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Cupric Decamolybdodivanadophosphate. A Coordination Polymer Heterogeneous Catalyst for Rapid, High Conversion, High Selectivity Sulfoxidation Using the Ambient Environment

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A new type of coordination network polymer involving the redox-active polyanion, $PV_2Mo_{10}O_{40}^{5-}$, and bridging $-Cu^{II}(OH_2)_4-$ units, $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$ (**1**), has been characterized by X-ray crystallography and several other methods. It is the first efficient heterogeneous (insoluble) catalyst for selective and rapid sulfoxidation using only the ambient environment (air at room temperature). Catalytic activity is enhanced by soluble nitrate in nontoxic perfluoropolyether (PFPE) media.

The development of catalysts for selective and reductant-free O_2/air-based oxidations under ambient conditions (1 atm of air; 25 °C) would have applications ranging from the green and energy-efficient production of chemicals to the realization of fabrics, coatings, personal care products, and porous solids that would remove toxic compounds in the air by O_2/air-based oxidative degradation. There are a few recent reports of molecules or materials that can catalyze reductant-free O_2-based (henceforth "aerobic") oxidations, but none are simultaneously heterogeneous (hence recoverable and extensively formulatable) yet fast using the ambient environment.[1−7] We report here the preparation and characterization of such a system: a coordination polymer composed of a mixed-addenda polyoxometalate (POM)[8] bridged by aquated Cu(II) units. This polymer, $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$ (**1**), is a particularly reactive catalyst for selective aerobic sulfoxidation of thioethers (organic sulfides).[9]

A broad spectrum screening of combinations of redox-active transition metal cations and oxidizing anions (including some families of POMs and common species such as NO_3^- and ClO_4^-) in acetonitrile solvent identified combinations of CuX_2 (where X is a minimally coordinating anion such as OTf^-, ClO_4^-, BF_4^-, or the POM $PV_2Mo_{10}O_{40}^{5-}$) and a nitrate salt as highly effective catalytic systems for selective aerobic sulfoxidation. The most reactive system proved to be **1** when suspended in nontoxic perfluoropolyether (PFPE) solvents[10−15] containing nitrate.

This coordination polymer is readily prepared and crystallized.[16] Compound **1** crystallizes in the monoclinic space group *C*2/*m* and contains α-$PV_2Mo_{10}O_{40}^{5-}$ Keggin anions[17,18]

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(9) CEES (2-chloroethyl ethyl sulfide) is a simulant for mustard and the rationale for selectivity is that the corresponding sulfoxide is relatively nontoxic (and far less so than the corresponding sulfone).

(10) PFPEs have been approved for use in personal care products including skin creams by the U.S. Food and Drug Administration.

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(16) Preparation of **1**: Copper nitrate (1.30 mmol) and copper triflate (1.95 mmol) were added to a solution of $H_5PV_2Mo_{10}O_{40}\cdot 10H_2O$ (0.26 mmol) in 90 mL of water, and the resulting solution was heated at 50 °C for 3 h. Crystals of **1** form slowly upon cooling to 15 °C (yield ~ 50%). Calcd for $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n\cdot 30H_2O$: Cu, 7.14; P, 1.16; V, 3.82. Found: Cu, 7.0; P, 1.2; V, 3.7.

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10.1021/ic0348953 CCC: $25.00

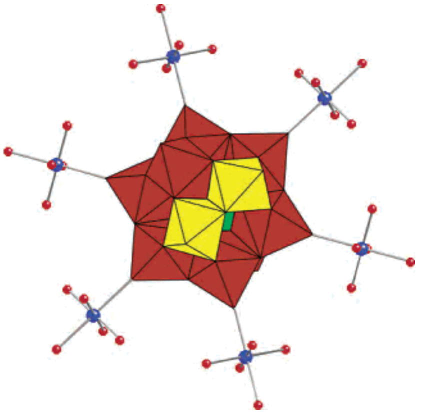

Figure 1. The coordination polymer $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$, **1**, in combination polyhedral/ball-and-stick notation (only one of five positional isomers of the POM unit is shown) illustrating the six Cu−O(POM) linkages. The Cu, P, V, O, and Mo atoms are blue, green, yellow, red, and orange, respectively.

linked through their terminal oxygen atoms by tetragonally distorted (POM)O−$Cu(OH_2)_4$−O(POM) moieties (Figure 1). Each $PV_2Mo_{10}O_{40}{}^{5-}$ is bound to six Cu(II) centers, each of which has four aqua ligands in an equatorial plane (bond lengths ~ 1.9 Å) and two longer axial bonds to the POM oxygens of ~2.5 Å. While one or two bonds between POM oxygens and counterion metal centers is a well-established structural paradigm[19] for POMs, it is unusual if not unprecedented to have six. The FTIR spectra, elemental analyses, and thermogravimetric (TGA) and differential scanning calorimetric (DSC) data are fully consistent with the structure determined by X-ray crystallography.[16,18]

Table 1 gives the initial rates of aerobic oxidation of one of the least reactive sulfides, 2-chloroethyl ethyl sulfide (CEES),[9] catalyzed by **1** suspended in PFPE solvents and by other soluble and insoluble catalyst systems. The rates of sulfoxidation for other dialkyl sulfides such as dimethyl sulfide are faster than for CEES. Importantly, the selectivity for sulfoxide in these oxidations, including CEES + $^1/_2O_2 \rightarrow$ CEESO, a reaction of considerable interest,[9] and the conversions of sulfide are both nearly quantitative for all these reactions so these data have been omitted from Table 1. No sulfoxidation is seen in only aerated solvent over the time scale of these experiments (1 h) nor when nitrate is present in the absence of metals (data not shown in Table 1). However, sulfoxidation catalyzed by all Cu complexes and/or the POM, $PV_2Mo_{10}O_{40}{}^{5-}$, is enhanced when nitrate is added. Coordinating solvents or ligands decrease or eliminate catalytic activity in all Cu(II)-containing systems. Specifically, CuX_2 species, X = $SO_4{}^{2-}$ or Cl^-, are catalytically inactive, whereas CuX_2 species, X = $NO_3{}^-$, $BF_4{}^-$, $ClO_4{}^-$, OTf^- (triflate), or $PV_2Mo_{10}O_{40}{}^{5-}$, are active. For the soluble $Cu(OTf)_2/NO_3{}^-$ system, there is no catalysis in MeOH, EtOH, Me_2CO, or CF_3CH_2OH (TFE), solvents that can coordinate to Cu(II) via oxygen lone pairs, or in CH_2Cl_2 or $C_2H_4Cl_2$, solvents that can form donor−acceptor complexes with Cu(II) species. There is reasonable activity in CH_3CN which coordinates weakly to Cu(II) and considerable activity in two PFPE solvents, Fomblin MF-300 or Fluorolink 7004.[20] These PFPE solvents coordinate to Cu(II) minimally if at all and consequently keep **1** totally insoluble as assessed by electronic absorption spectroscopy. The high activity in

Table 1. Aerobic Oxidation of 2-Chloroethyl Ethyl Sulfide (CEES)[a]

catalyst[b]	solvent	−(d[CEES]/d*t*) (10^5, mmol s^{-1})[c]
	Soluble (Homogeneous) Catalyst	
$Cu(OTf)_2/NO_3{}^-$	CH_3CN	6.45
	Insoluble (Heterogeneous) Catalysts	
$CuCl_2$	PFPE[d]	0
$CuSO_4$	PFPE[d]	0
$Cu(NO_3)_2$	PFPE[d]	0.13
$Cu(BF_4)_2$	PFPE[d]	0.11
$Cu(ClO_4)_2$	PFPE[d]	0.15
$Cu(OTf)_2$	PFPE[d]	0.21
$CuCl_2/NO_3{}^-$	PFPE[d]	0.80
$CuSO_4/NO_3{}^-$	PFPE[d]	1.30
$Cu(BF_4)_2/NO_3{}^-$	PFPE[d]	8.13
$Cu(ClO_4)_2/NO_3{}^-$	PFPE[d]	11.30
$Cu(OTf)_2/NO_3{}^-$	PFPE[d]	12.90
$Na_5PV_2Mo_{10}O_{40}$	PFPE[e]	3.4
1 only	PFPE[e]	4.86
$Na_5PV_2Mo_{10}O_{40}/NO_3{}^-$	PFPE[e]	12.4
1 $/NO_3{}^-$	PFPE[e]	17.26

[a] General conditions: 0.875 mmol (0.35 M) of CEES, 1 atm of air, and 0.876 mmol (0.35 M) of 1,3-dichlorobenzene (internal standard) were stirred in 2.5 mL of solvent at 25 °C for 1 h. [b] [Cu(II)] = 20 mM where present; [$TBANO_3$] = 16 mM in all reactions except in reaction 4 (reaction with only $Cu(NO_3)_2$); [$SO_4{}^{2-}$] = 20 mM in reactions with this anion; the total concentration of the other anions (OTf^-, $ClO_4{}^-$, $BF_4{}^-$, and/or Cl^-) = 40 mM in all reactions, no product was observed in the absence of Cu(II) salts (for example in the presence of only TBAX, X = $ClO_4{}^-$, OTf^-, $BF_4{}^-$, $NO_3{}^-$, Cl^-, or $SO_4{}^{2-}$). [c] Initial reaction conversion rate = mmol of CEES consumed s^{-1}. [d] 96% Fomblin MF-300/4% CH_3CN (4% CH_3CN used to ensure solubility). [e] 96% Fluorolink 7004/4% CH_3CN; 50 μmol of insoluble POM is present in reactions with these compounds, $Na_5PV_2Mo_{10}O_{40}$ or the $PV_2Mo_{10}O_{40}{}^{5-}$ repeating unit in **1**. See Supporting Information for more details.

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(18) Crystal data for $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$ (**1**): monoclinic space group $C2/m$, with a = 15.808(19) Å, b = 15.330 (17) Å, c = 11.0029(15) Å, β = 92.540(2)°, V = 2663.7(6) Å^3, and Z = 2. The data were collected on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo Kα (0.71073 Å) radiation. The structure was solved by direct methods and difference Fourier techniques (SHELXTL, V6.12). All non-hydrogen atoms were refined anisotropically except the vanadium atoms and O9W, O10W, and O11W. At final convergence, R1 = 8.83% and GOF = 1.248 on the basis of 2643 independent reflections with $F_o > 4\sigma(F_o)$. The structure was originally solved in space group $R\bar{3}$ and was refined to an R1 value of about 12%, with ~50 systematic absence violations. The monoclinic space group is related to the rhombohedral one, and there were no systematic absence violations with a final R1 of 9%. The structure could be reported as rhombohedral, but the statistics on the reflection data appeared to indicate that it was not the best choice. The complex α-$PV_2Mo_{10}O_{40}{}^{5-}$ is always present as a mixture of five positional isomers. Therefore, each of the 12 MO_6 centers of the anion is one-sixth vanadium and five-sixths molybdenum statistically. Recrystallization produces a microcrystalline compound of formula $Cu_2HPV_2Mo_{10}O_{40}\cdot 22H_2O$. IR (1% KBr pellet, 1200−400 cm^{-1}): 1179 (m), 1060 (sh), 1035 (s), 962 (s), 866 (m), 777 (m), 648 (s), 581 (w), and 520 (w). Anal. Calcd for $Cu_2HPV_2Mo_{10}O_{40}\cdot 22H_2O$: Cu, 5.53; P, 1.37; V, 4.51. Found: Cu, 5.5; P, 1.4; V, 4.6. The number of water molecules was confirmed by thermogravimetric analysis (TGA) [MW = 2586].

(19) Representative work includes: (a) Zheng, L.-M.; Wang, Y.; Wang, X.; Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **2001**, *40*, 1380−1385. (b) Zhang, X.; Chen, Q.; Duncan, D. C.; Campana, C.; Hill, C. L. *Inorg. Chem.* **1997**, *36*, 4208−4215. (c) Chen, Q.; Zubieta, J. *Coord. Chem. Rev.* **1992**, *114*, 107−167.

(20) A comparison of the data in ref 7 (Table 1) and this work reveals that high conversions can now be achieved in 1 h in PFPE rather than 20 h (in CH_3CN) while maintaining effectively quantitative selectivity for sulfoxide.

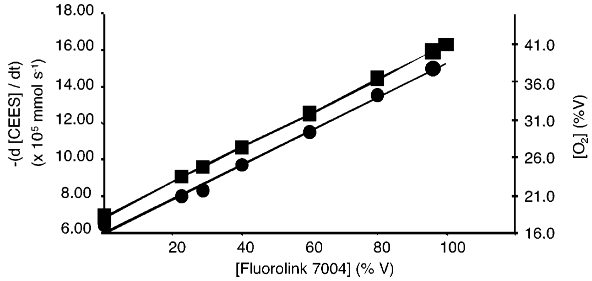

Figure 2. Effect of the relative concentration of Fluorolink 7004 solvent on the rate of Cu(II)/OTf$^-$/NO$_3$$^-$-catalyzed air oxidation of CEES (●) and solubility of O_2 (■) The latter is shown slightly offset to allow for comparison of the slopes. Conditions: 1 atm of air, 25 °C. [TBANO$_3$] = 16 mM. [Cu(OTf)$_2$] = 20 mM; [CEES] = 0.35 M. Stirring rate ~ 100 rpm.

the PFPE solvents also derives from the fact that O_2 is more soluble in them than in conventional solvents.[21,22] The data in Figure 2 (showing that an increase in the rate of CEES oxidation closely parallels the increase in dissolved O_2 concentration) are consistent with this and establish that O_2 is involved before or in the rate-determining step.

Significantly, **1** is active for selective aerobic sulfoxidation as a totally insoluble suspended material in the absence of any reagent or cocatalyst. The highest activity is seen for **1** suspended in PFPE containing nitrate (TBANO$_3$). Bosch and Kochi convincingly established that NO_2 can catalyze the O_2 oxidation of sulfides to sulfoxides in CH_2Cl_2 solution via [sulfide, NO$^+$]NO$_3$$^-$ electron donor−acceptor (EDA) intermediate complexes.[1] However, two factors argue that the homogeneous Cu(OTf)$_2$/NO$_3$$^-$ and the heterogeneous **1**/NO$_3$$^-$ systems reported here are substantially different chemistry than that of Bosch and Kochi. First, no oxidation of CEES is detectable by either of these systems in their solvent, CH_2Cl_2. Second, the reactivity of NO$_3$$^-$ from which NO$^+$ and NO_2 can form is either quite low (i.e., Cu(NO$_3$)$_2$ only versus Cu(OTf)$_2$/NO$_3$$^-$ or **1**/NO$_3$$^-$) or nonexistent (TBANO$_3$ only) under the conditions in Table 1. To assess the likelihood of intermediate electron donor−acceptor (EDA) complexes between CEES and Cu(II) in the soluble Cu(OTf)$_2$/NO$_3$$^-$ system, 1 equiv of CEES was mixed with 1 equiv of Cu(NO$_3$)$_2$, and separately with 1 equiv of Cu(OTf)$_2$ in PFPE under anaerobic conditions. While no apparent EDA complex forms with the far less active Cu(NO$_3$)$_2$, a transient one does appear to form with Cu(OTf)$_2$ under the same conditions indicated by an absorption band at 290 nm that decreases with time (Figure 3).

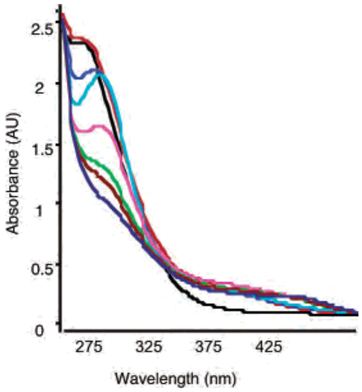

Figure 3. UV−vis spectra of an intermediate electron donor−acceptor (EDA) complex between CEES and Cu(II) in the Cu(OTf)$_2$/NO$_3$$^-$ system. The red line corresponds to the spectra of Cu(OTf)$_2$ alone while the black, medium blue, light blue, pink, green, brown, and dark blue lines correspond to the addition of CEES after 2, 10, 15, 25, 40, 50, and 120 min, respectively.

The mechanism of the optimally active heterogeneous catalyst, **1**/NO$_3$$^-$, is clearly complex and could well proceed by multiple mechanisms (oxygen transferring species). However, the data suggest that reversible displacement of the weakly associating $PV_2Mo_{10}O_{40}{}^{5-}$ unit from Cu(II) in the insoluble network **1** with formation of an intermediate Cu^{II}(CEES)(NO$_3$$^-$) EDA complex[23] and a slow step involving reoxidation by O_2 are likely operable.[24]

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Supporting Information Available: Structure determination parameters, crystal and structure refinement data, atomic coordinates and isotropic displacement parameters (in CIF format), and thermal ellipsoid plot for $\{[(Cu^{II}(OH_2)_4)_3(OH)]PV_2Mo_{10}O_{40}\}_n$ (**1**); plot of CEES consumption as a function of NO$_3$$^-$; plot of CEESO formation as a function of Cu(OTf)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Wesseler, E. P.; Iltis, R.; Clark, L. C., Jr. *J. Fluorine Chem.* **1977**, *9*, 137−146.

(22) Solvent polarity is also a factor that can affect oxidation rates. For example, see: Ogata, Y.; Kamei, T. *Tetrahedron* **1970**, *26*, 5667−5674.

(23) The POM catalyzes the reduction of NO$_3$$^-$ to NO_2/N_2O_4 by CEES and subsequent formation of an intermediate EDA complex.

(24) TBANO$_3$ alone does not affect the rate of CEES oxidation. However, when **1** is added to a mixture of TBANO$_3$ and CEES in PFPE, the system quickly turns brown (the color of an NO_2/N_2O_4−CEES intermediate). This is immediately followed by the formation of CEESO.