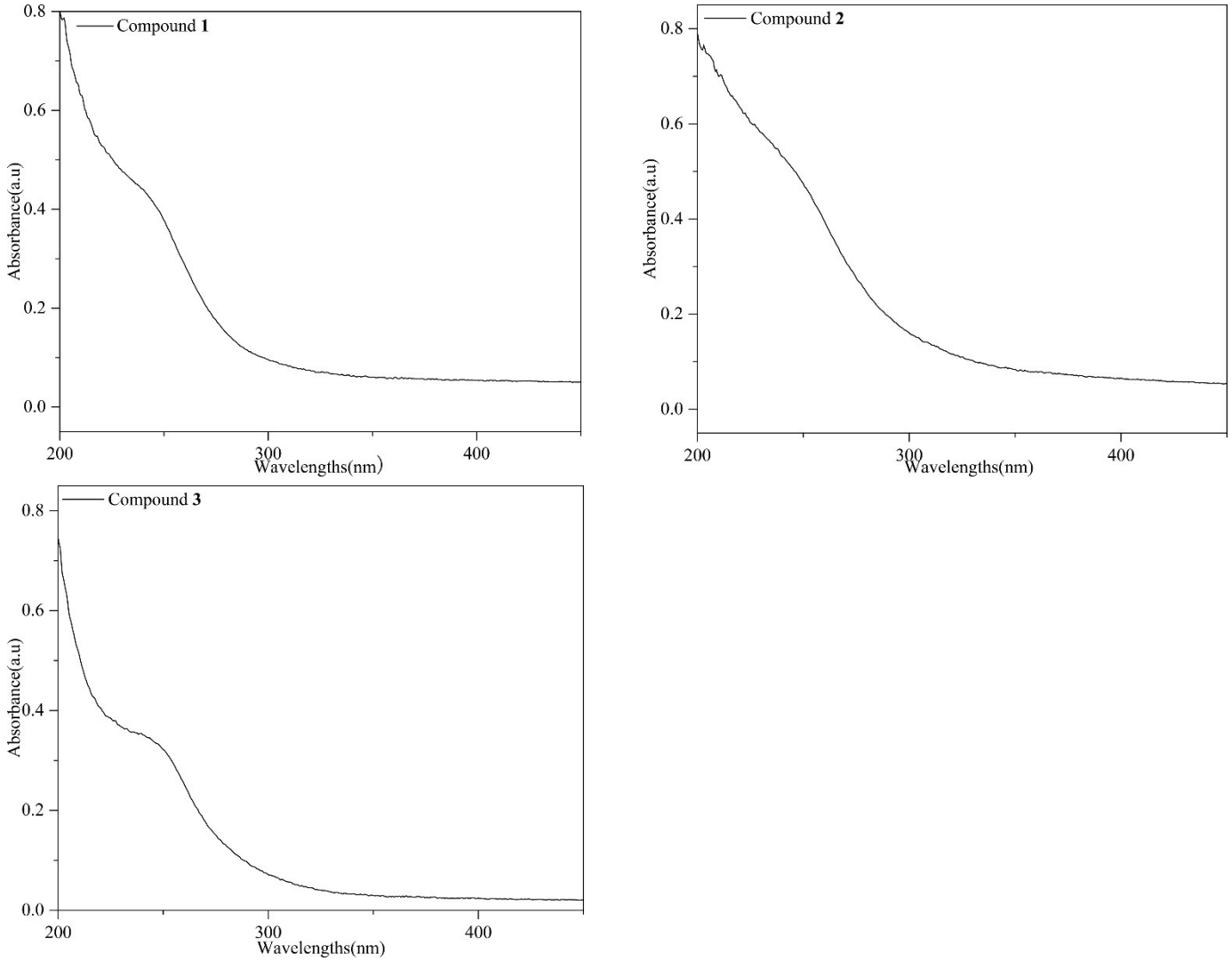

Fig. S2, The UV-Vis spectra of compounds **1**-**3**.

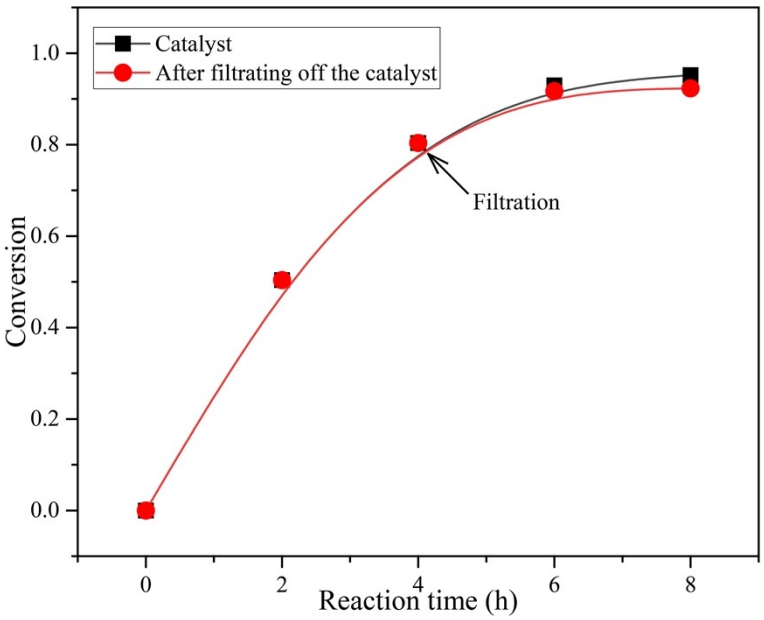

Fig. S3. Results of the hot filtration test of compound **1**.

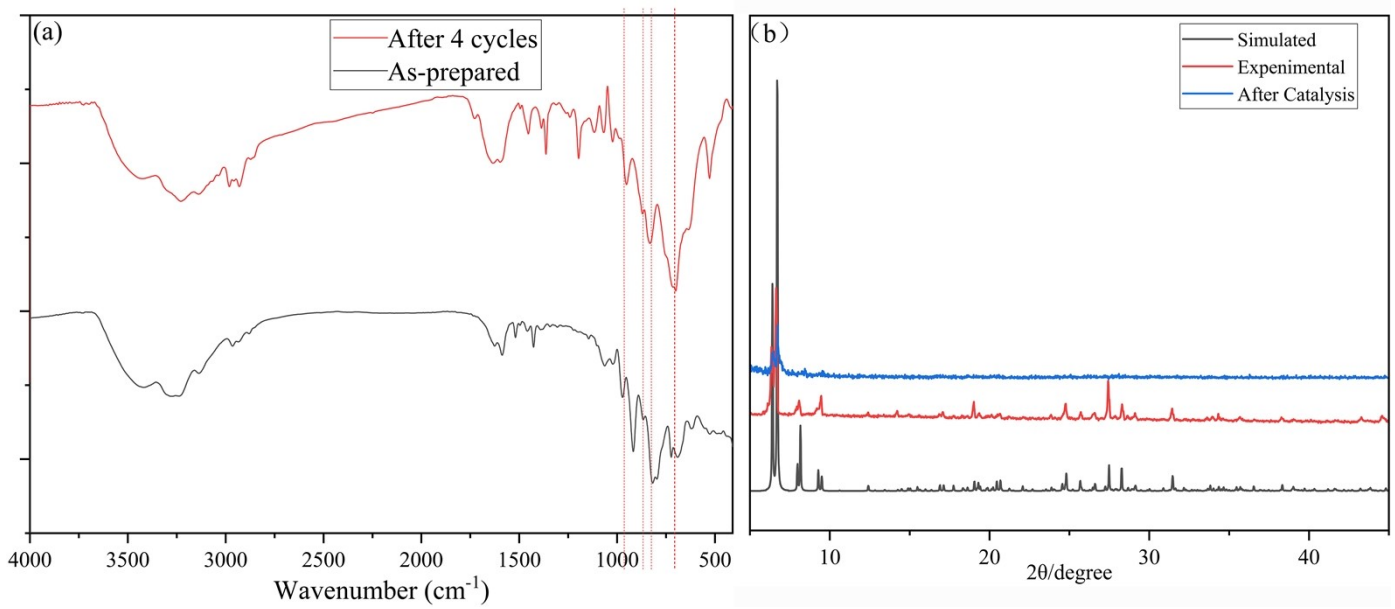

Fig. S4 Comparison of FT-IR spectra (a) and XRD patterns (b) of compound 1 before and after the 4 cycles.

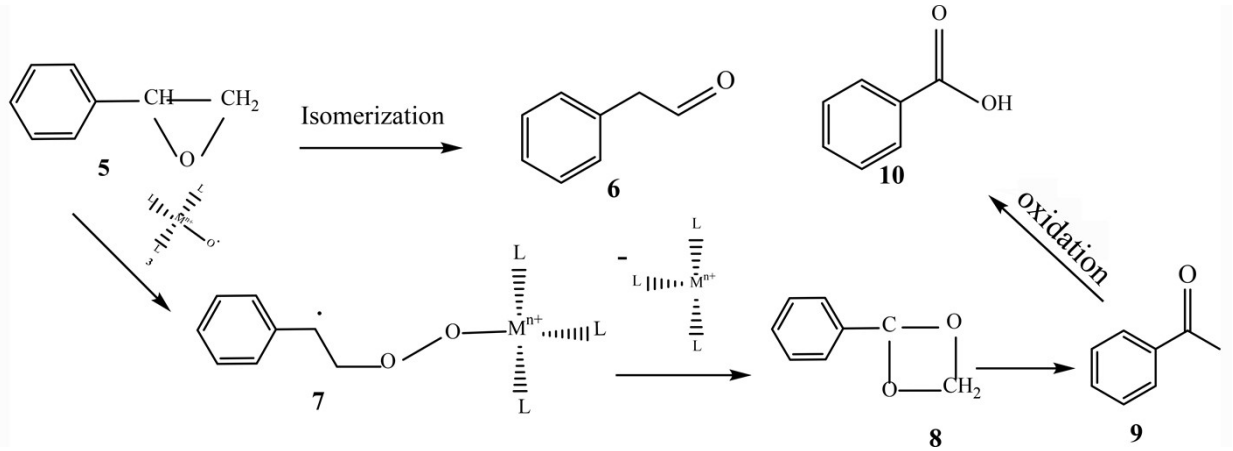

Fig. S5. The reactive metal cations present in the compounds undergoes a reaction with tert-butyl hydroperoxide (TBHP), resulting in the loss of a butanol molecule and the formation of a metal-containing oxygen radical. This radical subsequently interacts with the double-bonded carbon atom of styrene to form a metal epoxide intermediate (designated as species 4 in Fig 5 of the manuscript). Species 4 then undergoes O-M bond cleavage to form styrene oxide (5) and regenerate the catalyst. Within the catalytic process, the isomerization of styrene oxide can generate phenyl acetaldehyde (6), while Species 5 further reacts with metal oxygen radicals to generate Species 8, which then decomposes to form benzaldehyde (9). In addition, benzaldehyde can be further oxidized to produce benzoic acid (10) and so on.

Table S1 Crystal data and structure refinement for compounds **1-3**.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{48}H_{199}N_{32}O_{109.5}Si_2V_{8.5}Cu_8Nb_{24}K_2$	$C_{48}H_{214}N_{32}O_{109}P_2V_4Cu_8Nb_{24}K_2$	$C_{48}H_{214}Cu_8K_2N_{32}Nb_{24}O_{109}V_6$
Formula weight	6282.91	6066.56	6106.50
Crystal system	tetragonal	tetragonal	tetragonal
Space group	I4/mcm	I4/mcm	I4/mcm
a/Å	26.3310(12)	26.3917(6)	26.3856(7)
b/Å	26.3310(12)	26.3917(6)	26.3856(7)
c/Å	27.573(4)	27.4474(12)	27.5212(19)
Volume/Å^3	19117(3)	19117.7(12)	19160.3(17)
Z	4	4	4
ρ_{calc} g/cm^3	2.183	2.108	2.117
μ/mm^{-1}	16.827	2.585	2.654
F(000)	12258.0	11896.0	11960.0
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.746 to 127.93	4.88 to 50.73	4.882 to 50.724
Index ranges	-30≤ h≤ 27, -26≤k≤ 28, -31≤ l≤ 27	-31≤ h≤ 22, -24≤ k≤ 31, -32≤ l≤ 33	-31≤ h≤ 31, -27≤ k≤ 31, -33≤ l≤ 33

Reflections collected	28531	36985	60533
Independent reflections	4164 [R_{int}=0.0562, R_{sigma}=0.0413]	4613 [R_{int}=0.0474, R_{sigma}=0.0255]	4630 [R_{int}=0.0439, R_{sigma}=0.0179]
Data/restraints/parameters	4164/19/320	4613/0/321	4630/21/322
GOF on F^2	1.091	1.114	1.637
Final R indexes [I>=2σ (I)]	R_1 = 0.0622, wR_2 = 0.1753	R_1 = 0.0642, wR_2 = 0.1779	R_1 = 0.1007, wR_2 = 0.2867
Final R indexes [all data]	R_1 = 0.0812, wR_2 = 0.1894	R_1 = 0.0821, wR_2 = 0.2062	R_1 = 0.1367, wR_2 = 0.3811

We performed multiple single-crystal diffraction tests for compound **3**. However, all the results obtained were suboptimal, exhibiting relatively high R-values. The present data submitted for review is the best one. Compounds **2** and **3** are isostructural, and the single crystal data for compound **2** is good enough. A comparison of the two crystal data can demonstrate the accuracy of the crystal data pertaining to compound **3**.

Table S2. BVS results of the independent Nb and V atoms in compounds 1-3

Compound **1**			
Nb(1)	5.02	V(3)	3.84
Nb(2)	4.95	V(8)	3.85
Nb(3)	5.00		
Nb(4)	5.06		
Compound **2**			
Nb(1)	4.97	V(8)	3.92
0.Nb(3)	4.95		
Nb(4)	4.98		
Nb(5)	5.07		
Compound **3**			
Nb(2)	4.93	V(1)	4.27
Nb(3)	4.84	V(3)	5.37
Nb(4)	4.98		
Nb(5)	5.14		
For compound **1**, **2** and **3**, the equations used for the BVS of Nb are s=exp[(r_0-r)/0.37] (r_0=1.911),[1] the equations used for the BVS of V are s= exp[r_0-r)/0.37), and r_0=1.803.[1]			

Table S3. Catalytic performances with different olefin substrates.

Entry	Substrate	Conv. (%)	Sel. (%)
			1,2-Epoxycyclooctane(%)
1		76.2	42.4

Entry	Substrate	Conv. (%)	Sel. (%)		
			Cyclohexeneoxide	2-Cyclohexen-1-ol	2-Cyclohexen-1-one
2		95.7	0.8	22.7	2.2

Entry	Substrate	Conv. (%)	Sel. (%)				
			1,2-Epoxyoctae	Octanal	Heptanal	2-Octanone	n-Heptanoic acid
3		90.5	2.8	1.4	2.6	0	0

Reaction Conditions: substrate (1 mmol), catalyst (2.0 mg), TBHP (2 mM, 274 μL), acetonitrile (2 mL), toluene (1 mmol), 80 °C, 8 h reaction time.

1. I. D. Brown and D. Altermatt, Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database *Acta. Cryst.*, 1985, **B41**, 244-247.