7812 *Inorg. Chem.* **2009**, *48*, 7812–7817
DOI: 10.1021/ic9007729

Inorganic Chemistry
Article

Synthesis, Structure, and Magnetism of a Polyoxometalate with Coordinatively Unsaturated d-Electron-Transition Metal Centers

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Received April 21, 2009

A series of tetrabutylammonium salts of transition-metal substituted Wells−Dawson polyoxometalates has been synthesized by phase-transfer techniques and characterized by infrared spectroscopy, elemental analysis, and variable-temperature magnetic measurements. X-ray-quality crystals were obtained with a diffusion method using different organic solvents. The X-ray crystal structure of $[(n\text{-}C_4H_9)_4N]_{11}H_5[Cu_4(P_2W_{15}O_{56})_2]$ (**1**) (monoclinic, $P2(1)/n$, $Z = 2$, $a = 19.7269(6)$ Å, $b = 17.6602(5)$ Å, $c = 44.2525(11)$ Å, $\beta = 91.182(2)°$; $R_1 = 8.35\%$ based on 31 282 independent reflections) reveals the presence of two unusual coordinatively unsaturated Cu(II) centers. In the absence of cocatalysts, **1** does not catalyze the aerobic oxidation of organic substrates in organic solvents.

Introduction

The development of new materials to catalyze the selective aerobic oxidation of sulfur-based compounds under ambient conditions (1 atm air/O_2 and 25 °C) is of both intellectual and practical interest.[1−6] In recent years, several different catalytic systems based on polyoxometalates (POMs) have been investigated. Okun et al.[7−12] reported several bulk and cationic-silica-supported POMs that catalyze the selective aerobic oxidation of 2-chloroethyl ethyl sulfide (CEES, a mustard gas simulant) to 2-chloroethyl ethyl sulfoxide under ambient conditions. The most recent work[11,12] showed that tetrabutylammonium (TBA) salts of an iron(III)-substituted POM, $TBA_3[H_2Fe[H(ONO_2)_2]PW_{11}O_{39}]\cdot(HNO_3)$, and related Cu(II)-substituted derivatives are extremely fast and selective catalysts for aerobic (air-based) sulfoxidation. These studies indicate that the catalytic turnover frequency reflects a significant synergy between the d-electron-metal-substituted POM unit and nitrate. Unfortunately, the exact nature of this nitrate−POM interaction, despite considerable effort to clarify this issue experimentally, remains unclear for two reasons: (1) the X-ray structural determinations of these monosubstituted α-Keggin polyanions reveal that the substituted position (most frequently copper and iron in these highly active catalysts) is always 12-fold disordered, precluding identification of the terminal ligand, and (2) the paramagnetism of these highly active catalysts makes observation of the terminal ligands on the d-electron-metal centers impossible.

In the context of ongoing studies of metal-substituted POMs as catalysts for ambient-temperature, air-based oxidation of sulfides, trivacant $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ was chosen as the precursor to prevent disorder in the X-ray structures of the Cu- and Fe-substituted derivatives. We report here the synthesis of Cu_4-, Co_4-, Mn_4-, and Fe_4-substituted derivatives of $[P_2W_{15}O_{56}]^{12-}$ as their tetra-*n*-butylammonium (TBA) or tetra-*n*-heptylammonium (THpA) salts using a phase-transfer method that simulates the environment of the organic-solvent-soluble POM component of the highly active Cu- and Fe-substituted POM aerobic oxidation catalysts. The organic-soluble POMs were characterized by a range of techniques including magnetochemical analysis of the Cu(II)-based polyanion. We further report the provocative finding that the Cu(II) centers in the polyanion of **1**, namely, **1a**, are coordinatively unsaturated. The coexistence of unsaturated and saturated

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Cu(II) centers is reminiscent of the polyanion, $\{Cu_4(GeW_9O_{34})_2\}$, recently reported by Yamase and co-workers.[13]

Experimental Section

General Methods and Materials. $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 18H_2O$ and $Na_{14}Cu[Cu_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]\cdot 53H_2O$ were prepared according to literature methods,[14,15] and their purities were checked by FT-IR. All of the starting reagents, $Cr(NO_3)_3\cdot 9H_2O$, $Mn(NO_3)_2$, $Fe(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2$, $Cu(NO_3)_2\cdot 2.5H_2O$, $AgNO_3$, $CuBr_2$, $(n\text{-}C_4H_9)_4NBr$ (TBABr), $(n\text{-}C_4H_9)_4NNO_3$ (TBANO$_3$), $(n\text{-}C_7H_{15})_4NBr$, acetonitrile, dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, tetrahydrofuran, toluene, hexane, decane, octadecene, 1,3-dichlorobenzene, and CEES were purchased from Aldrich and used without further purification. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 5% phenyl methyl silicone capillary column, a flame ionization detector, and a Hewlett-Packard 3390A series integrator using N_2 as the carrier gas. Elemental analyses for K, Na, Cu, Si, and W were performed by Galbraith Laboratories (Knoxville, Tennessee). The infrared spectrum (2% sample in KBr pellet) was recorded on a Nicolet 6700 FT-IR spectrometer from ThermoElectron Corporation. The thermogravimetric data were collected on an ISI TGA 1000 instrument. Potentiometric titrations of the organic-solvent-soluble POMs in acetonitrile solution with 1.0 M methanolic $(n\text{-}C_4H_9)_4NOH$ to assess protonation states were carried out using a model 240 Corning pH meter equipped with a combination microglass electrode at room temperature. Magnetic susceptibility measurements were performed at applied fields of 0.1 to 5.0 T for the temperature range $T = 1.8-290$ K using a Quantum Design MPMS-5XL SQUID magnetometer.

General Method to Synthesize the Organic-Soluble POM Compounds. Phase transfer was used to produce the organic-solvent-soluble transition-metal-substituted POMs (TMSPs). The synthetic route to these compounds involves a metathetical exchange by adding and mixing a stoichiometric amount of TBA salt in organic solution to an aqueous solution of the potassium or sodium salt of the POMs with stringent control of the solution pH.[16] At the appropriate pH, the desired TBA^+/H^+ counterion combination associates and transfers the polyanions to the organic phase. The yield of the TBA salt is quite dependent on the pH. Optimizing the pH throughout the reaction can also minimize possible degradation or hydrolysis of the POMs.

Synthesis of $[(n\text{-}C_4H_9)_4N]_{11}H_5[Cu_4(P_2W_{15}O_{56})_2]$ (1). $Na_{14}Cu[Cu_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]\cdot 53H_2O$ (0.60 g, 0.066 mmol) was dissolved in 10 mL of deionized water. TBANO$_3$ (0.32 g, 1.06 mmol) was dissolved in 10 mL of CH_2Cl_2. These two solutions were mixed together with vigorous stirring. To this mixture was added a solution of 4 M HNO_3 dropwise under stirring until the solution became turbid. The final pH was 4.6. Upon standing, the solution separated into a cloudy, white aqueous layer and a clear green organic layer. The solution was then transferred to a separatory funnel, and the bottom layer (organic layer) was collected. The organic layer was transferred into a round-bottom flask and concentrated to a solid gel using a rotary evaporator. This green gel (0.90 g) was dissolved in a minimum amount of CH_3CN, and an excess quantity (ca. 50 mL) of deionized water was then added. The light-green precipitate that formed was collected, dried under a vacuum, and redissolved in a minimum amount of CH_2Cl_2, and anhydrous diethyl ether (ca. 100 mL) was added to afford a light-green powder (0.61 g, 88% yield). Crystals of this TBA salt were obtained by gas-phase (vapor) diffusion. Initially, the light-green powder of **1** (20 mg) was dissolved in 2 mL of $ClCH_2CH_2Cl$ in a 5 mL vial. This small vial was then moved into a 15 mL vial containing 5 mL of $CHCl_3$. The 15 mL vial was capped and placed in a dark cabinet. Green, blocklike crystals were obtained after one week. X-ray-quality single crystals were obtained by recrystallization using the same gas-phase diffusion method. The number of TBA cations, determined by the TGA measurement (S1, Supporting Information), was ca. 5.5 per P atom. The TGA measurement also indicates the presence of solvent molecules ($ClCH_2CH_2Cl$ and $CHCl_3$) in the freshly prepared **1**. However, the solvent molecules quickly evaporated under air, which caused cracks in the crystal of **1**. No Cl was found in the elemental analysis of the cracked crystals. Potentiometric titration of **1** indicated about five protons in the formulation (S2, Supporting Information). IR (2% KBr pellet, 1200−400 cm^{-1}): 1090 (s), 1060 (w, sh), 952 (s), 916 (w), 850 (w), 806 (s), 761 (s), 594 (w), 525 (w). Anal. Calcd for $C_{176}Cu_4H_{401}N_{11}O_{112}P_4W_{30}$, $[(n\text{-}C_4H_9)_4N]_{11}H_5[Cu_4(P_2W_{15}O_{56})_2]$: Cu, 2.45; P, 1.20; W, 53.25; C, 20.41; H, 3.90; N, 1.49. Found: Cu, 2.42; P, 1.1; W 50.2; C, 20.61; H, 3.75; N, 1.39. [MW = 10 357.705 g/mol]. The syntheses of Co-, Mn-, and Fe-substituted POMs are available in the Supporting Information (S3).

Magnetochemical Analysis. The magnetic susceptibility of **1** was recorded in the temperature interval 2−300 K, and applied fields ranged from 0.1 to 5.0 T. All data were corrected for diamagnetic and temperature-independent paramagnetic (TIP) contributions (the latter are significant for polyoxotungstates) that were partly derived from tabulated values and partly from measurements on similar yet diamagnetic polyoxotungstate compounds ($\chi_{dia/TIP}(\mathbf{1}) = -2.79 \times 10^{-5}$ cm^3 mol^{-1}). All simulations were performed using an extended version of the program CONDON for fully isotropic Heisenberg-type exchange.[17] Compound **1**, measured as a solid, is electron-spin-resonance-silent at room temperature (X-band).

X-Ray Crystallography. The X-ray-quality crystal of **1** was removed from the mother liquid and quickly coated with Paratone N oil. The coated crystal was mounted on a small fiber loop for index and intensity data collection. Because the crystals were prone to cracking quickly, extra care was needed when treating the organic-soluble crystals, especially the TBA salts obtained from chlorinated solvents. The X-ray diffraction data were collected under a nitrogen stream at 173 K on a Bruker D8 SMART APEX CCD single-crystal diffractometer using Mo Kα (0.71073 Å) radiation. Data collection, indexing, and initial cell refinements were processed using the SMART[18] software. Frame integration and final cell refinements were carried out using the SAINT[19] software. The final cell parameters were determined from the least-squares refinement of total reflections. The structures were determined through direct methods (SHELXS97) for locating the tungsten atoms and difference Fourier maps (SHELXL97). The hydrogen atoms of the water molecules were not located in the difference Fourier maps. The final results of the refinement are listed in Table 1.

Procedure for Catalytic Reactions. To 2.3 mL of acetonitrile was added 0.05 mmol of **1**, 0.875 mmol of CEES, and 0.876 mmol of 1,3-dichlorobenzene (internal standard). The solution was stirred in a 20 mL vial at room temperature under 1 atm of air. The products were then analyzed by gas chromatography after 20 h.

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Table 1. Crystal Data for **1**·$2ClCH_2CH_2Cl\cdot 2CHCl_3$

	1
empirical formula	$C_{182}Cl_{10}Cu_4H_{411}N_{11}O_{112}P_4W_{30}$
formula weight	10794.0 g mol^{-1}
space group	$P2(1)/n$
unit cell	$a = 19.7269(6)$ Å $b = 17.6602(5)$ Å $c = 44.2525(11)$ Å $\beta = 91.182(2)°$
volume	15413.5(7) $Å^3$
Z	2
temperature	173(2)K
wavelength	0.71073 Å
F(000)	9088
θ range	1.48−26.37°
abs. corr.	semiempirical
no. of total reflns	31282
no. of restraints	0
no. of params	814
abs. coeff.	11.588 mm^{-1}
GOF	1.006
final $R_1{}^a$ $[I > 2\sigma(I)]$	0.0835
final $wR_2{}^b$ $[I > 2\sigma(I)]$	0.1904

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]^{1/2}$.

Results and Discussion

Synthesis. The TBA salt of the copper-substituted phosphotungstate, **1**, was prepared using an improved phase-transfer method. In contrast to the general procedure in which a stoichiometric amount of TBABr is added to the aqueous solution of the polyoxometalate directly before the addition of organic solvent, we mixed a solution containing a stoichiometric amount of TBA salt in an organic solvent with an aqueous solution of the sodium salt of the polyoxometalate. The sequence change in the initial step helps avoid the formation of insoluble material induced by direct addition of TBA to the aqueous POM solution. The sequence change also results in a convenient route to optimize the amount of acid needed in the phase-transfer process. Initially, with the addition of acid into the mixture, white floccules form and disappear instantly with the vigorous stirring. After a certain amount of acid is added, one "extra" drop of acid results in a large amount of precipitate that does not redissolve, indicating that the optimal conditions have been reached. Absorption spectra showed that the concentration of POM in the organic layer reaches a maximum value at pH 4.6. The solution of the crude, phase-transferred product was collected and concentrated. One drawback of this phase-transfer method is the considerable amount of excess TBA cation present in the crude product and the less than quantitative transfer of the POM into the organic phase. However, the excess of TBA is also inevitable in the general literature method, and in either case the crude product must be purified before the final analysis. In the present study, the crude product was purified by repeated dissolving in a minimum amount of acetonitrile and then precipitation by the addition of excess water. The purified product was transferred to an anhydrous environment by dissolving it in a minimum amount of CH_2Cl_2 and then precipitating with a large amount of anhydrous diethyl ether before growing crystals. Similar methods were applied to the preparation of the TBA salts of cobalt- or manganese-substituted POMs and the THpA salt of iron-substituted POM.

Previously, Pope and co-workers[20−23] thoroughly studied the preparation of transition-metal-substituted POMs in anhydrous nonpolar solvents. They reported that the THpA cation can associate with the metal-substituted POMs, resulting in phase transfer of the polyanions from aqueous solution to highly nonpolar organic solvents such as toluene. These investigators prepared a series of THpA salts of $MXW_{11}O_{39}$, $MX_2W_{17}O_{61}$, and $M_4(XW_9)_2$ (M = Mn, Ni, Cu, Co; X = P, Si, Ge) in nonpolar solvents (benzene and toluene) using this phase-transfer method. A considerable amount of water (20−30 mol of water/mol of POM) was found in the transferred organic layer. Further, they argued, reasonably, that the low activity of water in highly nonpolar solutions favors dissociation of the water molecule coordinated to the d-electron transition metal center substituted in the POM unit. This group provided evidence from visible and EPR spectra for the existence of unsaturated positions on the substituted d-electron metals in the POMs. However, no X-ray crystal structures were presented.

Previously, Finke and co-workers[16] investigated the transfer of $\alpha_2\text{-}P_2W_{17}O_{61}(M^{n+}\cdot OH_2)^{n-10}$ ($M = Mn^{3+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) from aqueous solution to less polar organic solvents like CH_2Cl_2 by using TBABr. Two structurally distinct phosphorus atoms in this POM make NMR characterization possible even with the existence of proximal paramagnetic transition metal centers. Their studies of this system afforded isomerically pure TBA salts of the monosubsituted Wells−Dawson POMs as confirmed by ^{31}P NMR. Elemental analysis indicated that the TBA salts of their above monosubstituted Wells−Dawson POMs each contain exactly one extra equivalent of TBABr. This bromide was proposed to replace the terminal aqua ligand on the d-electron transition metal in the polyanion. These investigators verified the existence of the bromide ligand by absorption spectra and measured the ligand-association equilibrium constants. Again, no X-ray structures of these hydrophobic salts were reported.

The TBA salts of POMs play an important role in studying the catalytic properties of POMs in organic solvents. However, not many[24−32] tetraalkylammonium POM structures, especially of the Wells−Dawson type,

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have been reported, which reflects the challenges in growing diffraction-quality crystals of many classes of these polyanion salts. The formation of gels, the rapid cracking of effluorescent crystals after removal from the mother liquid, and the disorder of countercations are some of the factors that render acquisition of X-ray-quality crystals of the TBA salts problematic. We used both liquid- and gas-phase diffusion methods to grow crystals of the TBA salts in this work. Crystalline light-green blocks of **1** were obtained by gas-phase diffusion. Selecting the right solvents for gas-phase diffusion is crucial to obtaining suitable crystals. When CH_2Cl_2 was used as the principal solvent for the TBA salts, all of the crystals (obtained by diffusing THF or Et_2O into the CH_2Cl_2-based mother liquid) cracked in few minutes after removal from the mother liquid, ruining them for crystallographic study. The fast cracking of the TBA POM crystals is mainly attributed to the presence of low-boiling solvents and consequent very rapid evaporation. Several different organic solvents with higher boiling points were tested. The results showed that the crystals obtained by diffusing $CHCl_3$ into a $ClCH_2CH_2Cl$ solution of **1** are stable for at least 15 min, which is sufficient for crystal selection and mounting on the diffractometer. The THpA salts of the POMs are even harder to crystallize than the TBA salts. Both $THpANO_3$ and the THpA POM salts dissolve only in nonpolar solvents like toluene, and the resulting POM solutions are immiscible with most polar solvents, preventing facile further purification. To obtain an X-ray-quality crystal of the THpA POM salt, liquid-phase diffusion rather than gas-phase diffusion was used for crystal growth (see S3, Supporting Information).

Structural Features. The TBA salt of a copper-substituted Wells–Dawson sandwich-type POM, $[(n\text{-}C_4H_9)_4N]_{11}H_5[Cu_4(P_2W_{15}O_{56})_2]$, **1**, crystallizes in the monoclinic space group *P*2(1)/*n* and shows well-separated polyanions (**1a**), TBA cations, and solvent molecules ($ClCH_2CH_2Cl$ and $CHCl_3$). A total of 10 of 11 TBA counterions are clearly refined, and a fragment of one additional TBA is also found. The numbers of TBA counterions exactly match that found by both elemental analysis and thermogravimetric analysis. The polyanion, **1a**, which is a conventional Wells–Dawson sandwich structure with central β junctions,[33–56] contains two equivalent $[Cu_2P_2W_{15}O_{56}]^{8-}$ subunits related by an inversion center (C_i symmetry; Figure 1). The four Cu atoms in **1a** and the inversion center define a plane. Cu1 and Cu2 have different coordination environments. Cu2 is six-coordinate center internal to the structure and bonds to three oxygen atoms (O52, O53, and O56 or O50A, O51A, and O56A) in each $[P_2W_{15}O_{56}]^{10-}$ unit. Significantly, and distinct from the sodium salt analogue synthesized in aqueous solution, the terminal aqua group is absent on the two Cu(II) centers that reside in the outside positions of the central Cu_4 belt. Cu1 bonds to two oxygen atoms (O51 and O52) of $[P_2W_{15}O_{56}]^{10-}$ on one side of the Cu_4 plane and three oxygen atoms (O54A, O55A, and O56A) of $[P_2W_{15}O_{56}]^{10-}$ on the other side. The bond valence sum calculation[57] of the bridging oxygen atoms (Table 2) reveals that four protons locate on O53, O53A, O55, and O55A, and the remaining proton is disordered between O54 and O54A. Selected bond distances and bond angles are listed in Table 3. The absence of any diffraction peak proximal to these external Cu centers confirms that they are indeed five-coordinate and coordinately unsaturated. Evidence from decades of investigation (synthesis, spectroscopy, X-ray diffraction, and other studies) of d-electron TMSPs indicates that the d-electron centers always bear terminal ligands, with the exception of the toluene extracted systems reported by Pope and co-workers.[20–23] We now supply an X-ray crystallographic confirmation of coordinatively unsaturated d-electron centers in POMs present in nonpolar environments. Note that a POM with partially unsaturated (five-coordinate) Cu(II) centers obtained from an aqueous reaction solution has been reported very recently by Yamase and co-workers.[13] Previously, organic-solvent-soluble POM salts (especially TBA salts) were used during development of the catalytic aerobic oxidation systems by the Hill group. Nitrate salts of the d-electron transition metal were used most frequently as reactants in preparations of these POM catalysts. We proposed that nitrate could bond to the d-electron-metal in the POM and that this unit was likely involved in catalytic turnover.[11,12] In the phase-transfer step of preparing **1**, considerable nitrate is present in the organic phase, and bonding between nitrate and Cu atoms was expected. However, the X-ray

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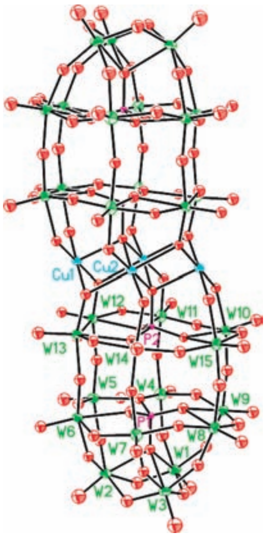

Figure 1. Ball-and-stick representation of $[Cu_4(P_2W_{15}O_{56})_2]^{16-}$ (polyanion **1a** of compound **1**) showing 50% probability ellipsoids and selected atomic labels.

Table 2. Bond Valence Sum of Selected Bridge Atom of **1**

O50	1.410	O53	1.282
O51	1.845	O54	1.337
O52	1.990	O55	1.185

Table 3. Select Bond Distances (Å) and Bond Angles (deg) for **1**

Cu1−Cu1A	5.532(16)	Cu1−O51−Cu2A	94.6(6)
Cu2−Cu2A	3.069(18)	Cu1−O52−Cu2	93.7(6)
Cu1−Cu2	3.155(15)	Cu2−O56−Cu2A	98.5(6)
Cu1−O51	1.945(14)	Cu1−O52	1.942(15)
Cu1−O54A	1.942(15)	Cu1−O55A	1.938(15)
Cu1−O56A	2.356(15)	Cu2−O50A	1.930(15)
Cu2−O51A	2.352(14)	Cu2−O52	2.365(16)
Cu2−O53	1.919(15)	Cu2−O56	2.036(14)
Cu2−O56A	2.015(14)	O50−W11	1.955(15)
O51−W12	1.851(14)	O52−W13	1.808(15)
O53−W14	2.019(14)	O54−W15	1.979(15)
O55−W10	2.055(14)	O56−P2	1.631(15)

structure of **1** clearly reveals that the external Cu(II) centers in the "belt" of the sandwich have no terminal ligands. The strong Jahn−Teller effect exhibited by d^9 Cu(II) centers certainly explains, in part, the coordinately unsaturated Cu centers in **1**. We prepared, purified, and characterized the structurally analogous Co(II)- and Mn(II)-substituted complexes by X-ray crystallography (S4 and S5 in the Supporting Information), and the external Co and Mn in both complexes bear terminal ligands. Interestingly, the nitrate group does not coordinate to any of these complexes. The d^7 Co(II) centers exhibit Jahn−Teller distortion but far less than d^9 Cu(II), and high-spin d^5 Mn(II) exhibits no Jahn−Teller distortion.

Sulfoxidation of Thioether by Air Catalyzed by 1. Initially, Okun and co-workers[11,12] proposed that the monoiron-substituted POM, $TBA_3H_2\{Fe[H(NO_3)_2]PW_{11}O_{39}\}$, is coordinated with a nitrate ligand, which makes the POM active in the catalytic aerobic sulfoxidation and other organic oxidation reactions. However, as noted above, the substituted α-Keggin structure precluded the use of both X-ray crystallography (positionally disordered structures are invariably produced) and NMR for structural confirmation. Extensive studies with Cu- and Fe-substituted $\{\gamma\text{-}SiW_{10}\}$ derivatives[58−76] conducted in media similar to those used in the catalytic aerobic oxidation studies also failed to provide insight into the structures of the highly reactive Cu/FePOM-NO_x aerobic oxidation catalysts. Instead, multicopper-substituted silicopolytungstates were obtained and characterized.[77,78] The latter Cu-substituted POMs were sufficiently insoluble that investigation of their homogeneous catalytic sulfoxidation chemistry in organic solvents was not possible.

The catalytic aerobic sulfoxidation activity of the tetracopper-substituted polyanion, **1a**, extracted into acetonitrile, was evaluated. No sulfoxide was found. In a second experiment, the addition of $TBANO_3$ to the halide-free solution of **1a** also resulted in a catalytically inactive solution.

Magnetic Properties. The observed magnetism of **1** indicates medium antiferromagnetic intramolecular exchange between the four Jahn−Teller-distorted $s = 1/2$ Cu(II) centers. The exchange, mediated by bridging oxo groups, primarily proceeds through the ligands binding to the equatorial coordination sites of the Cu centers since their magnetic orbitals are primarily of $3d_{x^2-y^2}$ character. Therefore, the exchange pathways in **1** can be grouped into three classes (Figure 2): (1) significant exchange via two μ_3-O centers (O56/O56A) bridging Cu2 and Cu2A (Cu···Cu, 3.07 Å; Cu−O−Cu, 98.5°); (2) weak exchange via μ_3-O centers (O51, O52, O56, and symmetry equivalents) that interlink all four Cu centers in the Cu_4 ring

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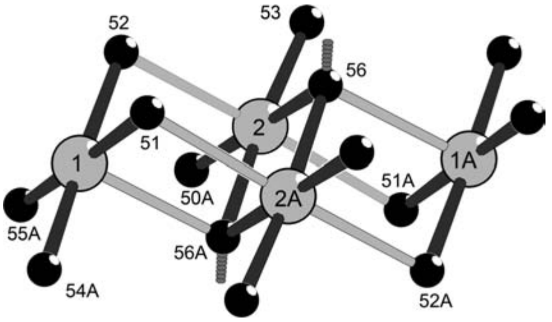

Figure 2. Coordination environments of the central Cu(II)$_4$ group in **1** with atom numbers of positions primarily involved in magnetic exchange (Cu, large gray circles; O, small black circles). Bonds to equatorial ligand positions are highlighted in dark gray. Dotted bond lines indicate bonds to the two proximal P centers of the $\{P_2W_{15}\}$ groups.

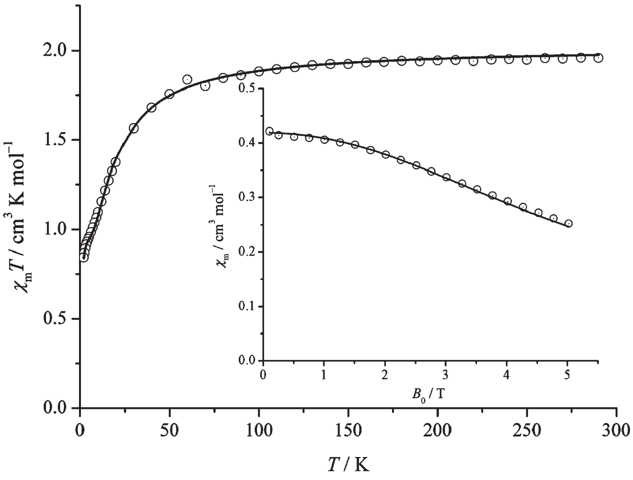

Figure 3. Temperature dependence of $\chi_m T$ for **1** at 0.1 T (2.0 K < T < 300 K). Inset: χ_m of **1** as a function of the applied field B_0 at 2.0 K, illustrating saturation effects. Experimental data, open circles; least-squares fit to the employed model (see text), blue line.

and assume both axial and equatorial coordination sites (Cu···Cu, 3.16 Å); and (3) very weak exchange between the distal Cu centers (Cu1/Cu1A) mediated by −O−W−O−P−O− pathways (Cu···Cu, 5.53 Å). Using an isotropic Heisenberg-type exchange Hamiltonian $\boldsymbol{H} = -J_1 S_2 \cdot S_{2A} - J_2(S_1 \cdot S_2 + S_1 \cdot S_{2A} + S_{1A} \cdot S_2 + S_{1A} \cdot S_{2A}) - J_3 S_1 \cdot S_{1A}$ augmented by a Zeeman operator, both the low-field susceptibility and the field dependence of the susceptibility at 2.0 K are best described for $J_1 = -10.05$ cm^{-1}, $J_2 = -2.08$ cm^{-1}, $J_3 = -0.41$ cm^{-1}, and $g = 2.23$ (Figure 3), in line with the expected coupling strengths. This concurrent fitting approach avoids overparametrization issues, contrary for example to a least-squares fit to the temperature dependence of the molar susceptibility, χ_m, for only a single applied field B_0. The increased g factor is common for Cu(II) complexes and results from an admixture of higher terms with orbital momenta to the ^2E_g ground state for Cu(II) in cubic and tetragonally distorted ligand fields. We compare the recently published $[Cu_4(GeW_9O_{34})_2]^{12-}$ polyanion[13] that features a similar pattern of an enlongated Cu_4 rhombus with two "external" five-coordinate Cu(II) centers (Cu···Cu, 3.11 Å) and two "internal" six-coordinate Cu(II) centers (equivalent to Cu2/Cu2A; Cu···Cu, 5.36 Å). Note that the connectivity of the Cu_4O_{14} core in both **1** and $[Cu_4(GeW_9O_{34})_2]^{12-}$ are identical, However, due to the geometric differences in bond lengths and angles, the coupling parameters J_{1-3} for **1** differ markedly from the reported values for $[Cu_4(GeW_9O_{34})_2]^{12-}$ ($J_1 = -49.6$ cm^{-1}, $J_2 = -12.1$ cm^{-1}, $J_3 = +0.02$ cm^{-1} for the spin Hamilton adopted above). Note that for both $[Cu_4(GeW_9O_{34})_2]^{12-}$ as well as its derivative containing two additional terminal H_2O ligands (completing the octahedral coordination environments of all four Cu centers) relatively high g factors are found (2.18 and 2.24, respectively) that compare well with the g value for **1**.

Conclusions

Four organic-solvent-soluble d-electron transition-metal-substituted derivatives of the trivacant POM, $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$, have been prepared using phase-transfer methods. By using $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}] \cdot 18H_2O$ as a precursor and gas- or liquid-phase diffusion techniques, the Cu_4, Co_4, Mn_4, and Fe_4 complexes have all yielded disorder-free X-ray crystal structures. All of the polyanions in these hydrophobic POM salts exhibit the conventional Wells−Dawson sandwich structure. Interestingly, the external Cu(II) centers in the central "belt" of the Cu_4-substituted compound, $[(n\text{-}C_4H_9)_4N]_{11}H_5[Cu_4(P_2W_{15}O_{56})_2]$, **1**, are coordinatively unsaturated. In contrast, the external Co, Mn, and Fe centers in the structurally analogous Co_4-, Mn_4-, and Fe_4-substituted complexes do have terminal aqua ligands. The temperature-dependent magnetism of **1** indicates medium-strength antiferromagnetic intramolecular exchange between the four Jahn−Teller-distorted $s = 1/2$ Cu(II) centers mediated by bridging oxo groups; the exchange proceeds primarily through the ligands binding to the equatorial coordination sites of the Cu centers. Significantly, there is no evidence from crystallographic or solution studies that nitrate binds competitively with the acetonitrile solvent molecules to the external Cu(II) centers in **1**. The crystals of **1** dissolved in acetonitrile, the principal solvent used in published studies of aerobic organic oxidations catalyzed by Cu(II)- or Fe(III)-POM/nitrate systems, in the absence of cocatalysts, show no catalytic activity. This implicates, at least for polyanion **1a**, a central role for the cocatalysts in these oxidation reactions.

Supporting Information Available: TGA and potentiometric titration of **1**. Preparation and crystallographic figures of the TBA salts of the structurally analogous Co_4 and Mn_4 POMs (and preparation of the THpA salt of structurally analogous Fe_4 POM). This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgment. We thank DTRA and TDA Research Corporation (HDTRA1-08-C-0032) for support of this work.