A new polymeric chain formed by paradodecatungstate clusters and [Cu(en)₂]²⁺ complexes: hydrothermal synthesis and characterization of [Cu(en)₂]₃[{Cu(en)₂}₂(H₂W₁₂O₄₂)]·12H₂O †

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The hydrothermal reaction of the mixture of $K_2WO_4 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, ethylenediamine and H_2O at 170 °C for 72 h yields purple needle-like crystals of $[Cu(en)_2]_3[\{Cu(en)_2\}_2(H_2W_{12}O_{42})] \cdot 12H_2O$. Single crystal X-ray diffraction reveals that the structure consists of one-dimensional $[\{Cu(en)_2\}_2(H_2W_{12}O_{42})]_n^{6n-}$ anions with discrete $[Cu(en)_2]^{2+}$ complex cations and crystallization water molecules occupying the interchain positions. In the polymeric chain each paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ cluster is connected to two neighbors through four μ_2-$[Cu(en)_2]^{2+}$ complex groups. The magnetic measurements show that the compound possesses well-separated Cu^{2+} centers. A probe reaction of the oxidation of cyclohexane with 760 Torr of O_2 indicates that the compound has good catalytic activity for the reaction.

Introduction

The contemporary interest in transition metal oxide clusters, or polyoxometalates, reflects their diverse properties, which endow them with applications in fields such as catalysis, medicine, analytical chemistry and photochemistry.[1] Recently, there has been growing interest in the synthesis of composite solids assembled by inorganic oxides and coordination complexes.[2] Owing to the remarkable features of transition metal oxide surfaces[3] and the proven roles of polyoxometalate clusters in several areas of current interest,[4] it is considerably attractive to exploit chemically robust polyoxometalate clusters as building blocks to design and prepare polyoxometalate-based composite materials with desired properties. The hydrothermal synthesis techniques, in combination with the organic templates, have been demonstrated to be a popular strategy in the isolation of metal oxides.[2,5] A number of such materials constructed from polyoxometalate clusters and transition metal coordination complexes have been hydrothermally synthesized. Typical examples with extended structures include $[\{Cu_3(4,7\text{-phen})_3\}_2\text{-}Mo_{14}O_{45}]$,[6] $[\{Cu(en)\}_2Mo_8O_{26}]$,[7] $[Zn_2(tp)(4,4'\text{-bpy})V_2O_6]$ (tp = terephthalate),[8] $[\{Cu(enMe)_2\}_4\{V_{18}O_{42}(H_2O)\}] \cdot 8H_2O$ (enMe = 1,2-diaminopropane)[9] and $[\{Cu(enMe)_2\}_7\{V_{16}O_{38}(H_2O)\}_2] \cdot 4H_2O$.[10] Although organic amines or coordination complexes have been extensively used as templating or structure-directing agents in hydrothermal reactions, little work has been reported on their use in hydrothermal syntheses of new polyoxo-tungstates with the exception of $[H_3N(CH_2)_6NH_3][W_{18}P_2O_{62}] \cdot H_2O$[11] and a few Keggin species.[12,13] The only reported compound consisting of polyoxotungstate clusters and co-ordination groups is $[Ni(2,2'\text{-bpy})_3]_{1.5}[Ni(2,2'\text{-bpy})_2(H_2O)(PW_{12}O_{40})] \cdot 0.5H_2O$,[13] but it exhibits a discrete cluster structure. Here we report the hydrothermal synthesis and structural characterization of a novel compound, $[Cu(en)_2]_3[\{Cu(en)_2\}_2(H_2W_{12}O_{42})] \cdot 12H_2O$ **1**, where the paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ clusters are interconnected through the bridging $[Cu(en)_2]^{2+}$ groups into a one-dimensional chain structure. Its catalytic activity has been explored by means of probe reaction of the oxidation of cyclohexane with 760 Torr of O_2 under photo-excitation.

† Electronic supplementary information (ESI) available: thermal variations of the magnetic susceptibility of compound **1**. See http://www.rsc.org/suppdata/dt/b3/b301917a/

Experimental

Materials and methods

Regents were purchased commercially and used without further purification. The hydrothermal reaction was carried out in 17 mL Teflon-lined stainless steel autoclaves under autogenous pressure with a fill factor of approximately 35%. The reactants were stirred briefly before heating. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer and inductively coupled plasma analysis on a Perkin-Elmer Optima 3300DV ICP spectrometer. The infrared spectrum was recorded at room temperature on a Nicolet 470 FTIR spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ region. Thermal analysis was performed in flowing N₂ with a heating rate of 10 °C min⁻¹ on a Universal V2.4F TA instrument. The magnetic susceptibility data were obtained on polycrystalline samples (25.31 mg) using a SQUID magnetometer in the temperature range from 4 to 290 K at an applied magnetic field of 5 kG. The diamagnetic contributions were estimated from Pascal's constants.

Hydrothermal synthesis

The hydrothermal reaction of a mixture of $K_2WO_4 \cdot 2H_2O$ (0.271 g), $CuSO_4 \cdot 5H_2O$ (0.189 g), ethylenediamine (0.075 mL) and water (5.5 mL) in the molar ratio 1 : 1 : 1.5 : 406 at 170 °C for 72 h resulted in purple needles of compound **1**. These crystals were filtered off, washed with distilled water and dried in a dessicator at ambient temperature. The yield was *ca.* 68% based on tungsten (Found: C, 6.04; H, 2.61; N, 6.94; Cu, 7.83; W, 54.87. Calc.: C, 5.98; H, 2.66; N, 6.98; Cu, 7.91; W, 54.95%). IR (KBr): 3446m, 3254m, 3214w, 2963w, 1587s, 1521w, 1458m, 1397w, 1276w, 1089m, 1040m, 952vs, 894s, 810s, 697m, 526m, 475w cm⁻¹.

X-Ray crystallography

The data on a crystal with dimensions 0.616 × 0.042 × 0.024 mm were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the ω-scan mode. The diffraction data were corrected for Lorentz factors, polarization, and absorption due to variation in the path length through the detector faceplate.[14] The structure was solved by direct methods and refined using SHELXL-97.[15] Anisotropic thermal parameters were refined

Table 1 Crystallographic data for compound **1**

Empirical formula	$C_{20}H_{106}Cu_5N_{20}O_{54}W_{12}$
M	4015.15
T/K	295(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.1989(7)
b/Å	14.0042(8)
c/Å	14.7254(9)
α/°	62.1440(10)
β/°	67.294(3)
γ/°	77.875(2)
V/Å³	2050.4(2)
Z	1
D_{calc}/Mg m^{-3}	3.252
μ(Mo-K$_a$)/mm^{-1}	18.121
Reflections collected	18810
Independent reflections	9153 (R_{int} = 0.0283)
GOF	1.049
R_1, wR_2 ($I > 2\sigma(I)$)	0.0275, 0.0738
R_1, wR_2 (all data)	0.0345, 0.0767

Table 2 Selected bond lengths (Å) for compound **1**

W(1)–O(1)	1.741(5)	W(1)–O(3)	1.848(4)
W(1)–O(2)	1.856(5)	W(1)–O(20a)	1.961(4)
W(1)–O(5)	1.967(5)	W(1)–O(4)	2.247(4)
W(2)–O(6)	1.719(5)	W(2)–O(8)	1.798(4)
W(2)–O(9)	1.890(4)	W(2)–O(7)	1.953(4)
W(2)–O(3)	2.100(4)	W(2)–O(4)	2.246(4)
W(3)–O(10)	1.749(5)	W(3)–O(11)	1.757(4)
W(3)–O(5)	1.865(5)	W(3)–O(13)	1.954(5)
W(3)–O(12)	2.164(4)	W(3)–O(9)	2.242(4)
W(4)–O(14)	1.735(4)	W(4)–O(15)	1.739(5)
W(4)–O(13)	1.896(4)	W(4)–O(16)	1.904(4)
W(4)–O(17)	2.273(4)	W(4)–O(9)	2.288(4)
W(5)–O(18)	1.736(5)	W(5)–O(19)	1.745(5)
W(5)–O(20)	1.876(4)	W(5)–O(16)	1.956(4)
W(5)–O(8)	2.194(4)	W(5)–O(17)	2.209(4)
W(6)–O(21)	1.719(5)	W(6)–O(12)	1.795(4)
W(6)–O(17)	1.921(4)	W(6)–O(7a)	1.942(4)
W(6)–O(2a)	2.073(5)	W(6)–O(4a)	2.271(4)
Cu(1)–O(10)	2.493(5)	Cu(1)–O(18b)	2.538(5)

Symmetry codes: (a) $-x +1$, $-y +1$, $-z$; (b) $x - 1$, y, z.

for all non-hydrogen atoms, except for the three water oxygen atoms (O(25), O(26), O(27)), which were refined isotropically. All hydrogen atoms were located in the difference Fourier maps or placed geometrically and refined isotropically. A summary of the crystallographic data is given in Table 1. Selected bond lengths are listed in Table 2.

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See http://www.rsc.org/suppdata/dt/b3/b301917a/ for crystallographic data in CIF or other electronic format.

Catalytic reaction

Compound **1** (2×10^{-3} mmol, powder), cyclohexane (4 mmol), and CH_2Cl_2 (10 mL) were added to a 50 mL three-necked quartz flask, which was placed on a magnetic stirrer. Under stirring, 760 Torr of O_2 and the irradiation of a mercury-vapor lamp ($\lambda \approx 360$ nm), the reaction was carried out at 30 °C for 2 h. When the reaction had reached completion the catalyst was separated off. The reactant solution was analyzed by gas chromatography on GC-9A capillary columns. The catalytic activity was evaluated by the quantity of cyclohexane oxidized.

Results and discussion

The isolation of compound **1** relies on hydrothermal synthesis techniques.[16] The hydrothermal conditions allow us to overcome problems associated with the differential solubilities of the reactants. Furthermore, the reduced viscosity of water

under these conditions enhances the solvent extraction of solids and the rate of crystallization from solution. Although the synthetic methodology depends on self-assembly of the products from the molecular precursors, the mechanism by which the assembly is organized remains elusive and the identity of the products under the employed conditions is often unpredictable.[17] The synthetic products, however, are sensitive to many parameters such as starting materials, temperature, pH, and pressure. The conditions for the preparation of **1** appear to be quite critical, and the solid is isolated only in a narrow region of the reaction domain. At 170 °C, substitution of WO_3 for $K_2WO_4\cdot2H_2O$ or of $CuCl_2\cdot2H_2O$ for $CuSO_4\cdot5H_2O$ generates amorphous mixtures. Compound **1** forms from $K_2WO_4\cdot2H_2O$ and $CuSO_4\cdot5H_2O$ only in the 160–175 °C temperature range. Nevertheless, the reaction of a mixture of $K_2WO_4\cdot2H_2O$, $CuSO_4\cdot5H_2O$, en and H_2O in the molar ratio of 1 : 1 : 1.5 : 406 at 170 °C for 72 h produced purple needle-like crystals of **1** in good yield.

The crystal structure of compound **1** is composed of one-dimensional $[\{Cu(en)_2\}_2(H_2W_{12}O_{42})]_n^{6n-}$ anions, discrete $[Cu(en)_2]^{2+}$ complex cations and H_2O molecules of crystallization. As shown in Fig. 1, the infinite one-dimensional chain is constructed from paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ clusters interconnected through $[Cu(en)_2]^{2+}$ bridging groups and runs parallel to the crystallographic a axis.

The skeleton of the core $[H_2W_{12}O_{42}]^{10-}$ is illustrated in Fig. 2 and is very similar to those in the known paradodecatungstates.[18–20] It is centrosymmetric and consists of four groups of two types with each type containing three edge-sharing WO_6 octahedra. In the upper or lower trimer of $[H_2W_{12}O_{42}]^{10-}$ depicted in Fig. 2a, the three tungsten atoms define a near-equilateral triangle with angles of 59.29(1), 59.60(1) and 61.11(1)°, while the three tungsten atoms in the left or right trimer define an open angle with a W_{side}–W_{middle}–W_{side} angle of 115.54(1)°. The two triangular units and the two open angular ones are held together through interconnecting corners into a cluster. The W–O bond distances range from 1.719(5) to 2.288(4) Å (Table 2), which are in accord with those in the known paradodecatungstates,[18–21] although the angle W_{side}–W_{middle}–W_{side} in the open angular trimer is somewhat smaller than that reported (115.72°).[21] In the polymeric anion chain in **1**, the $[H_2W_{12}O_{42}]^{10-}$ cluster acts as a tetradentate ligand coordinating to four copper(II) ions through the terminal oxygen atoms of four side WO_6 of the two open units (see Fig. 1, 2a), such that each $[H_2W_{12}O_{42}]^{10-}$ cluster is connected to two neighbors of the chain through four CuN_4O_2 octahedra. Bond valence sum calculations[22] resulted in each W atom having a valence sum ranging from 6.07 to 6.16, very close to the ideal value of 6 for W(VI). The bond valences of oxygen atoms in the polyanion are between 1.61 and 2.03, normal for oxo groups, except that the triply bridging O(4) atom has a sum of 1.21. This indicates that O(4) should be protonated and that the cluster unit in **1** should be $[H_2W_{12}O_{42}]^{10-}$, in accord with the formula given by X-ray structure determination and elemental analyses.

While the octahedral geometry around each Cu(II) atom in the polymer anion is completed by four equatorial N atoms from two en ligands and two *trans*-oxo groups from two adjacent paratungstate clusters with Cu–N distances of 1.987(7)–2.029(7) Å and Cu–O distances of 2.493(5) and 2.538(5) Å, the sphere around each Cu(II) site in the discrete cations exhibits planar square CuN_4 geometry formed by two en ligands with Cu–N distances of 1.935(12)–2.012(7) Å.

The chain structure of **1** is an example of a new topology in polyoxotungstates but is similar to that reported for $K_6[\{Co(H_2O)_4\}_2(H_2W_{12}O_{42})]\cdot14H_2O$.[21] In the latter chain, one of the two *trans*-oxo groups bonded to each Co(II) site comes from a triangular trimer of a paratungstate cluster, and the other from an open unit of a neighboring cluster. In contrast, in the chain of **1** the two *trans*-oxo atoms coordinated to each Cu(II) atom are both from the open units of two adjacent clusters. In the
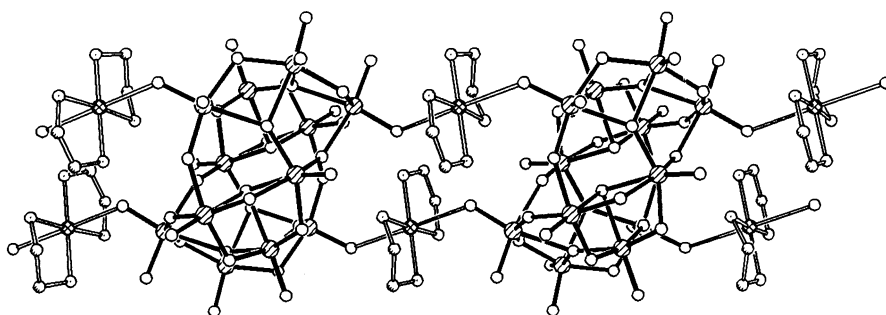
Fig. 1 The one-dimensional structure of **1** projected perpendicular to the *a* axis, with cross-hatched circles for Cu, striped ones for W, open ones for O, dotted ones for N and shaded ones for C.
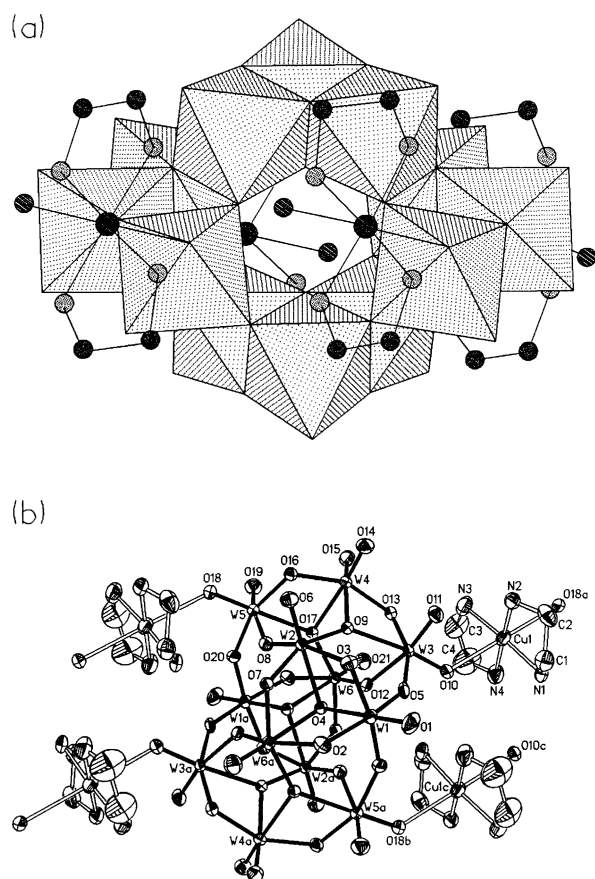

Fig. 2 (a) A polyhedral representation of the paradodecatungstate clusters in **1** showing the twelve WO_6 octahedral linkages and the four corner-sharing complexes. (b) A fragment of the $[\{Cu(en)_2\}_2\text{-}(H_2W_{12}O_{42})]_n^{6n-}$ chain in **1** with the atomic labeling scheme (thermal ellipsoids shown at 50% probability).

Fig. 3 TGA-TDA of compound **1** in flowing N_2 at 10 °C min^{-1}.

crystal structure of **1**, there is extensive hydrogen bonding among the H_2O molecules of crystallization, the N–H groups from the complexes and the oxygen atoms from the inorganic polyoxotungstate units with $N(O) \cdots O$ interatomic distances between 2.712(10) and 3.250(9) Å. These hydrogen bonds make the crystal structure of **1** more stable.

As documented in Fig. 3, the weight losses of compound **1** in the ranges 120–180 °C and 250–385 °C are 5.41 and 17.95%, respectively. These observed values are in agreement with the removal of the water molecules and the ethylenediamine ligands, respectively (cacld.: 5.38% for the former; 17.97% for the latter). The small weight loss of 0.51% between 485 and 540 °C is consistent with the release of one H_2O molecule (calcd. 0.45%), according to the decomposition reaction, $Cu_5[H_2W_{12}O_{42}] \rightarrow 5CuO \cdot 12WO_3 + H_2O$. The result of DTA showed three immediately subsequent steps. The first two are endothermic and accompanied by the evolution processes of water and ethylenediamine molecules, respectively. The third one is exothermic and corresponds to the formation of water.
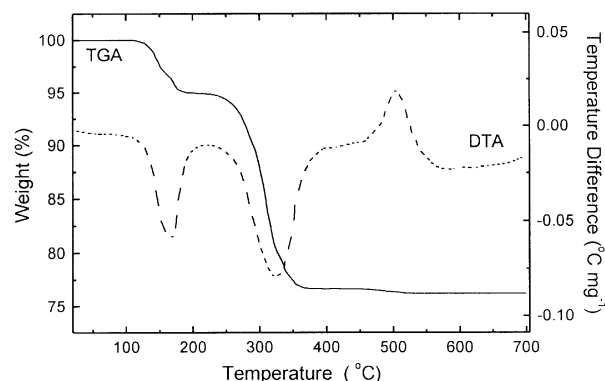
The copper centers in **1** are well separated with Cu $\cdots$ Cu distances longer than 7.61 Å. This fact leads to a good magnetic isolation of Cu^{2+} as demonstrated by the magnetic measurements. A nearly constant value of $\mu_{eff} = 1.86 \ \mu_B$ was observed in the range 4–290 K.

It has been illustrated that several polyoxotungstates have catalytic activity in the oxygenation of alkanes under photo-excitation.[23] To investigate the oxidative catalytic activity of compound **1**, we carried out a probe reaction of the photooxidation of cyclohexane with 760 Torr of O_2 using compound **1** as the catalyst. Under the above-mentioned experimental conditions, the overall oxidative conversion of cyclohexane was 36% yielding cyclohexanone and cyclohexanol in the ratio of about 2.5 : 1 as the products. In a comparative experiment, where no catalyst was added, the oxidative conversion of cyclohexane was observed only in a negligible amount (less than 3%). This suggests that compound **1** may be useful as an oxidative photocatalyst in some organic syntheses.

Acknowledgements

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