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Controllable Synthesis of Lindqvist Alkoxopolyoxovanadate Clusters as Heterogeneous Catalysts for Sulfoxidation of Sulfides

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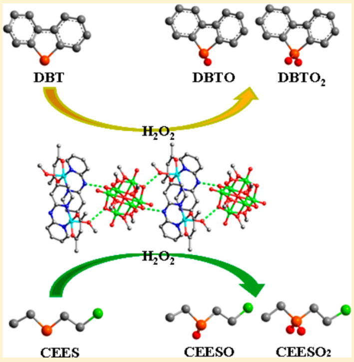
Supporting Information



ABSTRACT: Six alkoxohexavanadate-based Cu- or Co-POVs $[Cu(dpa)(acac)(H_2O)]_2[V_6O_{13}(OMe)_6]$ (**1**), $[Cu(phen)(acac)(MeOH)]_2[V_6O_{13}(OMe)_6]$ (**2**), $[Co(dpa)(acac)_2]_2[V_6O_{13}(OMe)_6]\cdot 2MeOH$ (**3**), $[Co(phen)(acac)_2]_2[V_6O_{13}(OMe)_6]$ (**4**), $[Cu(dpa)(acac)]_2[V^{IV}{}_2V^{V}{}_4O_{12}(OMe)_7]$ (**5**), and $[Cu(dpa)(acac)(MeOH)]_2[V^{IV}{}_2V^{V}{}_4O_{11}(OMe)_8]$ (**6**) (POV = polyoxovanadate; dpa = 2,2′-dipyridine amine; phen = 1,10-phenanthroline; acac = acetylacetone anion) have been synthesized by controlling the reaction conditions and characterized by single-crystal X-ray diffraction and powder X-ray diffraction analyses, FT-IR spectroscopy, element analyses, and X-ray photoelectron spectroscopy. In compounds **1**−**4** and **6**, Cu or Co complexes and alkoxohexavanadate anions are assembled through electrostatic interactions. Differently, in compound **5**, seven-methoxo-substituted Lindqvist-type $[V_6O_{12}(OMe)_7]^{2-}$ are bridged to Cu complex via terminal O atoms by coordination bonds. All compounds **1**−**6** exhibit excellent heterogeneous catalytic performance in oxidative desulfurization and CEES ((2-chloroethyl) ethyl sulfide, a sulfur mustard simulant) abatement with H_2O_2 as oxidant. Among them, the catalytic activity of **6** [conv. of DBT (dibenzothiophene) up to 100% in 6 h; conv. of CEES reached 100% and selectivity of CEESO ((2-chloroethyl) ethyl sulfoxide) up to 85% after 4 h] outperforms others and can be reused without losing its activity.

INTRODUCTION

Polyoxovanadates (POVs) as a unique branch of polyoxometalates (POMs), have recently become an area of great interest because of their enormous structural and chemical diversities leading to potential applications in many fields, such as catalysis, redox, molecular magnetism and drugs.[1] Among the POVs, alkoxopolyoxovanadate has attracted interest because of its potential catalytic applications and fascinating electronic, magnetic, or photochemical properties.[2,3] The alkoxide ligands serving to reduce the charge of polyanions are introduced into this system to stabilize the POVs clusters. Following this strategy, a series of multidentate trisalkoxo-ligand-substituted alkoxohexavanadates were synthesized after the first case $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{O_2NC(CH_2O)_3\}_2]$ contributed by Zubieta and co-workers.[4] Additionally, a surge of methoxo and ethoxo ligands substituted alkoxohexavanadates including $[V_6O_{13}(OMe)_6]^{2-}$,[5] $[V_6O_{12}(OMe)_7]^{-}$,[6] $[V_6O_{11}(OMe)_8]^{2-}$,[7] $[V_6O_8(OMe)_{11}]$,[8] $[V_6O_8(OMe)_{11}]^{+}$,[8] $[V_6O_7(OEt)_{12}]$,[9] $[V^{IV}{}_nV^{V}{}_{6-n}O_7(OMe)_{12}]^{(4-n)}$ (n = 3, 4, 5, 6),[10] and $[V^{IV}{}_{(4-n)}V^{V}{}_{(2+n)}O_7(OR)_{12}]^{n+}$ (R = −Me, n = 0, 1; R = −Et, n = 0, 1, 2)[11] have sprung up. In these compounds, however, very few alkoxohexavanadates examples with respect to their catalytic properties have been reported, although they are expected to have excellent performance as oxidation catalyst.[12] One important reason is that they are commonly highly reactive and extremely susceptible to hydrolysis by even a trace amount of water.[2,6] However, it is known that introducing water is often inevitable in most liquid-phase oxidation reactions. Therefore, it is essential to explore synthetic methods for more stable and highly active catalysts based on alkoxohexavanadates. We have succeeded in combining Pd-complex cation and alkoxohexavanadates to stabilize the POVs clusters and enable excellent catalytic activity for oxidation of benzyl-alkanes.[12d] However, the use of noble metal seems to limit its practical application to some degree. Therefore, to further obtain the more economical heterogeneous catalyst, here we moved forward this work to replace the noble ion of Pd with the transitional metal ions for the consideration of the potential applications.

On the other hand, reducing the level of sulfur content in fuel oils has become an attractive scientific field in recent years for environmental reasons.[13−16] Combustion of sulfur-containing fuels is responsible for the formation of sulfur oxides (SO_x), which can cause acid rain and lead to the growth of the PM (particulate matter), a serious environmental problem in developing country. Moreover, these sulfur-containing compounds can poison the catalysts used to remove hydrocarbons and nitrogen oxides derived from combustion reactions. Thus, it is an important work to remove sulfur from the original

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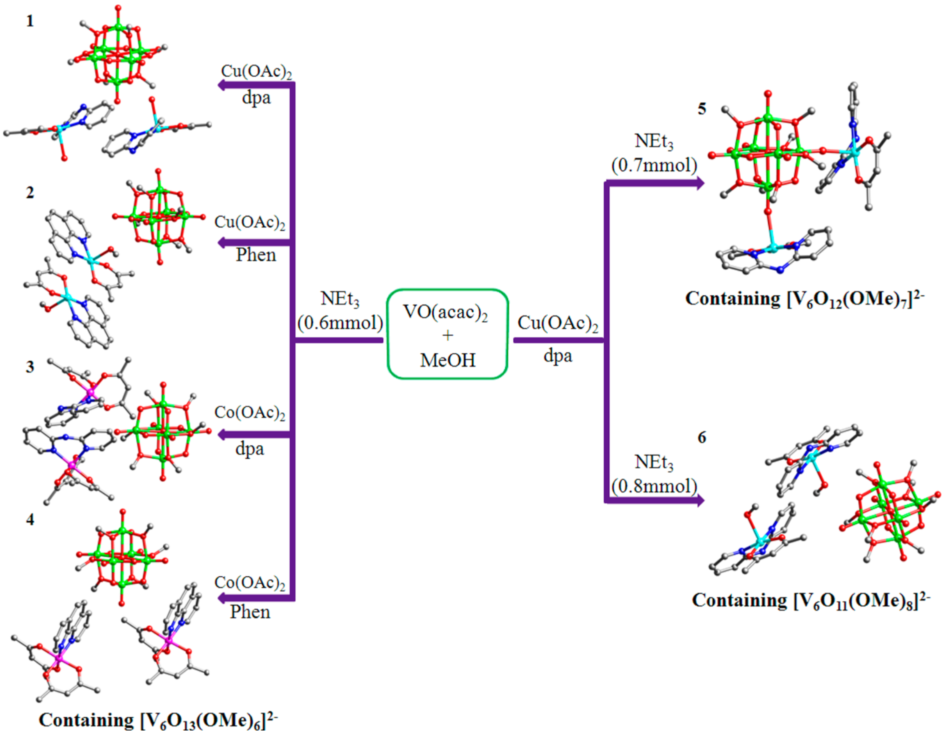
Scheme 1. Simplified Representation of the Controlling Synthesis of 1−6[a]



[a]Color code: Co, pink; Cu, light blue; V, green; N, blue; O, red; C, gray.

materials efficiently and in an environmentally friendly way. However, the traditional approach to removing sulfur-containing compounds, hydrodesulfurization (HDS), requires innovation not only for the rigorous operating conditions (such as high temperature and high pressure) but also for its ineffectiveness at removing the refractory sulfur-containing compounds, in particular, DBT, and its derivatives.[17,18] Thus, it is necessary to develop non-HDS methods, which have been long desired.[19] Oxidative desulfurization (ODS) is regarded as a promising strategy to obtain clean fuels because the refractory sulfur-containing compounds can be oxidized into the corresponding sulfoxides and sulfones under mild conditions using an ionic liquid[20] or a heteropolyacid[12b,21] as catalyst, which can be further removed by extraction. Therefore, we anticipated the alkoxohexavanadates species would also be a good candidate because of its good oxidation catalytic ability according to our previous work. Another case of bis(2-chloroethyl)sulfide, as typical sulfur-containing compound, is the main component of sulfur mustard (mustard gas or HD).[22] The decontamination of sulfur mustard to nontoxic products has also attracted significant attention. The common abatement methodologies are oxidation, dehydrohalogenation, and hydrolysis.[23] Among such methods, partial oxidation of sulfur mustard to the corresponding sulfoxide is the most promising route.[24]

With all the above in mind, as well as to advance our research in the field of oxidative catalytic activity of POVs[12d,25] and pursue more economical catalysts for the potential application, we synthesized six Cu- or Co-complexes instead of noble Pd-complex combined Lindqvist alkoxohexavanadates $[Cu(dpa)(acac)(H_2O)]_2[V^V{}_6O_{13}(OMe)_6]$ (**1**), $[Cu(phen)(acac)(MeOH)]_2[V^V{}_6O_{13}(OMe)_6]$ (**2**), $[Co(dpa)(acac)_2]_2[V^V{}_6O_{13}(OMe)_6]\cdot 2MeOH$ (**3**), $[Co(phen)(acac)_2]_2[V^V{}_6O_{13}(OMe)_6]$ (**4**), $[Cu(dpa)(acac)]_2[V^{IV}{}_2V^V{}_4O_{12}(OMe)_7]$ (**5**), and $[Cu(dpa)(acac)(MeOH)]_2[V^{IV}{}_2V^V{}_4O_{11}(OMe)_8]$ (**6**) by controlling the synthetic or crystallization conditions carefully. The new alkoxohexavanadate clusters were further used as highly efficient heterogeneous catalysts in sulfoxidation of sulfides with the environmentally benign H_2O_2 as the terminal oxidant, which has potential applications in oxidative desulfurization of fuel oil and sulfur mustard abatement.

■ RESULTS AND DISCUSSION

Synthesis. All compounds were synthesized by the reaction of $VO(acac)_2$, $Cu(OAc)_2$, or $Co(OAc)_2$ and N-donor ligands in the presence of Et_3N and methanol. As shown in Scheme 1, compounds **1**−**6** all contain a so-called Lindqvist type alkoxohexavanadate anion. As an organic base, Et_3N might facilitate the deprotonation of methanol, and thus, six-methoxo-substituted $[V_6O_{13}(OMe)_6]^{2-}$ cluster (in **1**, **2**, **3**, and **4**), seven-methoxo-substituted $[V_6O_{12}(OMe)_7]^{2-}$ (in **5**) and eight-methoxo-substituted $[V_6O_{11}(OMe)_8]^{2-}$ cluster (in **6**) can be obtained by carefully controlling the adding amounts of Et_3N. During the synthetic process, by changing the kinds of transition-metal ions (Cu^{2+} in **1** and **2**, Co^{2+} in **3** and **4**) and the N-donor ligands (dpa in **1** and **3**, phen in **2** and **4**) only under the equal amounts of Et_3N, we obtained compounds **1**−**4** all including a six-methoxo-substituted $[V_6O_{13}(OMe)_6]^{2-}$ cluster. From the above result, we can conclude that the countercation part has little effect on the structure of hexavanadate anion. Interestingly, due to the variability of the valence, Co^{2+} was oxidized to Co^{3+} under the synthetic conditions of **3** and **4**, which result in the different coordination environment with Cu^{2+} in **1** and **2**. To synthesize compounds **5** and **6**, we gradually increased the amounts of Et_3N under the same synthetic conditions of **1**. When the reaction completed, large amounts of precipitate were formed in the reactor of **5**, yet the solution of **6** remained clear. The precipitates were

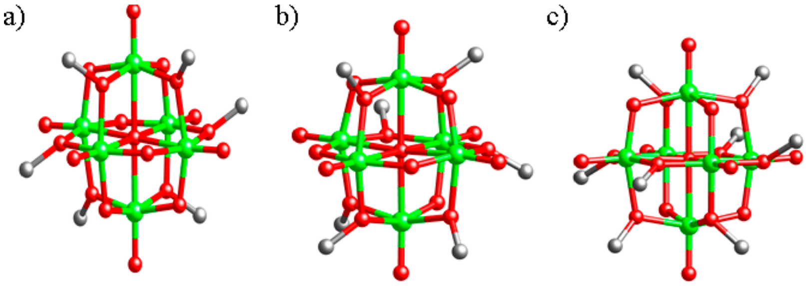


Figure 1. Methoxo-substituted hexavanadate anion in **1**–**6**. (a) $[V_6O_{13}(OMe)_6]^{2-}$ in **1**, **2**, **3**, and **4**; (b) $[V_6O_{12}(OMe)_7]^{2-}$ in **5**; and (c) $[V_6O_{11}(OMe)_8]^{2-}$ in **6**.

redissolved with DMSO and crystals of compound **5** were obtained after about 2 weeks. In addition, compounds **1**–**4** and **6** were all directly crystallized from the mother liquor.

FT-IR Spectra. IR spectroscopy can provide helpful information for the analysis of alkoxopolyoxovanadium clusters. Particularly, the 400–1200 cm^{-1} region is of interest and contains absorption bands due to metal–oxygen stretching vibrations, which are characteristic of POMs spectra in general. As can be seen from the IR spectra of compounds **1**–**6** (see Figure S1), the apparent absorption bands in the range of 1000–1100 cm^{-1} and 950–1000 cm^{-1} region are corresponding to the O–CH_3 and V═O stretching modes, respectively.[8] The 540–650 cm^{-1} region are ascribed to the V–O–V bending.[7] Further absorption located in the 935–950 cm^{-1} region are attributed to V═O vibration, whereas the 750–785 cm^{-1} region is assigned to V–O–V bridging fragments and the 650–695 cm^{-1} region to V-OCH_3 fragments, respectively.[7,26]

Crystal Structures of 1–4. Single-crystal X-ray diffraction (SXRD) shows that compounds **1**–**4** all consist of one Lindqvist type $[V_6O_{13}(OMe)_6]^{2-}$ polyanion (Figure 1a), which is comparable to $[Pd(dpa)(acac)]_2[V_6O_{13}(OMe)_6]$[12d] and $[\{VO(bmimpm)(acac)_2\}\{V_6O_{13}(OMe)_6\}]$ (bmimpm = bis(1-methylimidazol-2-yl)-4-methoxyphen-1-ylmethanol).[5a] The countercation parts in **1**–**4** are two five-coordinated Cu^{2+} (**1** and **2**) or six-coordinated Co^{3+} (**3** and **4**) complexes, respectively. The five-coordinated Cu^{2+} center is ligated by two N atoms from one dpa (in **1**) or phen (in **2**), two O atoms from $acac^-$ anion and one O atom from a water or methanol molecule. The structural index τ, $[\beta-\alpha]/60$ with α and β being two largest angles, is zero for an ideal square pyramid and becomes unity for an ideal trigonal bipyramid.[27] In compounds **1** and **2**, the value of structural index τ are 0.097 for **1** and 0.017 for **2**, respectively, indicating that they are in slightly distorted square pyramid geometry. The Co^{3+} center in **3** and **4** has a distorted-octahedral coordination environment, which bounds to four O atoms from two $acac^-$ anions and two N atoms from one dpa (in **3**) or phen (in **4**). The BVS calculations show that the oxidation states of all the vanadium atoms in compounds **1**–**4** are +V, which are in good agreement with the charge balance of the compounds (Table S1).

Besides electrostatic interactions, there exist strong hydrogen-bonding interactions between Cu- or Co-complex and polyanions in compounds **1**–**3**. Because of the diverse coordination environment, the hydrogen bonds in **1**–**3** are different from each other accordingly. In **1**, two μ_2-oxo atoms of $[V_6O_{13}(OMe)_6]^{2-}$ (O8 and O9A, symmetry code: A, $-x+1$, $-y+2$, $-z+1$) connect with O3 (derived from coordinated H_2O) and N3 (derived from dpa ligand) through hydrogen bonds with the O···O and O···N distances of 2.767(8) Å and 2.760(7) Å, respectively, and thus, a 1D chain supramolecular structure of **1** was formed (Figure S2a). As a result of the replacement of dpa by phen ligand, only one type of hydrogen bond exists in compound **2**. The distance of the μ_2-oxo (O6) and O3 (derived from coordinated MeOH) is 2.918(6) Å (Figure S2b). There is also only one type of hydrogen bonding interaction in compound **3** between the μ_2-oxo of $[V_6O_{13}(OMe)_6]^{2-}$ and the amino group (derived from dpa ligand) with the O···N distance of 2.805(3) Å (Figure S2c). No strong hydrogen bond exists in **4** because of the absence of dpa ligand and other coordinated solvent molecules. From the above result, we can see that the different N-donor ligands and coordination mode of the transition-metal center has a great impact on the supramolecular structures of compounds **1**–**4**.

Crystal Structure of 5. By increasing the amount of base (Et_3N), compound **5** instead of **1** was obtained under the same reaction conditions. Interestingly, the SXRD analysis shows that the number of the methoxo in **5** is found to be seven to form $[V_6O_{12}(OMe)_7]^{2-}$ polyanion, as scarcely reported except for $[V_6O_{12}(OMe)_7]^-$.[6] The five-coordinated Cu^{2+} center is ligated by two N atoms from one dpa, two O atoms from $acac^-$ anion, and the third O atom derived from the vanadate cluster. In this compound, the value of structural index τ is 0.023 for Cu1, indicating that it is in slightly distorted square pyramid geometry. As part of the $[V_6O_{12}(OMe)_7]^{2-}$ ion, one terminal oxygen atom O3 bridges the outer-shell Cu atom (Figure 2). Remarkably, the observed distance between V1 and O3 is

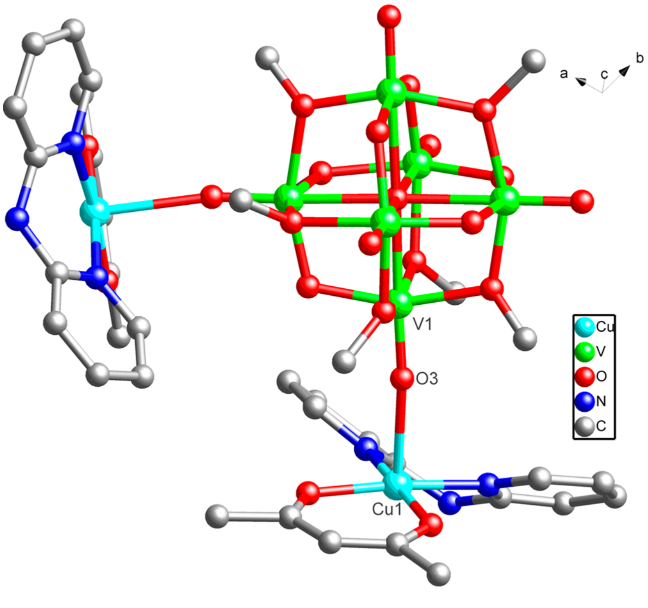


Figure 2. Crystal structure of **5**. All H atoms were omitted for clarity.

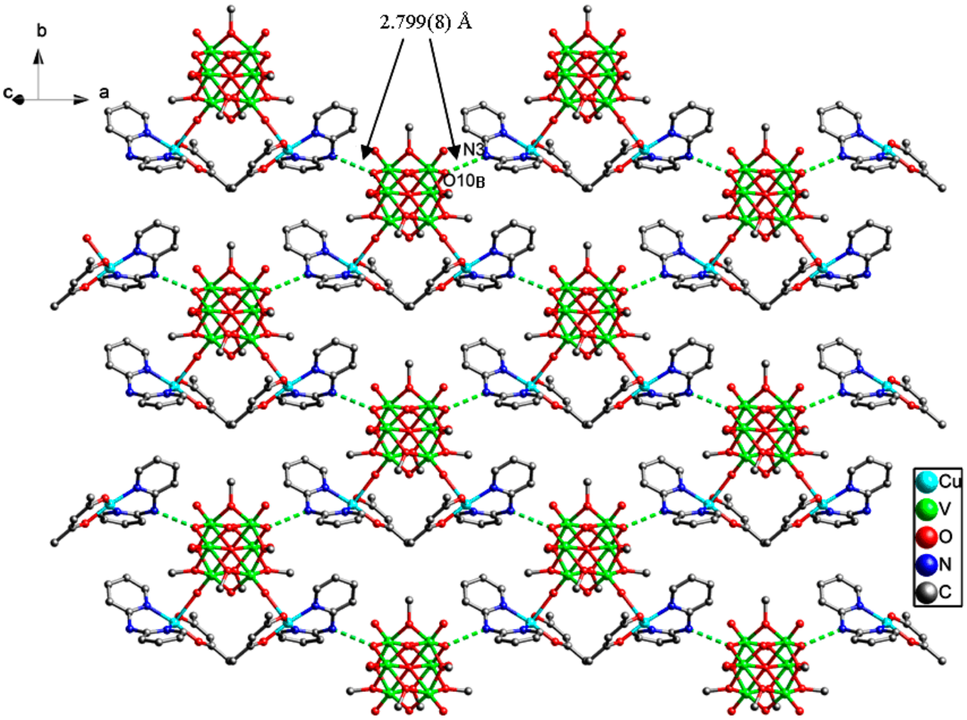


Figure 3. 2D planar supramolecular structure of **5**. The following symmetry transformation was used to generate equivalent atoms: B, −*x*+1/2, *y*−1/2, −*z*+1/2.

1.599(6) Å, which is expected for vanadyl bonds (V═O), whereas the Cu1−O3 bond is long (2.416(6) Å) because of the Jahn−Teller effect of the Cu^{2+} cation. The two copper complexes are attached to the hexavanadate core by O3 bridges as shown in Figure 2. To balance the charge of the cation in **5**, a mixed-valence state of vanadate anion containing two V^{IV} and four V^{V} are needed, which is further identified by both BVS calculations (Table S1) and XPS analysis (Figure S3).

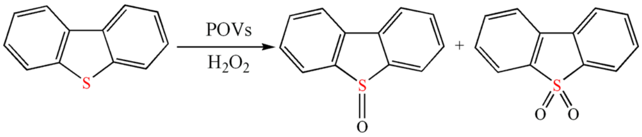
In addition, the coordination bonds between Cu center and μ_2-oxo atoms of $[V_6O_{12}(OMe)_7]^{2-}$, along with hydrogen bonds formed by μ_2-oxo atoms and −NH groups with the O10B···N3 (symmetry code: B, −*x*+1/2, *y*−1/2, −*z*+1/2) distance of 2.799(8) Å), leads to the resultant 2D planar supramolecular structure (Figure 3).

Crystal Structure of 6. Compared with the synthetic procedure of compound **5**, we further increased the adding amounts of Et_3N but keeping the other conditions unchanged. Compound **6**, consisting of two $[Cu(dpa)(acac)H_2O]^+$ and one $[V_6O_{11}(OMe)_8]^{2-}$ polyanion (Figure 1c), was obtained from the mother liquor. Herein, the interaction between Cu-complex and alkoxohexavanadate clusters is different from the coordination interaction of **5** but similar to **1**−**4** to be cationic−anionic electrostatic interaction, which is caused by one of the coordination sites of Cu in **6** is water oxygen atom instead of terminal oxygen derived from $[V_6O_{12}(OMe)_7]^{2-}$ in **5**. The geometry of five coordinated Cu1 is also a slightly distorted square pyramid indicated by the value of structural index τ being 0.018. Concerning with the polyanion moiety, it belongs to the eight-methoxo-substituted α-$[V_6O_{11}(OMe)_8]^{2-}$. All the eight methoxo groups are distributed in a symmetrical mode by taking the central O of Lindqvist cluster as the center, which is similar to the polyanion structure in our reported examples $[Pd(dpa)(acac)]_2[V_6O_{11}(OMe)_8]$ and $[Pd(DMAP)_2(acac)]_2[V_6O_{11}(OMe)_8]\cdot H_2O$ with only slight differences in bond lengths and bond angles.[12d] The BVS calculations (Table S1) and XPS analysis (Figure S3) investigations reveal that compound **6** also contains the mixed-valent $\{V^{IV}_2V^{V}_4\}$ to balance the charge of the cation.

There also exist two kinds of hydrogen bonds in compound **6**. Two μ_2-oxo atoms of $[V_6O_{11}(OMe)_8]^{2-}$ polyanion (O2C and O4D, symmetry code: C, *x*+1, *y*, *z*; D, −*x*, −*y*+2, −*z*+1) connect with O13 (derived from coordinated MeOH) and N2 (derived from dpa ligand) through hydrogen bonds with the O···O and O···N distances of 2.753(1) Å and 2.684(1) Å, respectively, forming a 1D chain supramolecular structure (Figure S2d).

Catalytic Activities of Cu or Co-POVs. The oxidation of DBT was selected as a model reaction to evaluate the catalytic activities of Cu- or Co-POVs (Scheme 2). The reaction was investigated first in acetonitrile with Cu-POVs catalyst $[Cu(dpa)(acac)(MeOH)]_2[V_6O_{11}(OMe)_8]$ (**6**) using H_2O_2 as oxidant. The gas chromatography (GC) analyses showed that DBT could be completely transformed to the corresponding sulfoxides and sulfones at 40 °C in 1.5 h. Thus, acetonitrile was selected as the appropriate solvent for the ODS process, in which the sulfur content was set by fixing the dosage of DBT (S content: 1000 ppm). A typical ODS process was performed as following: the model oil (decalin containing DBT) and acetonitrile mixture was stirred at 40 °C for 10 min, and subsequently, catalyst and 30% aqueous H_2O_2 were added to

Scheme 2. Oxidation of DBT Using POVs as Catalysts under Mild Conditions



initiate the reaction. At various time intervals, the mixture was quantitatively analyzed by GC. The different conversion of DBT catalyzed by **1**−**6** showed that the best result was achieved when using **6** as catalyst (Table 1, entries 1−6). From Figure 4 we can see that above 96% DBT was oxidized to the corresponding sulfoxide and sulfone after 4 h. Another 2 h later, the conversion of DBT reached 100% under the relatively mild conditions. The catalytic result of compounds **1**−**6** were almost the same as shown in Table 1 (entries 1−6), which indicated that the active center of the catalysts was the $\{V_6\}$ core and the slight difference in the types of the counter cations and the number of substituted methoxo had no obvious effect on the terminal catalytic performance of all the catalysts.

Table 1. Catalytic Oxidative Desulfurization of DBT by Different Catalysts[a]

entry	catalyst	conv. (%)	reaction system
1	**1**	98.5	heterogeneous
2	**2**	98	heterogeneous
3	**3**	97	heterogeneous
4	**4**	97	heterogeneous
5	**5**	96.5	heterogeneous
6	**6**	100	heterogeneous
7	$[NHEt_3]_2[V_6O_{13}(OMe)_6]$	100	homogeneous
8	$Cu(OAc)_2$+dpa	5	homogeneous
9	blank	<5	–

[a] Reaction conditions: model oil (2 mL), catalyst (1.5 mol %), acetonitrile (2 mL), and 30% H_2O_2 (0.5 mmol) at 40 °C for 6 h.

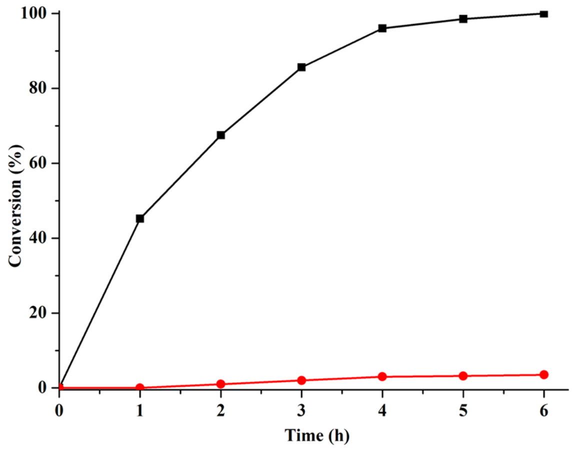


Figure 4. Time profile for the ODS using **6** as catalyst. Reaction conditions: model oil (2 mL), **6** (1.5 mol %), acetonitrile (2 mL), and 30% H_2O_2 (0.5 mmol) at 40 °C for 6 h. Black: with catalyst; red: blank.

Compound **6** with the best catalytic activity was selected as a representative to further investigate the ODS process. The test without catalyst (blank test) showing a negligible DBT removing (Figure 4), which demonstrated that the catalysts played a vital role in the ODS system. To further probe the role of the Cu-complex cation and hexavanadate anion in the catalytic reaction, control experiments were conducted. When $[NHEt_3]_2[V_6O_{13}(OMe)_6]$[12d] was used as homogeneous catalyst (Table 1, entry 7), the conversion of DBT reached 100% within 6 h, proving the present catalysis of **6** originated from the alkoxohexavanadate anion. When the mixture of $Cu(OAc)_2$ and dpa with the molar ration of 1:1 was involved (Table 1, entry 8), the conversion (5%) was comparable to that of blank experiment. The above results indicated that the Cu-complex nearly had no contribution to accelerate the ODS reaction rate. The combination of Cu-complex and alkoxohexavanadate cluster through electrostatic interaction or coordination bonds led to the formation of heterogeneous catalysts. Fortunately, the activity of alkoxohexavanadate was not reduced by the complexation.

To further elucidate the heterogeneity of **6** in the oxidative system, a hot leaching test was carried out. The solid catalyst **6** was filtrated off from the mixture after 1 h of reaction, and the filtrate was subsequently stirred at 40 °C for another 5 h. GC analysis of the resulting reaction mixture showed a negligible conversion after filtration (Figure S4). Atomic absorption analysis shows that there were no copper and vanadium ions in the filtrate of the reaction system (S5 in the Supporting Information). These results collectively confirmed that the catalytic system is heterogeneous in nature. Furthermore, **6** can be easily separated by centrifugation after the reaction and can be recycled at least 4 times without considerable decrease in activity (DBT conversion of the forth run remained above 98%,

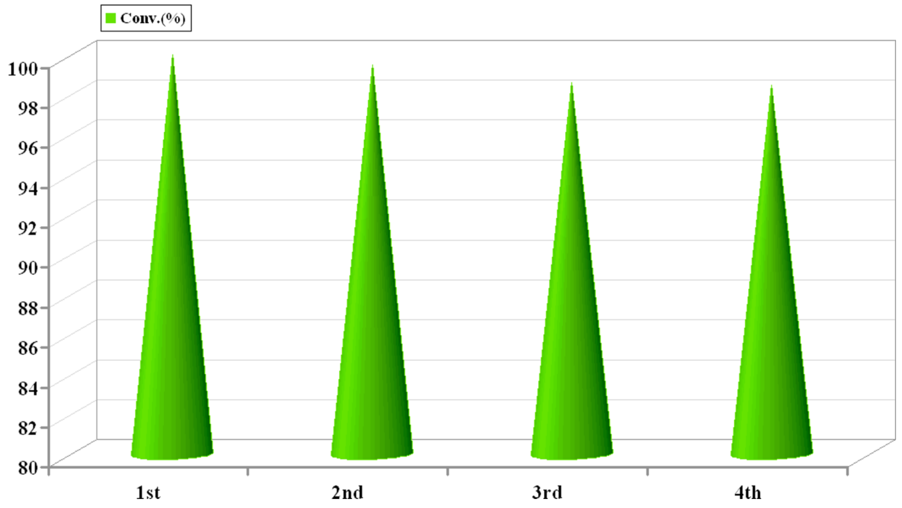


Figure 5. Recycling of **6** for oxidative desulfurization of DBT.

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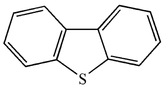
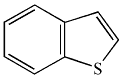
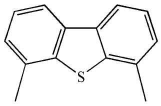
Figure 5). The PXRD patterns (Figure S6) together with IR spectrum (Figure S7) before and after catalysis demonstrated that the structure and the crystallinity of **6** was maintained during the reaction process.

From the point of practical applications, the broad-spectrum removing of refractory sulfur-containing compounds in fuel oils is desired. Benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4, 6-DMDBT) were also used to assess the general applicability of **6**. As shown in Table 2, BT and 4, 6-DMDBT were converted completely after 8 and 6.5 h, respectively. The above results show that the nature of the substrates is a critical factor influencing the desulfurization process. BT shows the lowest oxidative activity due to the lowest electron density on the S atom. Yet, compared with 4,6-DMDBT, DBT with lower electron density on the S atom shows a higher conversion to the corresponding suloxide and sulfone. The result indicates that the reactivity of the substrates not only ascribe to the electron density of sulfur atom but also to the steric hindrance (methyl group) on the sulfur atom, which is in line with the previous researches.[28,29]

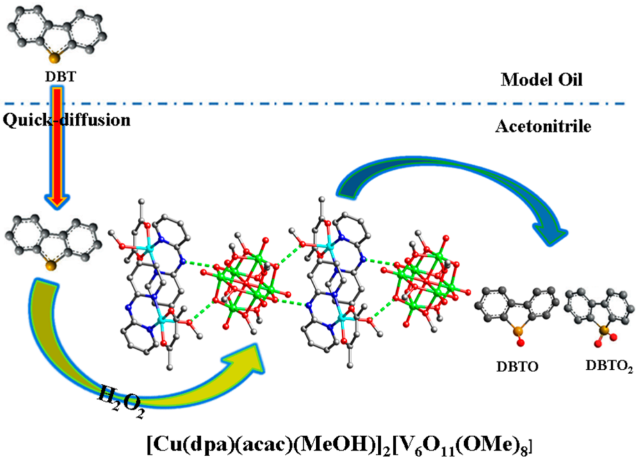
Table 2. Results of Oxidative Desulfurization of DBT and Its Derivatives Catalyzed by 6 using H_2O_2 Oxidant[a]

Entry	Substrate	Conv. (%)	Reaction time (h)
1		100	6
2		100	8
3		100	6.5

[a]Reaction conditions: model oil (2 mL), catalyst (1.5 mol %), acetonitrile (2 mL) and 30% H_2O_2 (0.5 mmol) at 40 °C.

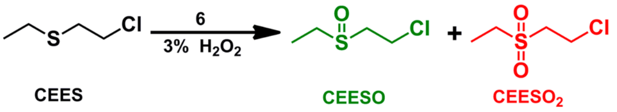
The proposed mechanism of the ODS process in the presence of **6** has also been preliminary studied. Comparative experiment using H_2O_2 and **6** in only decalin showed a negligible conversion because of the poor solubility of H_2O_2 in decalin. In acetonitrile, however, DBT was transformed completely within 1.5 h under the same conditions as the early experiment showed. An additional experiment showed that the distribution coefficient of DBT in equivalent acetonitrile and decalin was about 0.82, and it remained almost unchanged when the concentration of DBT reduced to half (Table S3). These results further supported our speculation that acetonitrile was an efficient solvent in the biphasic system, which is appropriate for liquid−liquid extraction as well as suitable for oxidative transformation. As shown in Scheme 3, the ODS process consists of two steps: DBT was extracted by acetonitrile from the decalin phase, and then, in the presence of **6**, it was oxidized to the sulfoxide or sulfone, which were maintained in the acetonitrile phase and separated from the model oil.

Scheme 3. Proposed Mechanism of the ODS Process in the Biphasic System



For the sulfur mustard abatement, taken into account the high toxicity of real agent, a sulfur mustard simulant, CEES, was selected as the substrate to further study the catalytic activities of **6** in the selective oxidation system (Scheme 4). To obtain higher sulfoxide selectivity, diluted H_2O_2 (3% in water) was used, which could also be used as a disinfectant for cuts and abrasion. As shown in Figure 6, CEES was converted completely within 4 h. During the first hour, CEESO was the only product as long as CEES was still present. After reaction for 1 h, a small amount of CEESO was further oxidized to the $CEESO_2$, which is as toxic as the pristine sulfur mustard. Fortunately, the selectivity of CEESO was still above 85% when CEES was completely consumed, and no dangerous polymerized sulfur-containing compounds were detected. As a heterogeneous catalyst, **6** can be reused at least three times without any appreciable loss of its high catalytic performance in the CEES oxidative abatement process (Figure S8).

Scheme 4. Oxidative Abatement of CEES to CEESO and $CEESO_2$ Catalyzed by Compound 6



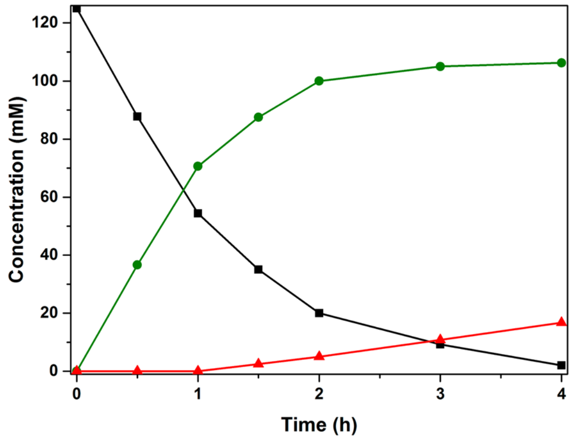


Figure 6. Catalytic abatement of CEES with **6**. Black: CEES; green: CEESO; red: $CEESO_2$. Reaction conditions: CEES (0.5 mmol), **6** (0.034 mmol), 1,3-dichlorobenzene (0.25 mmol), 3% H_2O_2 (0.525 mmol), and acetonitrile (4 mL) at room temperature for 4 h.

Table 3. Crystallographic Data for Compounds 1−6

	1	2	3	4	5	6
formula	$C_{36}H_{54}N_6O_{25}Cu_2V_6$	$C_{42}H_{56}N_4O_{25}Cu_2V_6$	$C_{48}H_{72}N_6O_{29}Co_2V_6$	$C_{50}H_{62}N_4O_{27}Co_2V_6$	$C_{37}H_{53}N_6O_{23}Cu_2V_6$	$C_{40}H_{64}N_6O_{25}Cu_2V_6$
M_r	1403.57	1449.62	1620.62	1574.53	1382.57	1461.69
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	*P*-1	*P*-1	*P*2(1)/*c*	*P*2(1)/*c*	*C*2/*c*	*P*-1
T (K)	296(2) K	296(2) K	296(2) K	296(2) K	296(2) K	296(2) K
a (Å)	9.831(3)	10.8434(18)	10.6093(3)	11.0869(4)	22.1519(6)	10.097(9)
b (Å)	12.003(4)	11.3914(18)	12.9751(4)	11.1026(4)	14.6490(6)	11.715(11)
c (Å)	13.179(4)	12.250(2)	23.5982(7)	24.7041(9)	18.5252(6)	12.835(12)
α (deg)	74.939(6)	82.018(6)	90	90	90	78.426(16)
β (deg)	70.669(6)	81.561(6)	92.4320(10)	90.3780(10)	121.271(2)	73.825(17)
γ (deg)	68.287(6)	64.109(5)	90	90	90	72.759(16)
V (Å^3)	1346.6(7)	1341.8(4)	3245.52(17)	3040.85(19)	5138.1(3)	1381(2)
Z	1	1	2	2	4	1
D_{calc} (g cm^{-3})	1.731	1.794	1.658	1.720	1.787	1.757
F(000)	708	732	1652	1596	2788	742
R_1 [$I > 2\sigma(I)$]	0.0707	0.0570	0.0397	0.0462	0.0540	0.0950
wR_2 [$I > 2\sigma(I)$]	0.1458	0.1343	0.1081	0.1191	0.1688	0.2604
R_1(all data)	0.1100	0.1064	0.0476	0.0560	0.0635	0.1546
wR_2 (all data)	0.1739	0.1581	0.1177	0.1285	0.1773	0.3163
GOF	1.043	0.993	1.076	1.099	1.117	1.012
CCDC no.	1523620	1464434	1460874	1469333	1523621	940415

■ CONCLUSIONS

In summary, by controlling the reaction conditions, we have synthesized six methoxohexavanadate compounds. The hexa-, hepta-, and octa-substituted methoxohexavanadate clusters could be obtained through varying amounts of Et_3N. The introduction of Cu- or Co-complexes make compounds **1−6** more stable, and they can be used as heterogeneous catalyst in the selective oxidation of sulfides using hydrogen peroxide with high catalytic activities. Specifically, compound **6** exhibits extraordinary efficiency in oxidative desulfurization (conv. of DBT up to 100% in 6 h) and CEES abatement (conv. of CEES reached 100% and selectivity of CEESO up to 85% after 4 h) and can be reused by filtration. Investigations on the use of these methoxohexavanadate catalysts for other potential catalytic reactions are in progress.

■ EXPERIMENTAL SECTION

General Methods and Materials. All reagents and solvents for synthesis were purchased from commercial suppliers and used as received unless otherwise noted. The metal content of the compounds **1−6** was measured by inductively coupled plasma (ICP) on a JY-ULTIMA2 analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. The powder X-ray diffraction pattern was collected by using a Rigaku D/max-2550 diffractometer with Cu Kα radiation and the XPS spectra were recorded on an ESAY ESCA spectrometer with an Mg Kα achromatic X-ray source. The resulting mixture was analyzed by GC-MS and GC using naphthalene as internal standard substrate after the catalytic reaction was completed. The GC analyses were performed on Shimadzu GC-2014C with a FID detector equipped with an Rtx-1701 Sil capillary column. The GC-MS spectra were recorded on Agilent 7890A-5975C at an ionization voltage of 1200 V. The C, H, and N elemental analyses were conducted on PerkinElmer 240C elemental analyzer.

*Synthesis of [Cu(dpa)(acac)(H$_2$O)]$_2$[V$_6$O$_{13}$(OMe)$_6$] (**1**).* VO(acac)$_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.6 mmol) were added to 8 mL of methanol. The resulting solution was stirred at 40 °C for 20 min, and then 2, 2′-dipyridine amine (34.3 mg, 0.2 mmol), Cu(OAc)$_2$·H$_2$O (39.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, green crystals suitable for X-ray diffraction grew upon after leaving the solution to stand for a week. Yield: 65.5%. Anal. Calcd for $C_{36}H_{54}N_6O_{25}V_6Cu_2$: C, 30.81 ; H, 3.88 ; N, 5.99 ; V, 21.78 ; Cu, 9.05. Found: C, 31.02; H, 4.11; N, 5.86; V, 22.04; Cu, 9.25. IR spectrum, ν (cm^{-1}): 3430 (O−H, s), 3190 (N−H, m), 3076 (Ar−H, w), 1645 (s), 1582 (C═N, s), 1525 (s), 1481 (C═C, s), 1430 (s), 1235 (s), 1166 (s), 1034 (s), 958 (s), 769 (s), 655400 (s), 450 (Cu−N, m).

*Synthesis of [Cu(phen)(acac)(MeOH)]$_2$[V$_6$O$_{13}$(OMe)$_6$] (**2**).* The synthetic procedure was the same as for compound **1**, except that 1,10-phenanthroline (36.1 mg, 0.2 mmol) was used instead of 2,2′-dipyridine amine. The reaction mixture was stirred for 12 h. From the resulting solution, green crystals suitable for X-ray diffraction grew upon after leaving the solution to stand for a week. Yield: 64.2%. Anal. Calcd for $C_{42}H_{56}N_4O_{25}V_6Cu_2$: C, 34.8; H, 3.89; N, 3.86; V, 21.11; Cu, 8.77. Found: C, 34.92; H, 3.91; N, 4.05; V, 22.38; Cu, 9.71. IR spectrum, ν (cm^{-1}): 3439 (O−H, s), 2914 (Ar−H, w), 1626 (s), 1581 (C═N, s), 1512 (s), 1428 (C═C, s), 1384 (s), 1143 (w), 1106 (w), 1035 (s), 954 (s), 846 (s), 757 (s), 719 (w), 668 (s), 445 (Cu−N, w).

*Synthesis of [Co(dpa)(acac)$_2$]$_2$[V$_6$O$_{13}$(OMe)$_6$]·2MeOH (**3**).* The synthetic procedure was similar to for compound **1**, only replacing Cu(OAc)$_2$·H$_2$O with Co(OAc)$_2$·4H$_2$O (49.8 mg, 0.2 mmol). The reaction mixture was stirred for 12 h. From the resulting solution, brown crystals suitable for X-ray diffraction grew upon after leaving the solution to stand for a week. Yield: 60.4%. Anal. Calcd for $C_{48}H_{72}N_6O_{29}V_6Co_2$: C, 35.57; H, 4.48; N, 5.19; V, 18.86; Co, 7.27. Found: C, 35.52; H, 4.15; N, 5.35; V, 17.38; Co, 6.92. IR spectrum, ν (cm^{-1}): 3443 (O−H, s), 3182 (N−H, w), 3064 (Ar−H, w), 1642 (s), 1564 (C═N, s), 1526 (s), 1473 (C═C, s), 1375 (s), 1290 (s), 1166 (s), 1030 (s), 951 (s), 755 (s), 657 (s), 448 (Co−N, m).

*Synthesis of [Co(phen)(acac)$_2$]$_2$[V$_6$O$_{13}$(OMe)$_6$] (**4**).* The synthetic procedure was similar to for compound **2**, only replacing Cu(OAc)$_2$·H$_2$O with Co(OAc)$_2$·4H$_2$O (49.8 mg, 0.2 mmol). The reaction mixture was stirred for 12 h. From the resulting solution, brown crystals suitable for X-ray diffraction grew upon after leaving the solution to stand for a week. Yield: 61.2%. Anal. Calcd for $C_{50}H_{62}N_4O_{27}V_6Co_2$: C, 38.14; H, 3.97; N, 3.56; V, 19.41; Co, 7.49. Found: C, 37.41; H, 3.40; N, 3.73; V, 18.57; Co, 7.52. IR spectrum, ν (cm^{-1}): 3052 (Ar−H, w), 1642 (w), 1570 (C═N, s), 1519 (s), 1428 (C═C, s), 1369 (s), 1284 (s), 1030 (s), 953 (s), 945 (s), 847 (s), 768 (s), 716 (m), 664 (s), 454 (Co−N, m).

*Synthesis of [Cu(dpa)(acac)]$_2$[V$_6$O$_{12}$(OMe)$_7$] (**5**).* VO(acac)$_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.7 mmol) were added to 8 mL of methanol. The resulting solution was stirred at 40 °C for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h, and the precipitate was filtrated and redissolved in DMSO. After about 2 weeks, brown crystals suitable for X-ray diffraction were obtained. Yield: 63.5%. Anal. Calcd for $C_{37}H_{53}N_6O_{23}V_6Cu_2$: C, 32.14; H, 3.86; N, 6.08; V, 22.11; Cu, 9.19. Found: C, 31.65; H, 3.91; N, 6.12; V, 21.06; Cu, 9.25. IR spectrum, ν (cm^{-1}): 3128 (N−H, w), 3076 (Ar−H, w), 1636 (s), 1585 (C═N, s), 1520 (s), 1474 (C═C, s), 1390 (s), 1273 (s), 1163 (s), 1027 (s), 955 (s), 787 (s), 728 (w), 650 (s), 585 (s), 448 (Cu−N, m).

*Synthesis of [Cu(dpa)(acac)(MeOH)]$_2$[V_6O_{11}(OMe)$_8$] (**6**).* $VO(acac)_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.8 mmol) were added to 8 mL of methanol. The resulting solution was stirred at 40 °C for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12h. From the resulting solution, green crystals suitable for X-ray diffraction grew upon after leaving the solution to stand for a week. Yield: 62.2%. Anal. Calcd (found) for $C_{40}H_{64}N_6O_{25}V_6Cu_2$: C, 32.87; H, 4.41; N, 5.75; V, 20.91; Cu, 8.69. Found: C, 32.65; H, 4.58; N, 5.56; V, 20.82; Cu, 8.52. IR spectrum, ν (cm^{-1}): 3325 (O−H, w), 3182 (N−H, m), 3068 (Ar−H, w), 1629 (s), 1572 (C═N, s), 1544 (s), 1459 (C═C, s), 1255 (s), 1168 (s), 1035 (s), 953 (s), 942 (s), 916 (s), 785 (s), 675 (s), 445 (Cu−N, m).

X-ray Crystallography. Single-crystal X-ray diffraction data for compounds **1**−**6** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 K. All absorption corrections were applied using the multiscan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package.[30,31] The hydrogen atoms of the organic ligands were refined as rigid groups. Crystallographic data for compounds **1**−**6** are summarized in Table 3. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries 1523620 (**1**), 1464434 (**2**), 1460874 (**3**), 1469333 (**4**), 1523621 (**5**), 940415 (**6**). The selected bond lengths and bond angles of compounds **1**−**6**, please see Table S2.

Catalytic Oxidative Desulfurization Process (ODS). DBT was dissolved in decalin to produce the model oil (S content: 1000 ppm). The mixture of model oil (2 mL) and acetonitrile (2 mL) was stirred at 40 °C for 10 min. After that, catalyst (1.5 mmol %) and 30% aqueous H_2O_2 (0.5 mmol) were added. The reaction was monitored by GC at various time intervals. Catalytic abatement of CEES: CEES (0.5 mmol) and 1, 3-dichlorobenzene (internal standard, 0.25 mmol) was dissolved in acetonitrile (4 mL), followed by addition of compound **6** (0.034 mmol). After stirring the mixture for 2 min at room temperature, 3% aqueous H_2O_2 (0.525 mmol) was added dropwise. The reaction was monitored by GC at various time intervals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00366.

Some structural figures, X-ray powder diffraction patterns, IR spectra, XPS spectra and ICP analysis (PDF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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