Synthesis and Structural Characterization of a Tetra-Cobalt(II)-substituted Sandwich-type Tungstophosphate, $(1,3\text{-}H_2dap)_2H_4[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]\cdot 3H_2O$

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A sandwich-type tungstophosphate, $(1,3\text{-}H_2dap)_2H_4[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]\cdot 3H_2O$ (1,3-dap = 1,3-diaminopropane), was hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, elemental and thermo-gravimetric analysis, and IR and UV spectroscopy. The compound presents a classical tetra-transition metal-substituted sandwich framework, $[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]^{8-}$, which contains two lacunary α-B-$[PW_9O_{34}]^{9-}$ Keggin units linked by a rhomb-like $Co_4O_{14}(1,3\text{-}dap)_2$ cluster lying across an inversion center. The Co^{2+} ions are coordinated by a mono-protonated dap ligand. Isolatedly protonated 1,3-dap units act as counter-ions interacting with the $[PW_9O_{34}]^{9-}$ polyanions *via* hydrogen bonds forming a three-dimensional framework.

Key words: Polyoxometalate, Crystal Structure, Tungstophosphate, Sandwich, Keggin

Introduction

The design and syntheses of hybrid polyoxometalates have been attracting extensive interest due to the rich architectures and potential applications of the products in chemistry, physics and material science [1]. Moreover, different polyanions, particularly vacant polyoxometalate clusters have different reactivity and can act as inorganic building blocks coordinating to transition metal or rare earth cations. The $[PW_9O_{34}]^{9-}$ anion is one of the important lacunary polyanions, obtained by losing three WO_6 octahedra from a Keggin anion $[PW_{12}O_{40}]^{3-}$. $[PW_9O_{34}]^{9-}$ still retains a large size and a high negative charge and possesses a large active gap so that the rare earth or transition metal can be easily captured constructing sandwich-type polyoxometalates. Moreover, these captured metals can be modified by organic ligands. Since Weakley *et al.* had discovered the first inorganic salt $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in 1973 [2], a number of hybrid species based on $[M_4(PW_9O_{34})_2]^{n-}$ (M = Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, *etc.*) building blocks have been consecutively reported [3 – 9].

Organic components are usually introduced into polyoxometalate systems as charge-compensating or space-filling constituents like in $[H_2en][Ni(en)_2]_2[\{(\alpha\text{-}B\text{-}PW_9O_{34})_2Ni_4(H_2O)_2\}\{Ni(en)_2(H_2O)\}_2]\cdot 5H_2O$ (en = ethylenediamine) [7]. Organic components attached to a transition metal as peripheral moieties or as complex bridging units can also act as ligands, an example being $[Zn(enMe)_2(H_2O)]_2\{[Zn(enMe)_2]_2[Zn_4(HenMe)_2(PW_9O_{34})_2]\}\cdot 8H_2O$ [6]. In addition, organic components have been introduced as ligands directly coordinated to the metal oxide substructure, as found in $\{[Ni(dap)_2(H_2O)]_2[Ni(dap)_2]_2[Ni_4(Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]\}\cdot H_2O$ (dap = 1,2-diaminopropane) [9]. It is very common to introduce organic ligands into polyoxometalates according to the first two aspects mentioned above. However, in previously reported compounds, most of the organic ligands were ethylenediamine, *N*,*N*-dimethylformamide, 2, 2′-bipyridine or 4,4′-bipyridine, while sandwich-type polyoxometalates associated with 1,3-diaminopropane have not been published. Herein we report a sandwich-type tungstophosphate, $(1,3\text{-}H_2dap)_2H_4[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]\cdot 3H_2O$ (1,3-dap = 1,3-diaminopropane).

Experimental Section

General

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H, N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The infrared spectrum was recorded from a KBr pellet on a Nicolet 170SXFT-IR spectrometer in the range of 400 – 4000 cm^{-1}. The UV spectrum was obtained on a Shimazu UV-250 spectrometer in the range 190 – 400 nm. TG measurements were performed on a Perkin-Elmer7 thermal analyzer in flowing nitrogen gas with a heating rate of 10 °C min^{-1}

Synthesis of
*(1,3-H_2dap)$_2$$H_4$[$Co_4$(1,3-Hdap)$_2$($\alpha$-B-$PW_9O_{34}$)$_2$]·3$H_2$O (**1**)*

A mixture of $Na_2WO_4 \cdot 2H_2O$ (1.0 g, 3.2 mmol), NaH_2PO_4 (0.15 g, 1.0 mmol), $CoCl_2 \cdot 6H_2O$ (0.10 g, 0.42 mmol), $Co(Ac)_2 \cdot 4H_2O$ (0.12 g, 0.48 mmol), 1,3-dap (0.06 g, 0.8 mmol), and H_2O (20 mL) was sealed in a Teflon-lined stainless-steel reactor and heated at 160 °C for 4 d with a starting pH of 4 adjusted with hydrochloric acid (6 mol L^{-1}). After cooling slowly to room temperature during about 24 h, red crystals were obtained, filtered, washed several times with distilled water, and dried in air (15.6% yield based on W). – Elemental analysis: calcd. C 2.86, H 0.92, N 2.22; found C 3.00, H 1.26, N 2.41.

Crystal structure determination

The data collection was made on a Bruker SMART APEX CCD area-detector diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293 (2) K. The intensities were corrected for Lorentz and polarization effects and empirically for absorption. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques on F^2 using the SHELX-97

Table 1. Crystallographic data for (H_2dap)$_2$$H_4$[$Co_4$(Hdap)$_2$($\alpha$-B-$PW_9O_{34}$)$_2$]·3$H_2$O (**1**).

Molecular formula	$C_{12}H_{46}Co_4N_8O_{71}P_2W_{18}$
M_r	5045.53
Crystal size, mm^3	0.18 × 0.21 × 0.23
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	12.004(3)
b, Å	20.015(4)
c, Å	19.407(4)
β, deg	105.510(4)
V, Å^3	4492.9(17)
Z	2
$D_{calcd.}$, g cm^{-3}	3.73
μ(MoK_α), mm^{-1}	23.8
F(000), e	4424
Refl. measured / unique / R_{int}	22643 / 7894 / 0.0576
Param. Refined	535
$R1$ / $wR2$ [$I > 2\sigma(I)$][a]	0.0432 / 0.1020
$R1$ / $wR2$ (all data)[a]	0.0640 / 0.1086
GoF (F^2)[b]	1.026
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	2.30 / −2.08

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$; [b] GoF = $[\Sigma w(F_o^2-F_c^2)^2/(n_{obs}-n_{param})]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) of **1**[a].

P(1)–O(34)	1.524(10)	P(1)–O(31)	1.545(10)
P(1)–O(33)	1.536(10)	P(1)–O(32)	1.551(10)
Co(1)–O(18)	2.025(10)	Co(1)–O(25)#1	2.126(10)
Co(1)–O(10)	2.045(10)	Co(1)–N(1)	2.146(13)
Co(1)–O(28)#1	2.118(10)	Co(1)–O(34)	2.250(10)
Co(2)–O(30)#1	2.013(9)	Co(2)–O(28)#1	2.085(10)
Co(2)–O(21)	2.022(10)	Co(2)–O(34)	2.221(9)
Co(2)–O(25)	2.073(11)	Co(2)–O(34)#1	2.238(10)
W(1)–O(1)	1.698(10)	W(2)–O(2)	1.703(10)
W(3)–O(3)	1.712(11)	W(4)–O(4)	1.714(10)
W(5)–O(5)	1.720(10)	W(6)–O(6)	1.704(10)
W(7)–O(7)	1.701(11)	W(8)–O(8)	1.703(11)
W(9)–O(9)	1.717(10)		
O(34)–P(1)–O(33)	111.4(5)	O(34)–P(1)–O(32)	110.1(5)
O(34)–P(1)–O(31)	111.5(5)	O(33)–P(1)–O(32)	108.5(6)
O(33)–P(1)–O(31)	107.8(5)	O(31)–P(1)–O(32)	107.3(5)
O(18)–Co(1)–O(10)	94.3(4)	O(10)–Co(1)–O(25)#1	90.0(4)
O(18)–Co(1)–O(28)#1	91.1(4)	O(28)#1–Co(1)–O(25)#1	83.1(4)
O(10)–Co(1)–O(28)#1	168.7(4)	O(18)–Co(1)–N(1)	88.2(5)
O(18)–Co(1)–O(25)#1	169.0(4)	O(10)–Co(1)–N(1)	
O(28)#1–Co(1)–N(1)	97.9(5)	O(18)–Co(1)–O(34)	
O(25)#1–Co(1)–N(1)	101.8(5)	O(10)–Co(1)–O(34)	
O(28)#1–Co(1)–O(34)	82.6(4)	N(1)–Co(1)–O(34)	
O(25)#1–Co(1)–O(34)	82.0(4)	O(30)#1–Co(2)–O(21)	
O(30)#1–Co(2)–O(25)	91.8(4)	O(30)#1–Co(2)–O(28)#1	
O(21)–Co(2)–O(25)	97.9(4)	O(21)–Co(2)–O(28)#1	
O(25)–Co(2)–O(28)#1	167.7(4)	O(25)–Co(2)–O(34)	
O(30)#1–Co(2)–O(34)	175.7(4)	O(28)#1–Co(2)–O(34)	
O(21)–Co(2)–O(34)	89.4(4)	O(30)#1–Co(2)–O(34)#1	
O(21)–Co(2)–O(34)#1	175.2(4)	O(28)#1–Co(2)–O(34)#1	
O(25)–Co(2)–O(34)#1	83.5(4)	O(34)–Co(2)–O(34)#1	

[a] Symmetry transformation used to generate equivalent atoms: #1 –x, –y, –z+1.

suite of programs [10]. All non-hydrogen atoms were refined anisotropically. Crystallographic data are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 871204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Crystal structure of $(1,3\text{-}H_2dap)_2H_4[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]\cdot 3H_2O$

As shown in Fig. 1, **1** is composed of three isolated water molecules, two diprotonated $1,3\text{-}H_2dap^{2+}$ cations and a sandwich-type polyanion $[Co_4(1,3\text{-}Hdap)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]^{8-}$ lying across an inversion center. Two $[\alpha\text{-}B\text{-}PW_9O_{34}]^{9-}$ anions are linked by a rhomb-like $Co_4O_{14}(1,3\text{-}dap)_2$ cluster in a centrosymmetric arrangement. Additionally, in the $Co_4O_{14}(1,3\text{-}dap)_2$ unit, Co(1) and Co(1A) ions are each coordinated by a nitrogen atom from a $1,3\text{-}Hdap^+$ cation (Fig. 2). The four Co atoms are all in a distorted octahedral geometry, with bond lengths of Co(1)–O 2.025(10) ∼ 2.250(10), Co(1)–N(1) 2.146(13) and Co(2)–O 2.013(9) ∼ 2.238(10) Å. The Co···Co separations in the $Co_4O_{14}(1,3\text{-}dap)_2$ moiety are: Co(1)···Co(1A) 5.598, Co(2)···Co(2A) 3.259 Å. Such a sandwich-type polyoxometalate in combination with 1,3-diaminopropane have not been seen previously, except for an isomeric 1,2-diaminopropane case. The reason might be the larger distance between the two terminal nitrogen atoms, which are more difficult to chelate to a metal atom. Compound **1** has two diprotonated dap cations acting as counter-ions, which interact with the $[PW_9O_{34}]^{9-}$ anion *via* hydrogen bonds leading to a three-dimensional framework (Fig. 3). PLATON [11] calculations indicate that the framework contains large solvent-accessible voids of 443 $Å^3$, so that it may act as a material for gas absorption. Regrettingly, the obtained yield is low so far thus preventing that gas absorption could be studied experimentally. Therefore, we will attempt to adjust the synthetic conditions and improve the yield in the future.

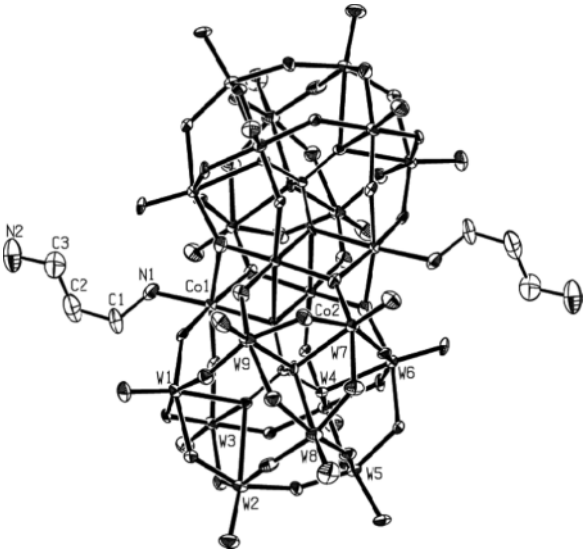

Fig. 1. Molecular unit of **1** showing the atom numbering scheme adopted. Displacement ellipsoids are drawn at the 30% probability level. Isolated water molecules and protonized dap ions are deleted for clarity.

IR spectrum of ***1***

The IR spectrum of **1** exhibits absorption peaks at 1494 and 1616 cm^{-1} associated with the 1,3-dap ligands. The band at 1034 cm^{-1} is characteristic of P–O stretching vibrations. The peak at 935 cm^{-1} corresponds to $\nu(W\text{–}O_t)$, that at 878 cm^{-1} is attributed to $\nu(W\text{–}O_b)$, and that at 735 cm^{-1} to $\nu(W\text{–}O_c)$. The results are in agreement with those in the literature [9].

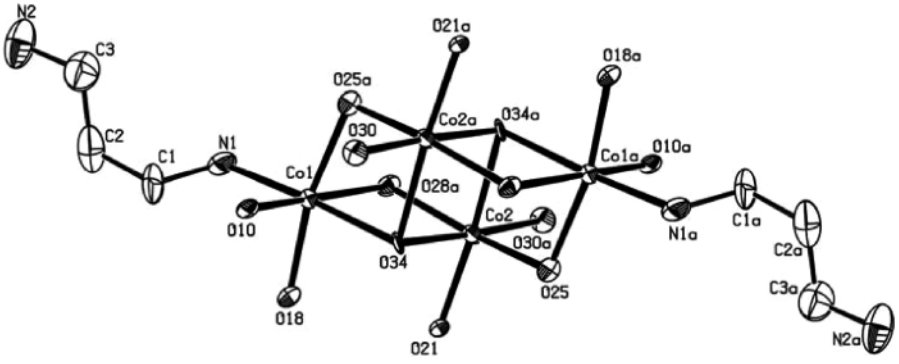

Fig. 2. View of the central $Co_4O_{14}(dap)_2$ unit of **1**.

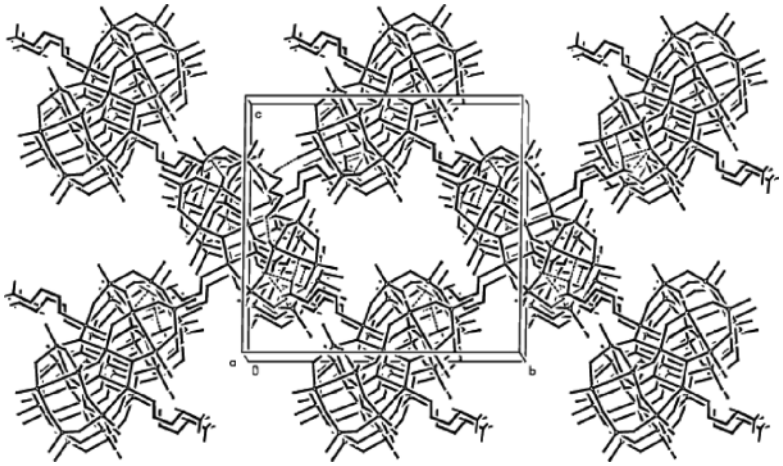

Fig. 3. The three-dimensional framework of **1** as viewed along the [100] direction.

*UV spectrum of **1***

The UV spectrum of **1** exhibits two intense absorption peaks at 206 and 260 nm corresponding to charge transfer $O_a \rightarrow W$ and $O_{b,c} \rightarrow W$, which is analogous to the two most intense absorption peaks for the Keggin anion [12], but the two bands are slightly shifted to the ultraviolet region.

*Thermal properties of **1***

The result of a thermo-gravimetric analysis (TGA) carried out under N_2 atmosphere shows two weight loss steps. The first rapid weight loss step of 2.5 % from room temperature to 150 °C corresponds to the loss of water caused by the humidification of the sample. A further weight loss of 9.0 % from 150 to 800 °C is due to the decomposition of the organic parts.

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