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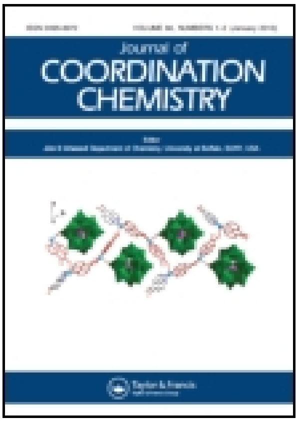

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Hydrolytic cleavage of a DNA-model phosphodiester: a new inorganic-organic hybrid constructed from a Zn-cluster with a polyoxometalate

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Hydrolytic cleavage of a DNA-model phosphodiester: a new inorganic–organic hybrid constructed from a Zn-cluster with a polyoxometalate

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An inorganic–organic hybrid constructed from a Zn-cluster with a polyoxometalate $\{[Zn_3Na_2(\mu\text{-OH})_2(bpdo)_6(H_2O)_{16}][PW_{12}O_{40}]_2\}\cdot(bpdo)_3\cdot C_2H_5OH\cdot 2H_2O$ (bpdo = 4,4′-bis(pyridine-N-oxide)) (**1**) has been synthesized by hydrothermal reaction and characterized by elemental analyses, IR spectra, and single crystal X-ray diffraction. The structural analysis indicates that **1** is an *S*-like complex constructed by $[Zn_3Na_2(\mu\text{-OH})_2(bpdo)_6(H_2O)_{16}]^{6-}$ with two $PW_{12}O_{40}{}^{3-}$ with water occupying several coordination sites and have the potential to act as labile ligands, allowing for substrate and nucleophile binding. Kinetic experiments for hydrolytic cleavage of the DNA-model phosphodiester bis(p-nitropheny1)phosphate (BNPP) were followed spectrophotometrically for absorbance increase at 400 nm in 4-(2-hydroxyethyl)piperazine-1–propane sulfonic acid (EPPS) buffer solution due to the formation of *p*-nitrophenoxide with **1** at pH 4.0 and 50 °C. UV spectroscopy indicates cleavage of the phosphodiester bond proceeds with pseudo-first-order rate constant $6.7(\pm 0.2)\times 10^{-7}\,s^{-1}$, giving an inorganic phosphate and *p*-nitrophenol as the final products of hydrolysis. The results demonstrate that **1** exhibits good catalytic activity and reusability for hydrolytic cleavage of BNPP.

Keywords: Polyoxometalate; Hybrid; Hydrolytic cleavage; Heterogeneous catalyst

1. Introduction

Rational approaches to the design of catalysts for hydrolysis of phosphate diesters have attracted research in bioorganic chemistry [1, 2]. The Lewis acidity of Zn^{2+}, together with its high coordination number, fast ligand-exchange rate, lack of toxicity, and absence of accessible redox chemistry provides an opportunity to mimic the activity of hydrolases to bind and activate the phosphate esters for cleavage. Zn^{2+} is the only metal frequently encountered in both natural and artificial agents. Thus, the development of Zn^{2+}-based artificial enzymes have been highly valued [3–5]. DNA is the most interesting substrate for hydrolytic agents. Since the first studies on DNA manipulation with artificial agents described in 2006 [6], considerable attention has been focused on homogeneous catalysts

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*Corresponding author. Email: hdhqx@henu.edu.cn for hydrolysis of phosphate diesters in aqueous solution [7]. However, due to its polyanionic nature, DNA is resistant to hydrolysis [8]. As a result, it is very difficult to perform mechanistic investigation on this substrate. BNPP as the most popular DNA model is still quite resistant to hydrolytic cleavage for notwithstanding the presence of two good leaving groups, of which the rate of spontaneous hydrolysis has been estimated to be $1.6 \times 10^{-11}\,s^{-1}$ in water at pH 7 and 25 °C, corresponding to a half-life of more than 1300 years.

Various catalysts namely welldefined molecular catalysts, biomimetic catalysts related to the heme enzyme of cytochrome P-450, and the nonheme enzyme of methane monooxygenase, and isolated single-site catalysts with high specific reactivity for cleavage of DNA-model phosphodiester reactions have been reported [9–11]. Heterogeneous catalysts have significant potential advantages over homogeneous catalysts, such as ease of separation, efficient recycling, and minimization of metal traces in the product [12]. However, heterogeneous catalysts for hydrolysis of phosphate diesters are scarce [13, 14]. The design of active, environmentally benign, and recyclable heterogeneous catalysts is expected to have a major impact on hydrolysis of phosphate diester applications.

Polyoxometalates (POMs), with versatile structural topologies, nucleophilic oxygen-enriched surfaces, and physicochemical properties in redox, photo and magnetic chemistry, represent excellent candidates for development of cluster architectures based on the building-block strategy [15–17]. Hybrid POMs have been studied as either acid or oxidation catalysts in homogeneous or heterogeneous catalysis [18–21]. The structure and properties of inorganic–organic hybrid materials depend on the nature of both components, and the search of multifunctional devices is often evoked as a motivation for their synthesis. In catalysis, study of organic–inorganic hybrids with POMs can help to understand the interactions between the organic molecules and the surface of oxides and can lead to more efficient recyclable multifunctional catalysts.

In this study, through combining a Keggin-type $PW_{12}O_{40}{}^{3-}$ and a Zn(II)-cluster, a new inorganic–organic hybrid $\{[Zn_3Na_2(\mu\text{-}OH)_2(bpdo)_6(H_2O)_{16}][PW_{12}O_{40}]_2\}\cdot(bpdo)_3\cdot C_2H_5OH\cdot 2H_2O$ (**1**) was obtained and explored for the catalysis of hydrolytic cleavage of BNPP. The results demonstrate that **1** has good catalytic activity and reusability for hydrolytic cleavage of BNPP.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were used as purchased. $H_3[PW_{12}O_{40}]\cdot 9H_2O$ [22], bpdo [23] and BNNP [24] were prepared according to literature methods and characterized by IR and MS, respectively. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 240C elemental analyzer. IR spectrum was recorded from a powder palletized with KBr on a Nicolet170 SXFT-IR spectrometer from 4000–400 cm^{-1}. UV–vis spectra were performed on a TU-1900 spectrophotometer.

2.2. *Preparation of 1*

$\{[Zn_3Na_2(\mu\text{-}OH)_2(bpdo)_6(H_2O)_{16}][PW_{12}O_{40}]_2\}\cdot(bpdo)_3\cdot C_2H_5OH\cdot 2H_2O$ (**1**). A mixture of $H_3PW_{12}O_{40}\cdot 9H_2O$ (67.0 mg, 0.022 mM), $Zn(ClO_4)_2\cdot 6H_2O$ (57.2 mg, 0.134 mM), bpdo

(20.4 mg, 0.108 mM) in mixed water (3 mL) and alcohol (5 mL) was stirred, and its pH was 5.8 without adjustment. The resulting suspension was sealed in a 25 mL Teflon-lined reactor and kept at 135 °C for four days. After cooling the autoclave to room temperature, colorless block single crystals of **1** were separated, washed with water, and air-dried (46% yield based on $H_3[\alpha\text{-}PW_{12}O_{40}]\cdot 9H_2O$). Anal. Calcd for $C_{92}H_{116}N_{18}Na_2O_{119}P_2W_{24}Zn_3$ (8094.46) (%): C, 17.01; N, 3.88; H, 1.80. Found (%): C, 17.24; N, 3.76; H, 1.90.

2.3. *Crystallographic data collection and refinement*

Intensity data for **1** were collected on Bruker CCD Apex-II diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structure of **1** was resolved by direct methods using SHELXTL-97 program package [25]. The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Lorentz polarization and multi-scan absorption corrections were applied. No hydrogens associated with water were located from the difference Fourier map. Positions of hydrogens attached to carbon were geometrically placed. All hydrogens were refined isotropically as a riding mode using the default SHELXTL parameters. Crystal data, data collection parameters, and details of the structure refinement are given in table 1. Relevant bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement for **1**.

Crystal data	
Chemical formula	$C_{92}H_{116}N_{18}Na_2O_{119}P_2W_{24}Zn_3$
Formula weight	8094.5
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Cell setting, space group	Triclinic, P-1
a (Å)	14.349
b (Å)	15.279
c (Å)	19.810
α (°)	87.908(1)
β (°)	86.299(1)
γ (°)	86.220(1)
V (Å^3)	4322.4(1)
Absorption coefficient (mm^{-1})	0.78
Z	1
$F(000)$	3664
Crystal size (mm)	0.25 × 0.23 × 0.18
θ range for data collection (°)	1.89–25.00
Index range	$-17 \leqslant h \leqslant 17$, $-18 \leqslant k \leqslant 17$, $-23 \leqslant l \leqslant 23$
Reflections collected	39,717
Reflections unique	15,148 [$R(\text{int}) = 0.0347$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15,148/66/1258
Goodness of fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$]^{a,b}	$R_1 = 0.0322$, $wR_2 = 0.0801$
R indices (all data)	$R_1 = 0.0440$, $wR_2 = 0.0844$
Largest diff. peak and hole (eÅ^{-3})	1.738 and −1.290

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where $x = 0.0450$, $y = 10.5523$ for **1**.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

P(1)–O(6)	1.621(6)	P(1)–O(28)	1.622(5)
P(1)–O(37)	1.622(5)	P(1)–O(18)	1.634(6)
W(1)–O(1)	1.710(7)	W(1)–O(4)	1.904(6)
W(1)–O(2)	1.914(6)	W(1)–O(5)	1.915(6)
W(1)–O(3)	1.924(6)	W(1)–O(6)	2.353(6)
W(2)–O(7)	1.698(6)	W(2)–O(10)	1.892(6)
W(2)–O(9)	1.897(6)	W(2)–O(8)	1.933(6)
W(2)–O(2)	1.948(6)	W(2)–O(6)	2.356(5)
W(3)–O(11)	1.708(6)	W(3)–O(12)	1.903(6)
W(3)–O(13)	1.904(6)	W(3)–O(8)	1.913(5)
W(3)–O(3)	1.930(6)	W(3)–O(6)	2.349(5)
Zn(2)–O(6 W)	2.024(7)	Zn(2)–O(51)	2.126(7)
Zn(2)–O(43)	2.175(7)	Zn(1)–O(2 W)	2.081(8)
Zn(1)–O(41)	2.083(8)	Zn(1)–O(5 W)	2.101(8)
Zn(1)–O(1 W)	2.113(11)	Zn(1)–O(4 W)	2.117(7)
Zn(1)–O(3 W)	2.122(8)	Na(1)–O(8 W)	2.747(14)
Na(1)–O(44)	2.762(12)	Na(1)–O(42)	2.993(15)
Na(2)–O(45)	2.827(11)	Na(2)–O(7 W)	2.853(17)
Na(2)–O(51)	2.908(12)	Na(2)–O(32)	3.013(11)
O(6)–P(1)–O(28)	109.6(3)	O(6)–P(1)–O(37)	109.7(3)
O(28)–P(1)–O(37)	109.0(3)	O(6)–P(1)–O(18)	109.3(3)
O(28)–P(1)–O(18)	109.8(3)	O(37)–P(1)–O(18)	109.4(3)
O(1)–W(1)–O(4)	102.2(3)	O(1)–W(1)–O(2)	100.8(3)
O(4)–W(1)–O(2)	89.6(3)	O(1)–W(1)–O(5)	101.2(3)
O(1)–W(1)–O(3)	99.4(3)	O(4)–W(1)–O(3)	158.4(3)
O(1)–W(1)–O(6)	171.1(3)	O(4)–W(1)–O(6)	85.1(2)
O(6 W)#1–Zn(2)–O(6 W)	180.000(1)	O(6 W)#1–Zn(2)–O(51)#1	89.6(3)
O(6 W)–Zn(2)–O(51)	89.6(3)	O(6 W)–Zn(2)–O(43)	89.4(3)
O(6 W)–Zn(2)–O(43)#1	90.6(3)	O(51)–Zn(2)–O(43)	87.8(3)
O(43)–Zn(2)–O(43)#1	180.000(2)	O(2 W)–Zn(1)–O(41)	89.2(4)
O(2 W)–Zn(1)–O(5 W)	87.1(4)	O(41)–Zn(1)–O(5 W)	95.1(3)
O(2 W)–Zn(1)–O(1 W)	87.0(4)	O(41)–Zn(1)–O(1 W)	175.5(4)
O(5 W)–Zn(1)–O(1 W)	87.1(4)	O(2 W)–Zn(1)–O(4 W)	171.5(4)
O(41)–Zn(1)–O(4 W)	95.4(3)	O(5 W)–Zn(1)–O(4 W)	85.3(3)
O(1 W)–Zn(1)–O(4 W)	88.7(4)	O(2 W)–Zn(1)–O(3 W)	95.4(4)
O(41)–Zn(1)–O(3 W)	83.3(3)	O(51)–Na(2)–O(32)	76.3(3)
O(8 W)–Na(1)–O(44)	141.5(5)	O(8 W)–Na(1)–O(42)	98.9(4)
O(44)–Na(1)–O(42)	90.6(4)	O(45)–Na(2)–O(7 W)	140.5(5)
O(45)–Na(2)–O(51)	81.8(3)	O(7 W)–Na(2)–O(51)	137.0(5)
O(45)–Na(2)–O(32)	74.5(3)	O(7 W)–Na(2)–O(32)	103.6(4)

Symmetry codes: #1 $-x,\ -y+2,\ -z+2$.

3. Results and discussion

3.1. *Spectroscopic study*

The IR spectrum of **1** displays characteristic vibrations from the Keggin framework. Four characteristic bands are observed at 1085, 967, 881, and 796 cm^{-1}, assigned to $\nu(\text{P–O}_a)$, $\nu(\text{W–O}_t)$, $\nu(\text{W–O}_b)$, and $\nu(\text{W–O}_c)$, respectively [22]. The observed strong and broad peak at 3440 cm^{-1} is attributed to O–H stretch of lattice water or coordination water in **1**. Four vibrations resulting from bpdo, namely, ν(N–O) (1220 cm^{-1}), ν(ring) (1640 cm^{-1}), δ(C–H, in plane) (1180 cm^{-1}), and δ(N–O) (841 cm^{-1}) are also observed. The IR spectrum is consistent with those of X-ray diffraction structural analysis.

3.2. *Description of the crystal structure of* $\{[Zn_3Na_2(\mu\text{-}OH)_2(bpdo)_6(H_2O)_{16}][PW_{12}O_{40}]_2\}\cdot(bpdo)_3\cdot C_2H_5OH\cdot 2H_2O$ *(1)*

Keggin-type heteropolyanions demonstrate a wide range of topologies and structures, with spherical surfaces giving an opportunity for forming coordination bonds or hydrogen bonds with organic or inorganic moieties [26–29]. In this work, the reaction system including $H_3PW_{12}O_{40}$, $Zn(ClO_4)_2$, and bpdo in H_2O and C_2H_5OH under hydrothermal conditions leads to a new inorganic–organic polyoxometalate. Structural analysis displays that **1** crystallizes in a triclinic space group $P\bar{1}$ and displays an *S*-like Zn-cluster with two polyanions decorated by terminal oxygens (figure 1). $PW_{12}O_{40}{}^{3-}$ exhibits a classical Keggin-type structure. In the skeleton, tetrahedral $\{PO_4\}$ resides in the center of the $[A\text{-}PW_{12}O_{40}]^{3-}$ Keggin cluster and shares four oxygens with four $\{W_3O_{13}\}$ groups. The BVS (bond valence sum) values for W indicate that all are + 6 [30]. Relevant W–O bond distances of $PW_{12}O_{40}{}^{3-}$ can be grouped into three sets: W–O$_t$ (terminal) 1.693(6)–1.713(6) Å; W–O$_{b,c}$ (bridge) 1.892(6)–1.948(6) Å; and W–Oa (central) 2.324 (5)–2.364(5) Å.

In $[Zn_3Na_2(\mu\text{-}OH)_2(bpdo)_6(H_2O)_{16}]^{6+}$, two crystallographic independent Zn(1) and Zn(2) centers are coordinated in distorted octahedral geometries, with Zn(1) coordinated by four oxygens from coordinated water in the equatorial plane with one oxygen from bpdo and another oxygen from coordinated water in axial positions (with Zn–O bond distances varying from 2.080(8)–2.123(8) Å), and six-coordinate Zn(2) is only one-half occupied, defined by two O from two bpdo [Zn(2)–O: 2.034(9)–2.202(9) Å] and two μ-OH (O51 and O51A) bridging to Na(2) building the equatorial plane, O6W and O6WA ($-x$, $2-y$, $2-z$) [Zn(2)–O(6W): 2.024(7) Å] lying on axial sites. In **1**, the coordination geometry of Zn ions is consistent with that of the DNA-Footprinting active cyclen-based Zn complexes [31]. Water molecules occupy several coordination sites and have the potential to act as labile ligands, allowing for substrate binding and the simultaneous metal bound nucleophile. Thus, **1** has potential to exhibit catalytic hydrolysis for modes of natural phosphate esters. Crystallographic independent Na(1) and Na(2) are half-occupied, the three-coordinate Na(1) adopts distorted trigonal geometry, coordinated by two O from two bpdo molecules [Na(1)–O: 2.762(12)–2.993(15) Å] and a water O8W [Na(1)–O(8W): 2.746(14) Å]. Na(2) adopts a

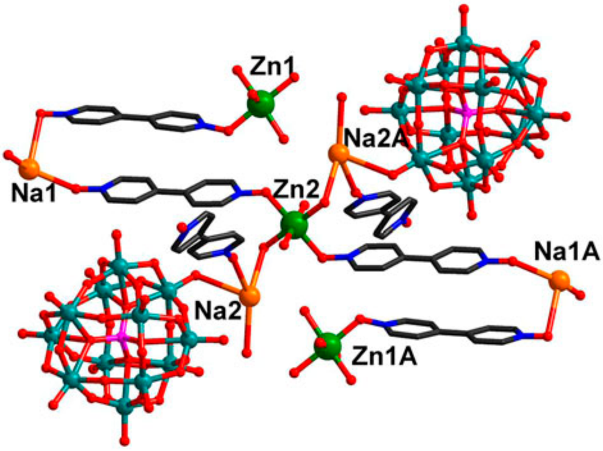

Figure 1. Wire-and-stick representation of **1**; symmetry code: A = $-x$, $2-y$, $2-z$. Hydrogens attached to carbon and nitrogen are omitted for clarity.

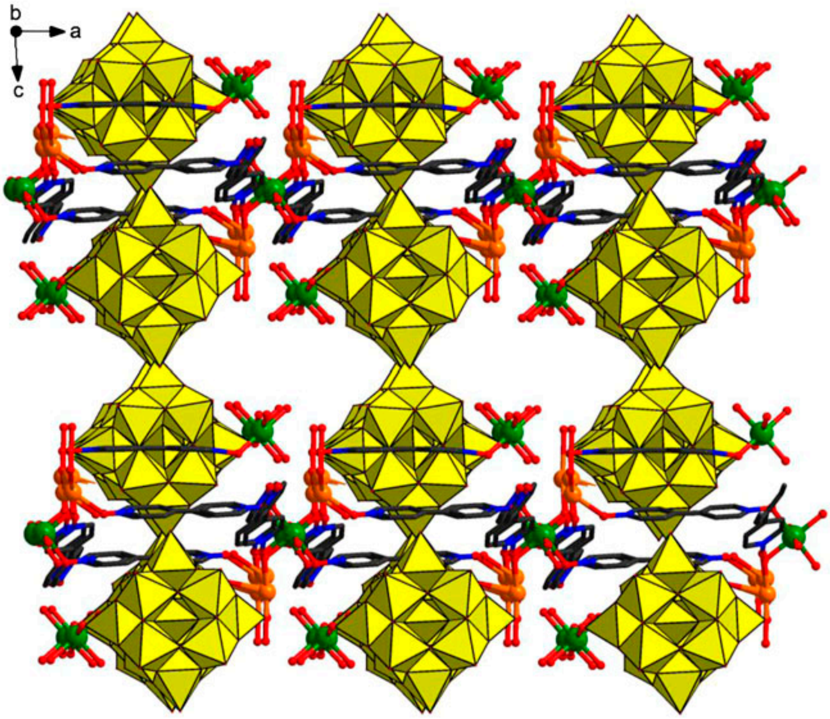

Figure 2. The 3D structure of **1** viewed down the *b*-axis.

seriously distorted tetrahedral geometry, coordinated by four oxygens from one bpdo [Na(2)–O: 2.827(11) Å], a bridging O51 [Na(2)–O(51): 2.908(12) Å], O7W [Na(2)–O(7W): 2.852(17) Å], and a terminal oxygen O32 [Na(2)–O(32): 3.013(11) Å]. By strong π…π–stacking interactions between adjacent pyridine rings, Na(1) and Zn(2) are linked by bridging ligand bpdo into an *S*-like chain. As can be seen from figure 2, these hybrids are stacked along the crystallographic *b*-axis parallel through interactions between $PW_{12}O_{40}^{3-}$, giving one-dimensional (1-D) channels along the *b*-axis with cross section about $15.1 \times 13.5\,Å^2$ allowing molecules such as BNNP and its hydrolyzates ingress and egress. The water coordinated Zn^{2+} ions are located in the channel, beneficial for contact with the substrate.

3.3. *Cleavage of a DNA-model phosphodiester*

Catalytic cleavage of BNPP was examined by using 10 M% of crystalline samples of **1** and 40.8 mg (0.12 mM) BNPP in 4 mL water through a heterogeneous system under stirring in an oil bath at 50 °C. Cleavage of BNPP was followed by monitoring increasing absorbance at 400 nm due to formation of 4-nitrophenoxide, and no obvious pH change was observed during the catalytic processes. The reaction mixture was withdrawn at regular intervals to study the progress of the reaction. Typically, 10 µL solution was taken out with the help of a micro syringe and then was injected into 3 mL EPPS buffer solution (pH 8.2). The monitoring continued 10 days until the absorbance did not increase. The

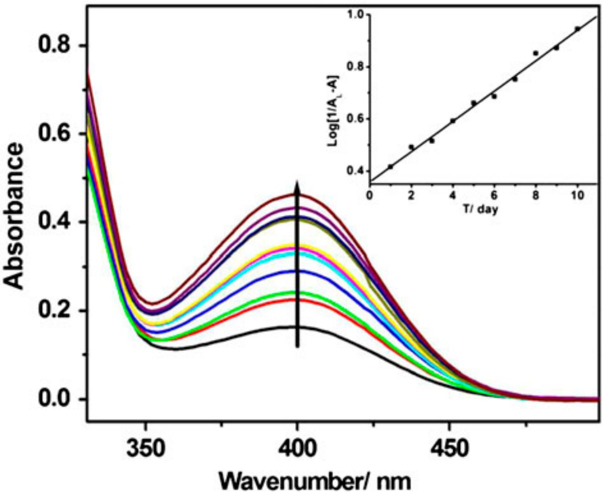

Figure 3. Family of UV–visible spectra of 4-nitrophenoxide formed from cleavage of BNPP in H_2O at 50 °C. Inset: Kinetic plot of hydrolysis of BNPP using **1** as the catalyst. A is the observed absorbance and A_L is the final absorbance at the end of the reaction.

pseudo-first-order rate constants k_{obsd} (s^{-1}) for these reactions were determined as the slopes of semilogarithmic plots of reaction progress ($A_L - A$) against time, where A is the observed absorbance at 400 nm and A_L is the final absorbance at the end of the reaction. As it can be seen in figure 3, a plot of the reaction progress $\log[1/(A_L - A)]$ against time fits well with the pseudo-first-order rate equation, giving a rate constant k_{obs} of $6.7(\pm 0.2) \times 10^{-7}\,s^{-1}$ and a half-life of 1.04×10^6 s. For this reaction, the values of k_{obsd} was reproducible to ± 4%. Crystals of **1** were easily isolated from the reaction suspension by filtration and reused three times, displaying only a slight decrease in activity, demonstrating this compound has great potential as a heterogeneous catalyst.

4. Conclusion

We have synthesized a new inorganic–organic hybrid constructed from a Zn-cluster with a polyoxometalate $\{[Zn_3Na_2(\mu\text{-}OH)_2(bpdo)_6(H_2O)_{16}][PW_{12}O_{40}]_2\}\cdot(bpdo)_3\cdot C_2H_5OH\cdot 2H_2O$ and explored it in hydrolysis of phosphodiester bond cleavage. It displayed high activity, suggesting a pseudo-first-order hydrolytic cleavage reaction in aqueous solution. The results confirmed that this compound has potential as a heterogeneous catalyst.

Supplementary data

Crystallographic data for the structural analysis have been deposited with The Cambridge Crystallographic Data Center, CCDC reference numbers 910621 for **1**. These data can obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif or from The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:+44–1223-336,033; E-mail: deposit@ccdc.cam.ac.uk).

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