

Unsymmetrical surface modification of a heteropolyoxotungstate *via in-situ* generation of monomeric and dimeric copper(II) species

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Unsymmetrical functionalization of a discrete α - $\{\text{SiW}_{12}\text{O}_{40}\}$ Keggin with two heterometallic building blocks, a Cu(II) dimer and a Cu(II) monomer, results in the formation of $\{[\text{Cu}_2(\text{O}_2\text{CMe})_2(5,5'$ -dimethyl-2,2'-bipy) $]\}_2\{\text{Cu}(5,5'$ -dimethyl-2,2'-bipy) $\}_2\{\text{SiW}_{12}\text{O}_{40}\}$ that displays interesting physical properties.

The modification of the surfaces of polyoxometalate clusters presents an important challenge as many of their potential applications, *e.g.* as molecular devices,^{1,2} anti viral agents,³ or catalysts,^{4,5} are directly related to their surface characteristics. However, the addition of heterometal groups, *e.g.* of specific Lewis acidities, to the stable $\{\text{XM}_{12}\text{O}_{40}\}$ Keggin structures usually favours symmetric substitution patterns that mirror the high symmetry of the Keggin groups.⁶ Thus, the controlled extension and functionalization of the Keggin framework remains an attractive synthetic goal. Of particular importance is the addition of transition metal ions onto the cluster surface,^{7,8} which even can result in the formation of novel metal-oxo frameworks.⁹ Our approach to this goal lies in the surface modification of heteropolyoxotungstates with transition metal complexes.

Herein, we report the synthesis, thermal and magnetic properties of an unsymmetrical molecular heteropolyoxotungstate Keggin cluster comprising three unique copper(II) centres, with monomeric and dimeric copper(II) groups, with the composition $\{[\text{Cu}_2(\text{O}_2\text{CMe})_2(5,5'$ -dimethyl-2,2'-bipy) $]\}_2\{\text{Cu}(5,5'$ -dimethyl-2,2'-bipy) $\}_2\{\text{SiW}_{12}\text{O}_{40}\}$ (**1**)[†]. Compound **1** was produced in a 44% yield as a green crystalline material from the hydrothermal reaction of copper(II) acetate, 5,5'-dimethyl-2,2'-bipyridyl, $\text{K}_8\text{SiW}_{10}\text{O}_{36}$ and glacial acetic acid over a period of 24 h.

Structural analysis of compound **1**[‡] (Fig. 1) shows that it is constructed from an α - $\{\text{SiW}_{12}\text{O}_{40}\}^{4-}$ Keggin cluster¹⁰ with two crystallographically unique copper sites located on opposite poles of the cluster. Each of the copper sites binds to the cluster through corner-sharing Cu–O–W bonds. Cu(1) bonds to the cluster through a terminal oxo-group $\{\text{O}=\text{W}\}$, with a Cu(1)– μ_2 -O(1) distance of 2.232(7) Å, leading to an elongation of the $\{\text{O}=\text{W}\}$ bond toward Cu(1), $\{\text{O}=\text{W}\} = 1.721(7)$ Å, $\{\text{W}=\text{O}_{\text{ave}}\} = 1.704(5)$ Å. Cu(3) coordinates through a bridging oxo-group $\{\text{W}-\text{O}-\text{W}\}$, with a Cu(3)– μ_3 -O(20) distance 2.489(7) Å.

The three copper atoms are segregated to distinct positions on the cluster as a $\{\text{Cu}_2(\text{O}_2\text{CMe})_2(5,5'$ -dimethyl-2,2'-bipy) $\}_2^{2+}$ dimer

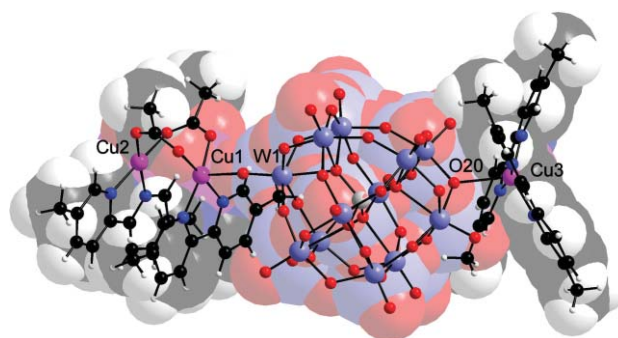


Fig. 1 Structure of the complex $\{[\text{Cu}_2(\text{O}_2\text{CMe})_2(5,5'$ -dimethyl-2,2'-bipy) $]\}_2\{\text{Cu}(5,5'$ -dimethyl-2,2'-bipy) $\}_2\{\text{SiW}_{12}\text{O}_{40}\}$. The following colour scheme is used above: tungsten, pale blue spheres; copper, purple spheres; oxygen, red spheres; nitrogen, dark blue spheres; carbon, black spheres and hydrogen, white spheres.

and a $\{\text{Cu}(5,5'$ -dimethyl-2,2'-bipy) $\}_2^{2+}$ monomer. The dimeric copper(II) ions are composed of two unique coordination environments. The Cu(1) coordination sphere displays a $\{\text{CuN}_2\text{O}_3\}$ square pyramidal geometry with two nitrogen donors from one 5,5'-dimethyl-2,2'-bipy ligand, and two oxygen atoms from two different *cis*- $\{\text{CH}_3\text{CO}_2\}^-$ ligands that bridge to the second copper centre of the dimer unit and the apical oxygen atom from the terminal oxo-group $\{\text{O}=\text{W}\}$ of the cluster. Cu(2) has a square planar geometry $\{\text{CuN}_2\text{O}_2\}$ defined by two nitrogen donors from the second 5,5'-dimethyl-2,2'-bipy ligand of the dimer and the two remaining oxygen atoms from the *cis*- $\{\text{CH}_3\text{CO}_2\}^-$ groups, with a Cu–Cu distance of 2.953(2) Å. The plane is defined by the nitrogen atoms of the bipyridyl ligand and oxygen atoms of the acetate groups for Cu(1) has the copper atom displaced out of the plane towards the cluster by 0.16 Å whereas the related plane for Cu(2) has the copper centre displaced out of the plane by 0.05 Å away from Cu(1).

Typically, transition metal dimers consisting of multiple acetate groups form a paddle-wheel type shape, such as $\text{Na}[\text{Rh}_2(\text{O}_2\text{CMe})_4\text{Cl}_2]$, with four acetate groups defining the wheel and the two auxiliary ligands capping the paddle-wheel.¹¹ Apart from compound **1**, there are only a few examples that contain two acetate groups with additional co-ligands while retaining the paddle-wheel geometry around the metal centres, *e.g.* platinum(II) complexes of the type $[\text{Pt}_2(\text{O}_2\text{CtBu})_2(\text{NH}_3)_4][\text{X}]_n$, where $\text{X} = \text{SO}_4$, $n = 1$ and ClO_4 , $n = 2$.¹² It is also possible for a polyoxometalate to act as an equatorial co-ligand.¹³

The monomeric copper site, Cu(3), has a $\{\text{CuN}_4\text{O}\}$ distorted square pyramidal geometry with four nitrogen atoms from two 5,5'-dimethyl-2,2'-bipy defining the equatorial plane and the apical

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position occupied by a bridging oxygen atom {W–O–W} from the cluster. The distortion of the square pyramid arises from the dipyriddy ligands which are canted with respect to each other out of the plane (defined by the four nitrogen atoms), and this is due to the steric interactions between each of the dipyriddy ligands (average Cu–N distances are 1.998(5) Å).

Although polyoxometalates are known as linker groups that can be efficient in mediating magnetic superexchange, the magnetic susceptibility data of **1** shows that the two magnetic addenda do not significantly interact through the {SiW₁₂} Keggin unit. This is due to (1) the fact that even the shortest possible exchange pathway involves an extended–O–W–O–Si–O–W–O–bridging motif and (2) the apical coordination modes of both Jahn–Teller–distorted Cu groups to the relevant oxo centres of the Keggin unit (this geometry minimizes the overlap of magnetic Cu(3d) orbitals with the Keggin unit). Therefore, the observed susceptibility can be represented as the sum of an antiferromagnetically coupled {Cu₂} group and an uncoupled, Jahn–Teller–distorted single $S = 1/2$ Cu(II) ion. Using an isotropic Bleaney–Bowers equation augmented by a Curie term correspondingly reproduces the experimental data with a singlet–triplet splitting of $J/k_B = -128$ K for the {Cu₂} group and an isotropic average $g = 2.15$.

The thermal decomposition of **1** (Fig. 2) exhibits a plateau of stability from room temperature up to 315 °C followed by the loss of both acetate groups from the copper dimer with the process ending at 375 °C; acetate loss experimental (calcd) %: 2.80 (3.01).

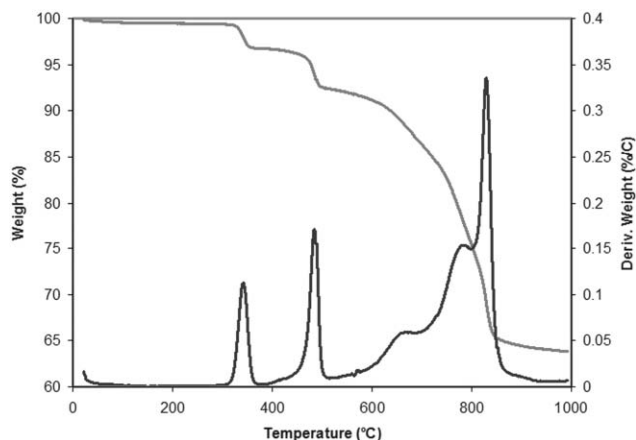


Fig. 2 The TGA of **1** showing the three step weight loss (grey) and the corresponding first derivative (black).

A second decomposition process begins at 400 °C and is completed at 510 °C, corresponding to the loss of one molecule of 5,5'-dimethyl-2,2'-bipy, experimental (calcd) %: 4.39 (4.69). Finally, the weight loss of 28% from 575–950 °C accounts for the loss of the remaining molecules of 5,5'-dimethyl-2,2'-bipy. The DSC of **1** also agrees with the loss of acetate at 315 °C followed by the loss of one 5,5'-dimethyl-2,2'-bipy at 470 °C. Temperature variable powder diffraction measurements show that there is no change in the diffraction pattern prior to the loss of acetate ligands (line d, 300 °C). However, the pattern changes upon loss of acetate and a new phase develops (line c in Fig. 3, 400 °C). The material then proceeds through an amorphous phase (line b, 550 °C) associated with the loss of the 5,5'-dimethyl-2,2'-bipy before finally transforming into a new CuWO phase that develops

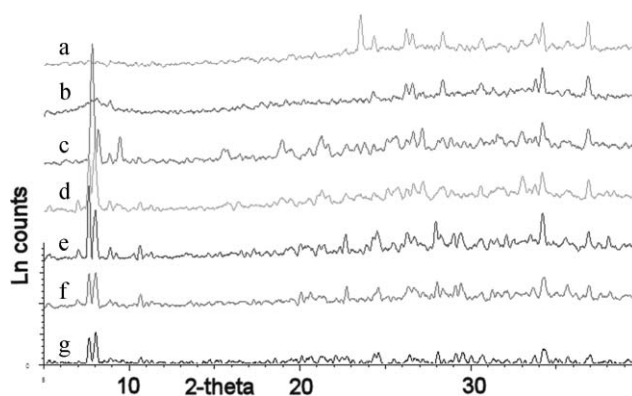


Fig. 3 Powder diffraction as a function of T , from 40 °C to 650 °C. The pattern was measured from 5° to 45° in 2θ under an argon atmosphere (g–a is 40, 100, 200, 300, 400, 550, 650 °C respectively).

at 650 °C (line a). The process between 315–375 °C is interesting since only the loss of acetate is observed here producing formally two doubly coordinatively unsaturated Cu(II) centres which then rearrange to produce a new phase (the loss of only acetate was confirmed by elemental analysis, TGA, and *in-situ* TOF-MS) and this results in transformation to a new structure type as shown by powder diffraction.

In summary we have synthesised and characterised a novel unsymmetrical surface-modified tungstosilicate. The thermal decomposition of the $\{[Cu_2(O_2CMe)_2(5,5\text{-dimethyl-}2,2\text{-bipy})_2]\{Cu(5,5\text{-dimethyl-}2,2\text{-bipy})_2\}SiW_{12}O_{40}\}$ complex has been shown to proceed *via* the stepwise loss of acetates and 5,5'-dimethyl-2,2'-bipy ligands before decomposing into an unidentified copper–tungsten oxide. This result is interesting because of the unsymmetrical nature of the complex formed which has promise in the design of functional hybrid polyoxometalate–transition metal complexes with labile coordination sites.

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Notes and references

† *Synthesis*. The reaction of $Cu(O_2CMe)_2 \cdot H_2O$ (0.043 g, 0.22 mmol), 5,5'-dimethyl-2,2'-bipy (0.026 g, 0.14 mmol), $K_8SiW_{10}O_{36}$ (0.214 g, 0.078 mmol), distilled H_2O (10 ml) and glacial acetic acid (500 μ l) was performed by heating the solution to 150 °C in a Parr acid digestion vessel for 24 h, which upon cooling yielded green crystals of **1** in 44% yield based on Cu that were suitable for X-ray diffraction.

‡ *Analysis*. $\{[Cu_2(O_2CMe)_2(5,5\text{-dimethyl-}2,2\text{-bipy})_2]\{Cu(5,5\text{-dimethyl-}2,2\text{-bipy})_2\}SiW_{12}O_{40}\}$ (**1**): Elemental calcd (found) %: C 15.96 (15.74), H 1.24 (1.23), N 2.86 (2.68). FTIR (KBr pellet), cm^{-1} : 3432 s, 2924 w, 1582 m, 1476 m, 1442 m, 1249 w, 1160 w, 1053 w, 1013 w, 965 m, 915 s, 793 s, 723 m and 527 m. *Crystal data*: monoclinic, $P2_1/n$, $a = 14.082(2)$ Å, $b = 21.908(3)$ Å, $c = 25.635(3)$ Å, $\beta = 103.888(4)^\circ$, $V = 7677.2(2)$ Å³, $Z = 4$, $T = 150$ K, $\rho_{calcd} = 3.391$ g cm⁻³, $\mu(Mo-K\alpha) = 1.882$ mm⁻¹, 88894 reflections measured, 19095 unique ($R_{int} = 0.0791$) which were used in all calculations. Final $R1 = 0.0720$ and $wR2 = 0.0930$ (all data). Data was measured on a Bruker Nonius X8 Advance diffractometer equipped with an APEX II CCD detector [$\lambda(Mo-K\alpha) = 0.71073$ Å], graphite monochromator. Structure solution and refinement were performed by using SHELXTL *via* APEX2 software package.¹⁴ CCDC reference number 292969. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b518316b. *Powder data*: Performed on a Bruker D5000 equipped with a PARR temperature

stage. The XRD patterns were measured from 5° to 45° in 2 θ , under an argon atmosphere, at 0.02° increments with a collection time of 3 s per step. *TGA data*: Data were measured on a TA Q500 instrument under a nitrogen atmosphere. The initial heating range was from RT to 150 °C at 2.00 °C per min followed by a second range from 150 to 1000 °C at 5.00 °C per min. *DSC data*: Performed on TA Q100 instrument under a nitrogen atmosphere measured from 40 to 540 °C at 10.00 °C per min. *Magnetic data*: recorded on a 60 mg polycrystalline sample of **1** in the 2–290 K temperature range, using a Quantum Design MPMS-XL spectrometer. The temperature dependent magnetic data were obtained at a magnetic field of 0.1 Tesla.

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