Hydrothermal synthesis, crystal structure and electrochemical properties of a novel 3D Dawson-type polyoxometalate supramolecular network

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A novel Dawson-type polyoxometalate supramolecular architecture of the formula $[4,4'\text{-}H_2bipy]_{2.5}\cdot[4,4'\text{-}Hbipy]\cdot[P_2W_{18}O_{62}]\cdot6.25H_2O$ (4,4'-bipy = 4,4'-bipyridine) has been hydrothermally synthesised and characterised by means of elemental analysis, IR, CV and X-ray single-crystal diffraction. X-ray crystallography indicates that the title compound consists of Dawson-type polyoxoaions $[P_2W_{18}O_{62}]^{6-}$, water molecules and 4,4'-bipy units. The polyoxoanion clusters together with 4,4'-bipy units and water molecules to construct the three-dimensional supramolecular network through hydrogen bonds. The crystal structure analyses reveal that water molecules and 4,4'-bipy units play the important role on the packing arrangements of crystals. Cyclic voltammetry shows that the title compound exhibits three chemically reversible steps

Key words: Dawson-type polyoxometalate, supramolecular compound, hydrothermal synthesis, crystal structure, electrochemical behaviour

In recent years, supramolecular chemistry has developed at a tremendous rate. This expansion has been driven by growing knowledge regarding synthetic and characterisation methods for complex structures.[1–3] The directed assembly of supramolecular arrays from discrete molecular building blocks is a topic of significant interest with potential applications in the areas of catalysis, molecular electronics, sensor design, and optics.[4–6] Polyoxometalates (POMs) are a unique class of ligands characterised by their discrete size, high symmetry, large anionic charge, aqueous stability, and various redox activities.[6] Due to these features, POMs have been found to be extremely versatile inorganic building blocks for the construction of supramolecular architectures.[7–10] To the best of our knowledge, the most employed POM candidates are the saturated Keggin-type polyoxoanions, which can be formulated as $[XM_{12}O_{40}]^{n-}$ (X = P^V, As^V, Si^{IV}, Ge^{IV} or B^{III}; M = Mo^{VI}, W^{VI} or Nb^V), partly because the charge density of the surface oxygen atoms on them can be increased either by reducing some metal centres or replacing higher-valent metal centres with lower valent metal centres.[11] In contrast, the investigations on supramolecular complexes based on Dawson-type polyoxoanions $[X_2M_{18}O_{62}]^{n-}$ (X = P^V or As^V; M = Mo^{VI} or W^{VI}) remain much less developed. Moreover, most saturated Dawson-type compounds that have been reported previously are zero- or one-dimensional structures.[12-17]

4,4'-bipyridine is an excellent planar aromatic electron donor rod-like ligand, which has been extensively employed as the rigid organic building block for the construction of infinite one-, two- or three-dimensional coordination polymeric frameworks.[18] Because of the excellent features of 4,4'-bipyridine and the fact that the spherical surface of the POM anions can give a better opportunity in forming hydrogen bonds with the organic/inorganic moieties, it is interesting to prepare the supramolecular compound based on Dawson-type POMs. Here, we obtained a novel supramolecular compound $[4,4'\text{-}H_2bipy]_{2..5}\cdot[4,4'\text{-}Hbipy]\cdot[P_2W_{18}O_{62}]\cdot6.25H_2O$ (4,4'-bipy = 4,4'-bipyridine) by hydrothermal synthesis, which showed a 3-D framework.

Experimental

Preparation of the title compound

A mixture of $Na_2WO_4\cdot2H_2O$ (0.9896 g, 3.0 mmol), H_3PO_4 (0.2 ml, 85%), and $C_{10}H_8N_2\cdot10H_2O$ (0.0096 g, 0.04 mmol) was dissolved in 10 ml of water, and the pH value of the solution was adjusted to 3.8 with 0.5 mol l^{-1} KOH solution. The cloudy solution was stirred for 30 min in air, then transferred to a 25-ml Teflon-lined stainless-steel autoclave with a filling capacity of approximately 50% and held at 433K for 6 days. After the mixture was slowly cooled to room temperature, light yellow block-shaped crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 50% based on W. Elemental analysis. Calcd for $C_{35}H_{46.\,5}N_7O_{68..25}P_2W_{18}$: C, 8.35; H, 0.92; N, 1.95. Found: C, 8.42; H, 0.89; N, 2.02%.

Materials and physical measurements

All materials were of chemical grade and used without further purification. Elemental analysis (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyser. The water content was determined from thermogravimetric analysis of the sample. IR spectra were recorded on a Hitachi X-650 FT-IR. spectrometer using KBr discs in the range 4000–400 cm^{-1}. TG-DTA measurements were performed on a TGA-7 thermal analyser in flowing nitrogen gas with a heating rate of 5K min^{-1}. Cyclic voltammograms were obtained on a model CHI630 electrochemical analyser (CH Instruments, Austin, TX, USA) controlled by a personal computer at room temperature. A three-electrode system was used for the measurements, with a bare GCE (3 mm diameter) or C-Ni/GCE used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. All experiments were performed at room temperature.

X-ray crystal structure determination

X-ray single crystal data were collected with a Bruker SMART CCD area detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically on $|F|^2$ by full-matrix least-squares methods using SHELXL-97.[19] Hydrogen atoms were introduced in calculated positions and refined isotropically. The refinement converged at $R = 0.0442$ over 17666 reflections with $I>2\sigma(I)$, $wR = 0.1113$, $w = 1/[\sigma^2(F^2_o) + (0.0632P)^2 + 12.7227P]$, where $P = (F_o^2 + 2F_c^2)/3$. The crystal data and structure refinement are listed in Table 1. Selected bond lengths and bond angles are provided in Table 2.

Results and discussion

Description of the crystal structure

The basic motif of the structure is shown in Fig.1. The polyoxoanion of the title compound retains the parent structure which formally consists of two $[\alpha\text{-}PW_9O_{34}]^{9-}$ units linked by almost linear M–O–M bonds (~162 °) arranged in approximately D_{3h} symmetry.[20] There are two kinds of W atom in the polyoxoanion skeleton: six polar W atoms on vertical mirror planes grouped in two sets of three, and twelve equatorial W atoms that do not lie on mirror planes grouped in two sets of six. The polyoxoanion consists of eighteen WO_6 octahedrons and two PO_4 units. The oxygen atoms in the $[P_2W_{18}O_{62}]^{6-}$ anion can be divided into four groups according to their coordination number:[21,22] O_t (terminal oxygen atoms connecting only one W atom), O_b (oxygen atoms located in the shared corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge-sharing WO_6 octahedrons in the

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Table 1 Crystal data and structure refinement

Compound	$C_{35}H_{46\cdot 5}N_7O_{68\cdot 25}P_2W_{18}$
Colour/shape	Light-yellow/block
CCDC deposite no.	CCDC-284236
Formula weight	5028.53
Temperature	293(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 13.2673(12)$Å, $\alpha = 78.266(10)°$ $b = 14.1638(12)$Å, $\beta = 83.892(2)°$ $c = 26.950(2)$ Å, $\gamma = 68.3190(10)°$
Volume	4605.0(7) Å 3
Z	2
Dx	3.636 g. cm^{-1}
Absorption coefficient	22.515 mm^{-1}
F(000)	4452
λ	0.71073 Å
Crystal size	0.28 x 0.15 × 0.07 mm^3
θ range for data collection	1.54 to 26.02°
Index ranges	$-16 \le h \le 6, -17 \le k \le 17, -32 \le l \le 33$
Reflections collected	26066
Independent reflections	17666
Completeness to θ = 26.02°	97.30%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17666/0/1090
Goodness-of-fit on F^2	1.033
Final *R* indices [I>$2\sigma(I)$]	$R_a = 0.0442$, $wR_b = 0.1113$
R indices (all data)	$R_a = 0.0593$, $wR_b = 0.1202$
$(\Delta/\sigma)_{max}$	0.013
Largest diffraction peak and hole	2.511 and −2.388 e · Å^{-3}

Table 2 Selected bond lengths (Å) and bond angles (°) for the title compound

P1–O20	1.528(8)	P1–O22	1.527(9)
P1–O21	1.538(8)	P1–O9	1.592(8)
P2–O43	1.517(8)	P2–O41	1.521(9)
P2–O35	1.553(9)	P2–O54	1.584(8)
W1–O1	1.701(9)	W1–O5	1.894(9)
W1–O8	1.924(8)	W1–O2	1.928(8)
W1–O3	1.949(9)	W1–O9	2.370(9)
W2–O6	1.732(9)	W2–O13	1.899(9)
W2–O2	1.925(9)	W2–O10	1.926(9)
W2–O4	1.941(9)	W2–O9	2.383(8)
W3–O15	1.701(10)	W3–O18	1.883(8)
W3–O16	1.906(9)	W3–O14	1.894(9)
W3–O5	1.939(8)	W3–O20	2.351(8)
W4–O25	1.702(9)	W4–O14	1.903(9)
W4–O8	1.902(8)	W4–O23	1.922(10)
W4–O28	1.930(9)	W4–O21	2.353(9)
W5–O24	1.709(9)	W5–O29	1.898(8)
W5–O12	1.906(8)	W5–O23	1.901(10)
W5–O31	1.937(8)	W5–O21	2.387(9)
W6–O7	1.707(9)	W6–O11	1.896(9)
W6–O3	1.898(9)	W6–O4	1.907(8)
W6–O12	1.914(8)	W6–O9	2.376(8)
O1–W1–O5	102.9(4)	O1–W1–O8	100.7(4)
O5–W1–O8	86.1(4)	O1–W1–O2	101.6(4)
O5–W1–O2	89.7(4)	O8–W1–O2	157.7(4)
O1–W1–O3	101.3(4)	O5–W1–O3	155.8(4)
O8–W1–O3	87.8(4)	O2–W1–O3	87.2(4)
O1–W1–O9	171.5(4)	O5–W1–O9	83.9(3)
O8–W1–O9	84.7(3)	O2–W1–O9	73.1(3)
O3–W1–O9	72.2(3)	O20–P1–O22	112.7(5)
O20–P1–O21	111.4(5)	O22–P1–O21	112.0(5)
O20–P1–O9	106.1(5)	O22–P1–O9	107.5(5)
O21–P1–O9	106.7(5)		

same W_3O_{13} unit) and O_a (oxygen atoms connecting the P heteroatom and W atoms). Relevant W–O bond distances in the anion can be classified into three groups: W–O_t distances vary from 1.686(9) to 1.735(9) Å; W– $O_{b,c}$ distances vary between 1.861(8) and 2.398(8) Å; and W– O_a distances vary between from 2.37(9) to 2.383(8) Å. Their average bond distances are 1.706(9), 1.9763(1) and 2.376(8) Å respectively. The O–W–O angles vary from 73.1(3) to 171.5(4)°. These results indicate that all W atoms are in a distorted geometric environment.

Interestingly, except for the N5 atom, the nitrogen atoms of the 4,4'-bipy molecules in compound **1** are protonated, with a total positive charge balancing the negative charges on the polyoxoanion $[P_2W_{18}O_{62}]^{6-}$ to give compound **1** electric neutrality. All protonated nitrogen atoms exhibit + 1 oxidation state. As shown in Fig.2, each polyoxoanion cluster is connected to one $[4,4\text{-Hbipy}]^+$ unit and two lattice waters through hydrogen bonds with O2WA…O2 = 2.955 Å, N6A…O3 = 3.002 Å and O5WA…O17B = 3.020 Å, respectively. The detailed analysis shows that there are two kinds of strong hydrogen bond; between lattice water and lattice water, lattice water and N atom from 4,4'-bipy. An infinite one-dimensional chain is formed through hydrogen bonds with O5W…O4WA = 2.766Å, O4W…O2WA = 2.815 Å and O4W…N6A = 2.656 Å, respectively. Figure 3 shows a two-dimensional layer of two chains where a pair of anions are bridged by two $[4,4\text{-}H_2\text{bipy}]^{2+}$ units through hydrogen bonding interactions with N4A…O36B = 2.618 Å, N2…N3A = 2.753 Å and N1A…O46C = 3.043Å, respectively. Moreover, each pair of anions has another bridge to two $[4,4\text{-}H_2\text{bipy}]^{2+}$units on their other sides.

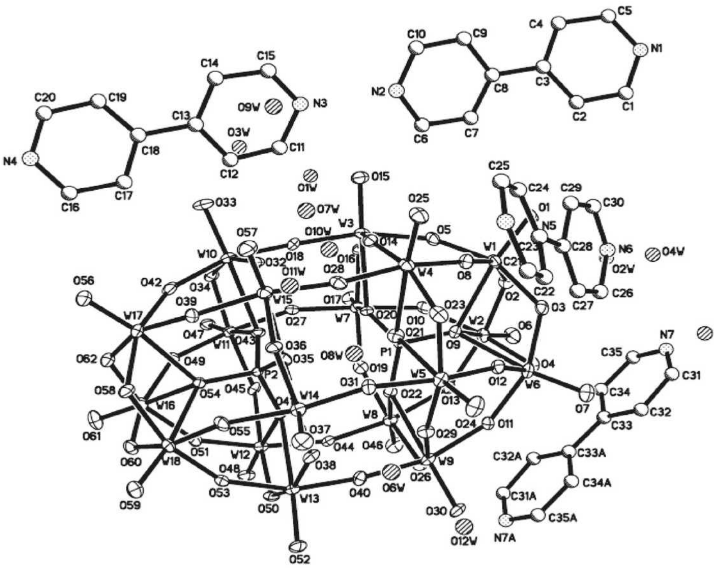

Fig. 1 Ball and stick drawing of the title compound. Hydrogen atoms have been omitted for clarity.

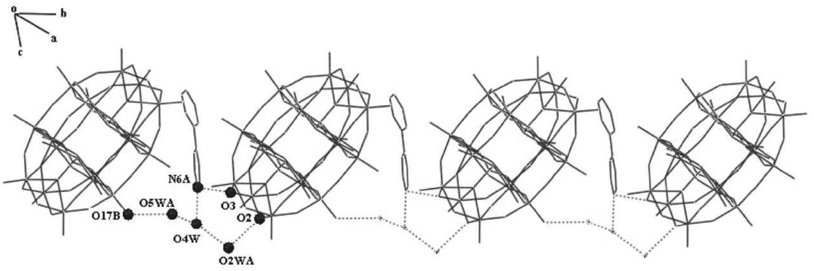

Fig. 2 The infinite one-dimensional chain in the title compound through hydrogen bonds (dashed lines). All hydrogen atoms have been omitted for clarity. Symmetry codes: A (1–*x*, 1–*y*, 1–*z*), B(1–*x*, –*y*, 1–*z*).

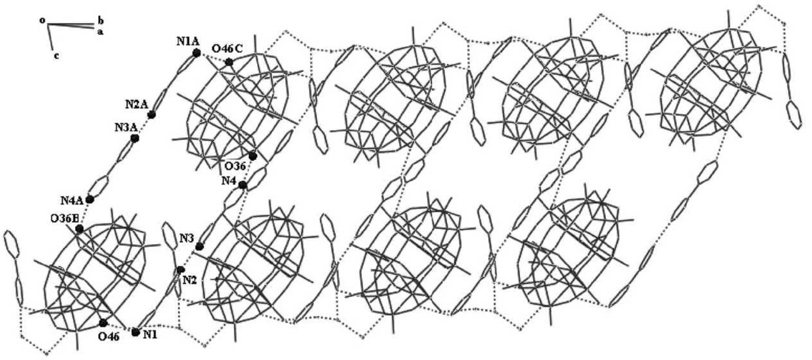

Fig. 3 The two-dimensional layer of two chains formed through hydrogen bonding interactions (dashed lines) between polyoxoanions and 4,4-bipy. All hydrogen atoms have been omitted for clarity. Symmetry codes: A(*x*, *y*,–1+*z*), B (1–*x*, –*y*, –*z*), C (–1+*x*, 1+*y*, –1+*z*).

Another interesting structural feature is that the layers are further linked by strong hydrogen bonds into a 3D supramolecular network. As shown in Fig. 4, the layers are connected by hydrogen bonding interactions between N1 atoms from bi-protonated 4,4'-bipy, with distance of 2.637 Å, into a stepped multilayer framework, (Fig. 4a). In addition, two anions from adjacent layers are connected by another bi-protonated 4,4-bipy and water molecules. The stepped multilayer frameworks are further extended through hydrogen bonds with O3WA...O33 = 2.954Å, O1W...O16 = 2.954Å, O1W···O3W = 2.742 Å and O1W···N7B = 2.790 Å, respectively (Fig. 4b). Thus a three-

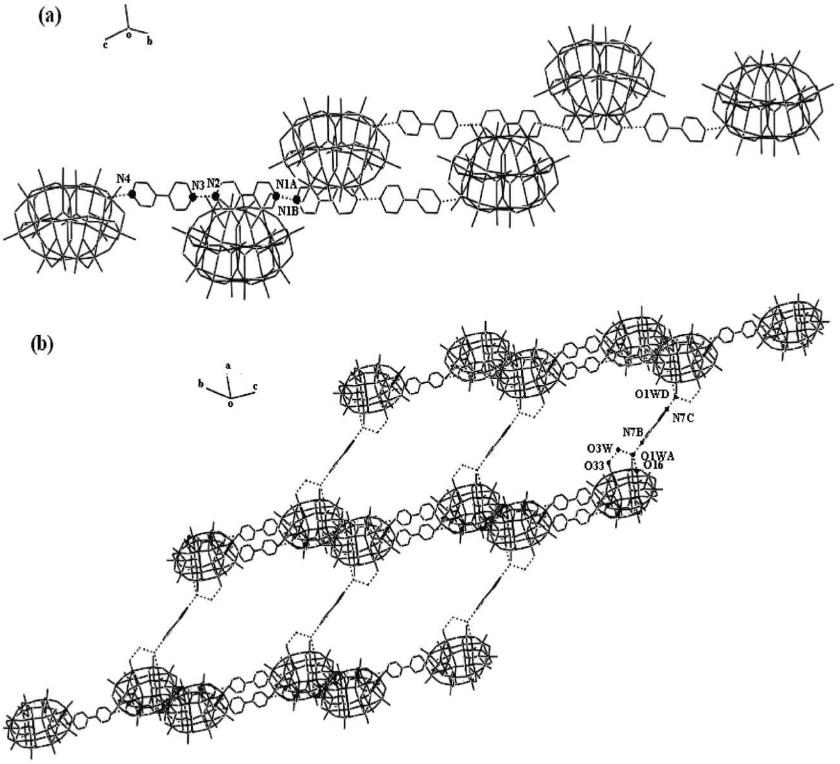

Fig. 4 (a) The two-dimensional layers connected into a stepped multilayer framework through hydrogen bonds (dashed lines) between N1 atoms. Symmetry codes: A (–*x*, 3–*y*, –*z*), B(*x*, 1+*y*, *z*). (b) The stepped multilayer frameworks connected by hydrogen bonding interactions (dashed lines) between water molecules and N atoms from one bi-protoned 4,4-bipy to build up a 3D network. All hydrogen atoms and some [4,4-Hbipy]$^+$ units have been omitted for clarity. Symmetry codes: A (1–*x*, 1–*y*, 1–*z*), B(*x*, *y*, 1+*z*), C(2–*x*,1–*y*,1–*z*), D(1+*x*, 1+*y*, *z*).

dimensional supramolecular network comes into being. In general, hydrogen bonding interactions play rather important roles in the formation of three-dimensional framework in the title compound.

IR spectra of compound **1**

In the IR spectra of compound **1** there are four characteristic vibration bands resulting from the Dawson-type polyoxoanion, namely, ν(P–Oa), ν(W–O_t), ν(W–Ob) and ν(W–Oc). Comparing the IR data to those of α-$H_6P_2W_{18}O_{62}\cdot nH_2O$, the W–$O_t$ vibration band has a red-shift from 961 to 957 cm^{-1}, the W–Ob vibration band has a red-shift from 912 to 910 cm^{-1}, and the W–Oc vibration band has also a red-shift from 780 to 776 cm^{-1}. The P–Oa vibration band appears nearly identical to the parent acid α-$H_6P_2W_{18}O_{62}.nH_2O$.[23] The results indicate that the polyoxoanions in compound **1** are somewhat distorted due to the strong interactions between polyoxoanions and 4,4'-bipy groups. Bands at 1410, 1490 and 1610 cm^{-1} belong to the characteristic vibrations of the 4,4'-bipy groups.

Thermal properties of compound **1**

The TG curve of compound **1** shows two weight-loss stages (Fig. 5, see Supplementary data available from the author), giving a total loss of 12.28% of initial weight in the range 23–800 °C. The first weight loss is 3.64% in the range of 23–197 °C, corresponding to the release of crystallisation water molecules. The second weight loss of 8.64% from 197 to 576 °C is attributed to the combustion of 4,4'-bipy molecules. A very strong exothermic peak appearing at 699 °C indicates the decomposition of the title polyoxoanion. The results shows that the thermal stability of the title compound is higher than that of the parent heteropolyoxoanion, which decomposes at *ca.*500 °C.

Electrochemical behaviour of compound **1**

Figure 6 (see Supplementary data available from the author) shows a cyclic voltammogram of 0.5 mmol compound **1**, in DMF containing H_2SO_4, with scan rate (υ) of 100 mV s^{-1} in the potential range from 0.3 to –0.9 V. The cyclic voltammogram displays three reduction peaks (reduction potentials: –0.34, –0.54 and –0.76V) and three corresponding oxidation peaks (oxidation potentials: –0.31, –0.51 and –0.73V). The $E_{1/2}$ values are –0.33, –0.53 and –0.75V respectively, which agree with the literature.[24] The peak potential separations of the three redox peaks are all 30 mV, which indicate the three reversible steps are involved in two-electron transfer processes.

Conclusion

In conclusion, a novel hydrogen-bonded high dimensional supramolecular structure has been synthesised and structurally characterised. In the compound, supramolecular interactions among the organic molecules, inorganic polyanions and water molecule play significant roles in stabilisation of the overall high-dimensional supramolecular network. Extended researches are underway to reveal the synthetic rules and explore its attractive properties.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No.284236. Copies of the data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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