



Synthesis and structural characterization of a monomeric di-copper-substituted silicotungstate $[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]^{4-}$ and the catalysis of oxidative homocoupling of alkynes

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ABSTRACT

The di-copper-substituted γ -Keggin silicotungstate with bis- μ -1,1-azido ligands $\text{TBA}_4[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]$ (**1**, TBA = tetra-*n*-butylammonium) was synthesized in an aqueous medium. The crystal structure of the anion part of **1** was a monomer of the basal-basal end-on diazido-bridged di-copper-substituted γ -Keggin silicotungstate. The NMR and CSI-MS spectra of **1** in organic solvents, such as acetonitrile, benzonitrile, and 1,2-dichloroethane, showed that complex **1** was present as a monomer of the di-copper-substituted γ -Keggin silicotungstate. Complex **1** could act as an effective homogeneous catalyst for the oxidative homocoupling of various types of alkynes, including aromatic, aliphatic, and heteroatom-containing ones. The reaction possibly proceeds as follows: First, the ligand exchange proceeds between the azido groups in **1** and alkynyl groups to form the corresponding diyne with the reduced copper(I) species via the di-copper(II)-alkynyl intermediate, then the reduced species is reoxidized by molecular oxygen, and the oxidized species reacts with an alkyne to regenerate the alkynyl intermediate.

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1. Introduction

Polyoxometalates are attractive compounds used in various fields, including analytical chemistry, medicine, electrochemistry, photochemistry, and especially catalysis [1–8]. Recently, interest in the catalysis of transition metal-substituted polyoxometalates, synthesized by the introduction of substituent metal ions into the vacant site(s) of lacunary polyoxometalates, has been growing because of their unique reactivity, which depends on the composition and structure of the active sites [1–8]. Since the synthesis of the di-lacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ was reported by Tézé and Hervé [9], several di-metal-substituted polyoxometalates with the γ -Keggin framework have been synthesized and applied to the selective “green” oxidation reactions with molecular oxygen or hydrogen peroxide as the sole oxidant [1–8].

The azido ion (N_3^-) is well known to be a versatile ligand that can bridge two or more transition metals [10,11]. Recently, various transition metal-substituted polyoxometalates with azido ligands have been synthesized [12–15]. Mialane et al. reported a mono- μ -1,1-azido-bridged di-nickel-substituted phos-

photungstate $\text{KRB}_5[(\alpha\text{-PW}_{10}\text{O}_{37})(\text{Ni}(\text{H}_2\text{O}))_2(\mu\text{-}1,1\text{-N}_3)]\cdot 19\text{H}_2\text{O}$ [12]. Successively, di-copper-substituted silicotungstates, $\text{KNaCs}_{10}\{[\gamma\text{-SiW}_{10}\text{O}_{36}\text{Cu}_2(\text{H}_2\text{O})(\mu\text{-}1,1\text{-N}_3)_2]_2\}\cdot 26\text{H}_2\text{O}$ (**2**) [13] and $\text{TEA}_4\text{TBA}_4\text{H}_2\text{O}\{[\gamma\text{-SiW}_{10}\text{O}_{36}]_2\text{Cu}_4(\mu\text{-}1,1,1\text{-N}_3)_2(\mu\text{-}1,1\text{-N}_3)_2\}$ (**3**, TEA = tetraethylammonium) [14], were reported by the same group (Fig. 1). Complexes **2** and **3** have dimeric structures and are composed of two $[\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\text{N}_3)_2]^{6-}$ subunits, with differing connection modes of the ligands [13,14].

Recently, many applications of 1,3-diyne derivatives (both symmetric and nonsymmetric ones) as key structural elements for natural product synthesis, polymer chemistry, supramolecular chemistry, and material science have been reported [16–18]. In addition, electronic and optical properties of extensively π -conjugated systems have spurred research into new linear origoacetylenic compounds in which 1,3-diyne derivatives can be used as precursors [16]. Consequently, much attention has been given to the efficient and selective synthesis of 1,3-diyne derivatives. One of the most widely used synthesis procedures for synthesizing 1,3-diyne derivatives is an oxidative alkyne–alkyne homocoupling reaction. Stoichiometric amounts of copper salts generally have been used under Glaser conditions [19], and, alternatively, catalytic amounts of copper salts with appropriate nitrogen bases (ligands or solvents) and molecular oxygen have been used under Hay [20] or Eglinton conditions [21] for the oxidative alkyne–alkyne homocoupling reactions [22–28]. But the yields of aliphatic 1,3-diynes by

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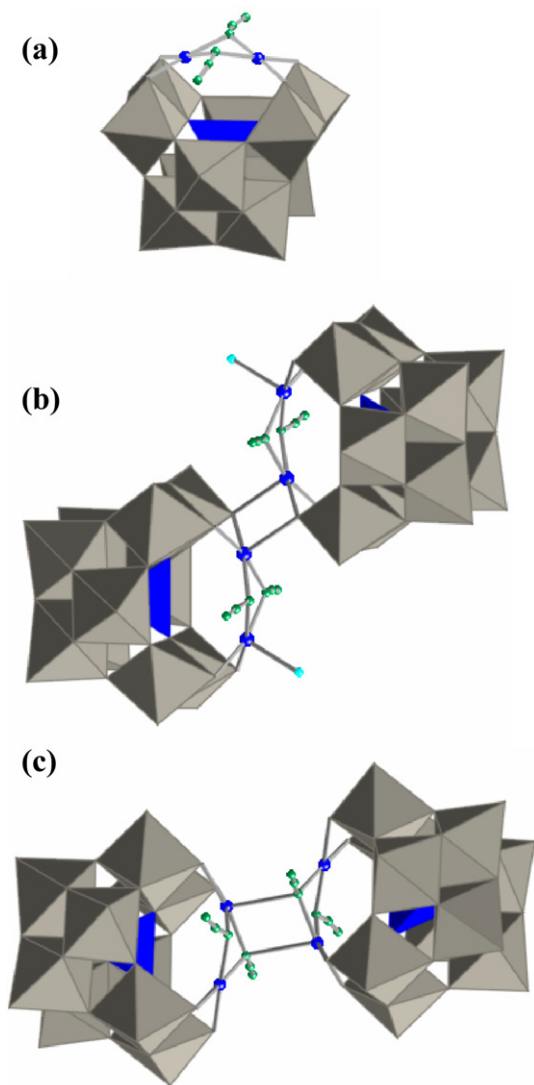


Fig. 1. Polyhedral representations of the anion parts of (a) $\text{TBA}_4[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]$ (this study) (**1**) [36], (b) $\text{KNaCs}_{10}[\gamma\text{-SiW}_{10}\text{O}_{36}\text{Cu}_2(\text{H}_2\text{O})(\mu\text{-}1,1\text{-N}_3)_2] \cdot 26\text{H}_2\text{O}$ (**2**) [13], and (c) $\text{TEA}_4\text{TBA}_2\text{H}_2[\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Cu}_4(\mu\text{-}1,1,1\text{-N}_3)_2(\mu\text{-}1,1\text{-N}_3)_2]$ (**3**) [14]. Gray octahedra and blue tetrahedra show the $[\text{WO}_6]$ and $[\text{SiO}_4]$ units, respectively. Blue, green, and light blue spheres show the copper, nitrogen (azido), oxygen (water) atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the homocoupling reactions of aliphatic alkynes under the Hay or Eglinton conditions in the presence of copper salts generally have been only low to moderate [19–28]. Although the oxidative homocoupling of aliphatic alkynes with combined catalysts of copper and palladium salts can proceed efficiently, these systems have several disadvantages, including (i) the use of expensive palladium catalysts, (ii) the need for bases and co-catalysts (copper salts), and (iii) difficult catalyst recovery [29–35]. Thus, the development of the widely usable efficient alkyne–alkyne homocoupling systems remains a challenge. The scope and limitations of copper- and/or palladium-mediated homocoupling systems have been reviewed in more detail previously [16].

Recently, we reported that a di-copper-substituted γ -Keggin silicotungstate $\text{TBA}_4[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]$ (**1**) acts as an effective homogeneous catalyst for the oxidative alkyne–alkyne homocoupling reactions [Eq. (1)] [36]. In this paper, we report details of the synthesis procedure and structural characterization of the di-copper-substituted γ -Keggin silicotungstate **1** in solid and so-

lution states. Furthermore, the scope of the **1**-catalyzed oxidative alkyne–alkyne homocoupling is extended, and 13 new entries are added [36]. We also discuss the possible reaction mechanism for the present **1**-catalyzed homocoupling in more detail [36].



2. Experimental

2.1. General

IR spectra were measured with a Jasco FT/IR-460 Plus device using KBr disks. NMR spectra were recorded at 298 K on JEOL JNM-EX-270 spectrometer (^1H , 270 MHz; ^{13}C , 67.8 MHz; ^{29}Si , 53.45 MHz; ^{183}W , 11.20 MHz). Chemical shifts (δ) were reported in ppm downfield from the internal TMS for ^1H and ^{13}C , external TMS (in CDCl_3) for ^{29}Si , and external Na_2WO_4 (in D_2O) for ^{183}W . UV–vis spectra were recorded on a Jasco V-570 spectrometer with a Unisoku thermostatic cell holder (USP-203). GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with a TC-5 capillary column (internal diameter = 0.25 mm, length = 60 m) or a TC-1 capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column (internal diameter = 0.25 mm, length = 30 m). CSI-MS spectra were recorded on JEOL JMS-T100LC. Typical measurement conditions were orifice voltage, -95 V; spray temperature, 263 K; and ion source temperature, room temperature. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, NaN_3 , and copper salts were obtained from Wako or Kanto (reagent grade) and used as received. Copper(I) phenylacetylide was obtained from Alfa Aesar (reagent grade) and used as received. Solvents and alkynes were obtained from Tokyo Kasei or Aldrich (reagent grade) and purified before use [37]. The di-copper-substituted silicotungstate **1** was synthesized as described previously [36] (see Supporting information).

2.2. Procedure for oxidative alkyne–alkyne homocoupling

The oxidative alkyne–alkyne homocoupling was carried out as follows. First, **1** (2.2 mol% with respect to alkyne), alkyne (1 mmol), and benzonitrile (1 mL) were successively placed into a glass reactor. The reaction mixture was stirred at 373 K under 1 atm of molecular oxygen. The yield was periodically determined by GC analysis. After the reaction was completed, 20 mL of diethylether was added to the solution. The precipitated catalyst was recovered by filtration (95% recovery), washed with diethylether (ca. 50 mL), and dried in vacuo before being recycled. Isolation and purification of diynes were carried out by column chromatography on silica gel, using *n*-hexane as an eluent. All products were confirmed by comparing their GC retention times, mass, and NMR spectra with those of authentic samples. The purity of isolated products was determined by ^1H NMR and was >95% in all cases.

3. Results and discussion

3.1. Synthesis and characterization of $\text{TBA}_4[\gamma\text{-H}_2\text{SiW}_{10}\text{O}_{36}\text{Cu}_2(\mu\text{-}1,1\text{-N}_3)_2]$ (**1**)

The TBA salt of a di-copper-substituted silicotungstate with bis- μ -1,1-azido ligands (**1**) was obtained by the reaction of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]$ with two equivalents of CuCl_2 and an excess amount of NaN_3 in aqueous solution at room temperature, followed by the addition of TBABr. The detailed procedure is as follows. First, CuCl_2 (0.090 g, 0.67 mmol, two equivalents with respect to $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$) in water (20 mL) was added to a suspension of

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