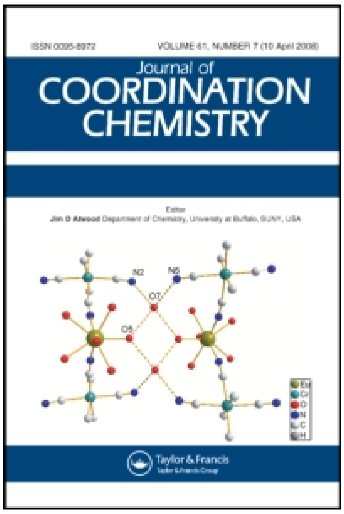

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Synthesis, characterization and crystal structure of a 1D heteropolytungstate $[4,4'\text{-bipyH}_2]_2[4,4'\text{-bipyH}][PCoW_{11}O_{39}]\cdot H_2O$

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Synthesis, characterization and crystal structure of a 1D heteropolytungstate $[4,4'\text{-bipyH}_2]_2$ $[4,4'\text{-bipyH}][\text{PCoW}_{11}\text{O}_{39}]\cdot\text{H}_2\text{O}$

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A chain-like structure compound $[4,4'\text{-bipyH}_2]_2[4,4'\text{-bipyH}][\text{PCoW}_{11}\text{O}_{39}]\cdot\text{H}_2\text{O}$, in which lacunary polyoxoanions are joined by a Co–O–W bridge, was prepared through the hydrothermal method and characterized by IR, and X-ray crystallography. The title compound crystallizes in a monoclinic lattice, $P2_1/n$ space group, with $a = 13.643$ (3), $b = 27.052(5)$, $c = 15.180(3)$ Å, $\beta = 100.63(3)^\circ$, $V = 5506.2(19)$ Å^3, $Z = 4$, $R_1 = 0.0792$, $wR_2 = 0.1532$. Cobalt-substituted Keggin-type subunits are connected via Co–O–W bridges to form a 1D, chainlike, polymolecular Keggin POM. TG-DTA analysis indicates the title compound decomposes at 553°C.

Keywords: Polyoxometalates; Keggin structure; Crystal structure; Monovalant derivative

1. Introduction

Hybrid inorganic–orangic materials have attracted increasing interest in recent years, due to the potential, perceived and realized, applications in many areas, especially catalysis, separations, ion exchange, imaging, sorption, medicine, functional materials and molecular electronics in addition to optical, electrical, magnetic and supraconductive fields [1–20]. Polyoxometalates have recently been employed as versatile inorganic building blocks for the construction of molecular-based materials with various transition metal complexes [21]. The monovacant, lacunary polyoxoanion $[\text{XW}_{11}\text{O}_{39}]^{n-}$ ($\text{X} = \text{B}^{\text{III}}$, P^{V}, Si^{IV}, Ge^{IV}, As^{V}, etc.) is obtained by removal of one $[\text{W(VI)=O}]^{4+}$ group from the saturated Keggin-type $[\text{XW}_{12}\text{O}_{40}]^{-n+4}$ anion and respresents a unique class of ligand [22]. Transition metal substituted polyoxometalates based on the monovacant, lacunary polyoxoanion possess many interesting structures [23–29].

Here, we report the hydrothermal synthesis and single crystal structure analysis of a heteropolytungstate showing a chain-like structure: $[4,4'\text{-bipyH}_2]_2[4,4'\text{-bipyH}]$ $[\text{PCoW}_{11}\text{O}_{39}]\cdot\text{H}_2\text{O}$, in which lacunary polyoxoanions are joined by Co–O–W bridges.

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2. Experimental section

2.1. *General remarks*

All chemicals used for synthesis were of reagent grade and used without further purification.

2.2. *Synthesis of the title compound*

Compound **1** was prepared by the hydrothermal method from a mixture of $Co(CH_3COO)_2 \cdot 4H_2O$, $CoCl_2 \cdot 2H_2O$, TiO_2, $Na_2WO_4 \cdot 2H_2O$, 4,4′-bipyridine, and H_2O in the molar ratio of 1 : 1 : 11 : 1 : 1.1 : 4167 heated in a Teflon-lined acid digestion bomb inside a programmable electric furnace at 160°C for four days with starting pH = 3.97 adjusted by phosphoric acid (85%). After cooling the autoclave to room temperature for two days, black crystals were obtained. Elemental analysis: Calcd: C, 11.27; H, 0.98; N, 2.63%. Found: C, 11.32; H, 1.01; N, 2.61%.

2.3. *Physical measurements*

C, H and N elemental analyses were preformed with a Perkin-Elmer 240C elemental analyzer. Thermogravimetric measurements were performed on an Exstar 6000 thermal analytical system in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$. The IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrometer ($4000–400\,cm^{-1}$).

2.4. *Crystal structure determination*

A black polyhedral single crystal with dimension $0.18 \times 0.16 \times 0.13\,mm^3$ was mounted on a glass fiber for intensity data collection on Rigaku-RAXIS-IV image plate area detector equipped with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range of $1.53 < \theta < 25.00^{\circ}$. A total of 15,201 independent reflections were collected in the range of $-15 \leq h \leq 16$, $-32 \leq k \leq 32$, $-18 \leq l \leq 0$, of which all observed reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement after the *Lp* corrections. The structures were solved by direct methods and refined using full-matrix least-squares calculations with anistropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were performed using the SHELXTL-97 program [30]. Crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Structure description*

The asymmetric unit of the title compound (figure 1) consists of a monosubtituted Keggin structure, $[PCoW_{11}O_{39}]^{5-}$, two diprotonated and one monoprotonated 4,4′-bipyridine molecules (according to an empirical bond valence calculation [30],

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{30}H_{31}CoN_6O_{40}W_{11}$
Fw	3227.86
Temperature (K)	293(2)
Space group	$P2_1/n$
Crystal system (nm, °)	Monoclinic
a	1.3643(3)
b	2.7052(5)
c	1.5180(3)
β	100.63(3)
Volume (nm^3),	5.506(19)
Z	4
D_c ($Mg\,m^{-3}$)	3.893
μ (mm^{-1})	23.126
Reflns collected	15201
Indep. reflns	8213($R_{int} = 0.0863$)
Params	811
GOF on F^2	1.114
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0792$, $wR_2 = 0.1532$
R indices (all data)	$R_1 = 0.1050$, $wR_2 = 0.1636$

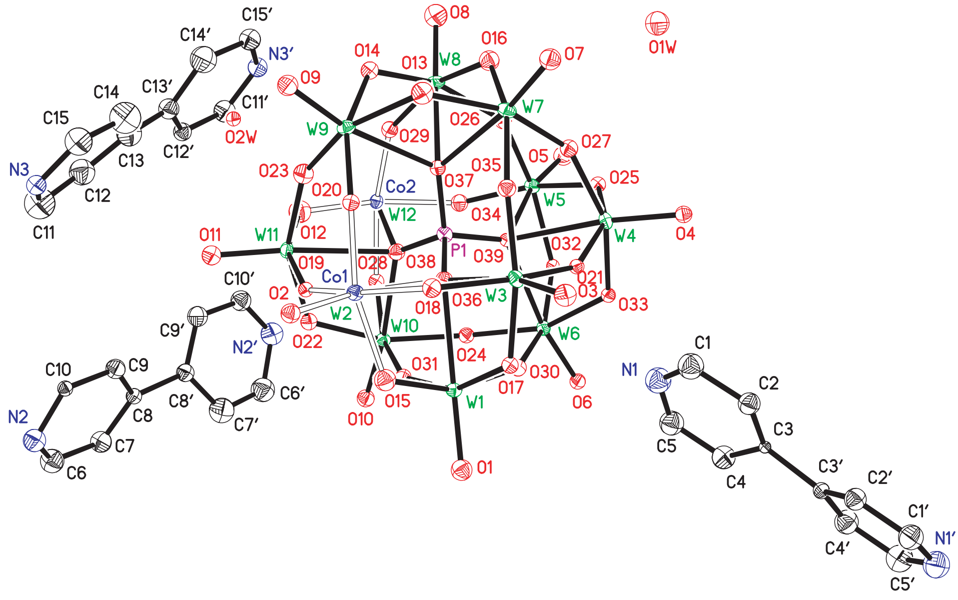

Figure 1. An ORTEP view of the title compound.

bond valence values for N(1′), N(1) ~ N(3′), N(3) are 2.540, 2.831, 2.748, 2.611, 2.540, 2.744, respectively, show that there are five protonated N atoms.). The $[PCoW_{11}O_{39}]^{5-}$ fragment derives from the well-known Keggin $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ [24] anion formed by a central PO_4 tetrahedron surrounded in an ideal Cs symmetry by four, vertex-sharing W_3O_{13} trimers of edge-sharing WO_6 octahedra, the W atoms forming a cubic-octahedral framework. These W_3O_{13} trimers are composed of three

WO_6 octahedra sharing edges via W–O_c–W connections, and linked to the encapsulated P atoms via a W–O_a–P bond. The W_3O_{13} groups are connected to each other by vertices via O_b atoms. A terminal oxygen O_d completes the coordination sphere of the W centers. In the fragment $[PCoW_{11}O_{39}]^{5-}$, the mono-lacunary species is obtained by removal of a $[W{=}O_d]^{4+}$ group. The P atom resides in the center of the PO_4 tetrahedron, which has been somewhat deformed from removal of one $[W{=}O_d]^{4+}$ group and the complete incorporation of a Co(III) into the monovacant polyoxometalate framework. In comparison with the well-known Keggin structure $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ [24], the P–O bond distances in the PO_4 polyhedron vary from 1.531(19) to 1.569(18) Å with av. 1.552 Å, which is in good agreement with the literature, and the O–P–O bond angles are in the range of 107.8(10)–112.3 (10)°. In addition, the oxygen atoms in the fragment of $[PCoW_{11}O_{39}]^{5-}$ can be classified into five types, O_a, $O_{b(c)}$, O_d, and O_e according to their coordination numbers and types of coordination atoms. O_a is bound to the central P atom and three W atoms [d(W–O_a) 2.374(19)–2.454(16) Å, av. 2.424 Å], which is 0.016 Å shorter than the literature, while, $O_{b(c)}$ is shared by two W atoms (O_b atom is shared by two W atoms of different W_3O_{13} clusters, O_c atom is shared by two W atoms inside each W_3O_{13} unit [d(W–$O_{b(c)}$) 1.847(18)–1.987(16) Å]), O_d is the terminal oxygen atom bonded to only one W atom [d(W–O_d) 1.673(18)–1.73(2) Å], O_e is shared by a W atom and a Co atom [d(W–O_e) 1.834(18)–1.845(18) Å] (table 2).

Each Keggin unit shows a preference for Co(1) at the W(2) octahedron and the Co(2) at the W(12) octahedron with the population factor equal to 50%, which means the bridge between the Keggin units is always of Co–O–W type (Co(2)–O(2)–W(2)=160°) [27]. The bond lengths of W(2)–O and W(12)–O are in the range of 1.834(18) ~ 2.387(17) and 1.845(18) ~ 2.413(18) Å with mean bond distances 2.001 and 2.002 Å, respectively. These units are connected via Co–O–W bridges to form a 1D chainlike polymolecular Keggin POM. In addition, there are some protonated 4,4′-bipyridine molecules around the chain figure 2.

3.2. *IR spectra*

The IR spectrum of the title compound using KBr pellet exhibits absorptions: 484(m), 513(m), 703(s), 789(s), 865(m), 893(s), 955(s), 1058(s), 1076(m), 1396(s), 1457(s), 1492(s), 1626(s). Compared with the literature [24], the IR spectrum of the title compound using KBr pellet exhibits distinctive differences: the vibration peak of the W=O_d bonds have a red shift from 986 to 955 cm^{-1}; the W–O_b bonds have a blue shift from 890 to 893 cm^{-1}, too; and the W–O_c bonds have a red shift from 810 to 789 cm^{-1}. The results show that the polyoxoanion is distorted due to the monsubstituted polyanion with the Co atom. Bands at 1625, 1492, 1457 cm^{-1} are assigned to characteristic vibrational modes of 2,2′-bipyridine, 1625 and 1457 cm^{-1} are attributed to C=N and C–N stretches.

3.3. *Electron paramagnetic resonance spectra*

The EPR spectra of the title compound show that the Co atom is in the low spin state [32]. The nine hyperfine splitting signals of $g = 2.11$, 2.09, 2.07, 2.05, 2.02, 1.98, 1.95,

Table 2. Main bond lengths (Å) and main angles (°) for the title compound.

W(1)–O(1)	1.73(2)	W(1)–O(17)	1.922(17)
W(1)–O(31)	1.883(17)	W(1)–O(30)	1.922(18)
W(1)–O(15)	1.90(2)	W(1)–O(36)	2.399(19)
W(2)–O(2)	1.834(18)	W(2)–O(18)	1.987(18)
W(2)–O(20)	1.887(18)	W(2)–O(15)	2.00(2)
W(2)–O(19)	1.940(16)	W(2)–O(36)	2.387(17)
W(3)–O(3)	1.700(2)	W(3)–O(17)	1.938(18)
W(3)–O(18)	1.884(18)	W(3)–O(32)	1.990(16)
W(3)–O(35)	1.888(18)	W(3)–O(36)	2.430(17)
W(4)–O(27)	1.919(19)	W(4)–O(4)	1.732(17)
W(4)–O(33)	1.926(17)	W(4)–O(32)	1.870(16)
W(4)–O(39)	2.407(16)	W(4)–O(25)	1.862(17)
W(5)–O(5)	1.70(2)	W(5)–O(21)	1.950(17)
W(5)–O(34)	1.854(18)	W(5)–O(25)	1.961(17)
W(5)–O(26)	1.913(19)	W(5)–O(39)	2.454(16)
W(6)–O(6)	1.700(18)	W(6)–O(30)	1.926(17)
W(6)–O(24)	1.886(17)	W(6)–O(33)	1.926(16)
W(6)–O(21)	1.897(16)	W(6)–O(39)	2.440(17)
W(7)–O(7)	1.70(2)	W(7)–O(16)	1.92(19)
W(7)–O(27)	1.885(18)	W(7)–O(35)	1.937(18)
W(7)–O(13)	1.90(2)	W(7)–O(37)	2.428(17)
W(8)–O(8)	1.73(2)	W(8)–O(14)	1.911(18)
W(8)–O(29)	1.847(18)	W(8)–O(16)	1.937(19)
W(8)–O(26)	1.912(18)	W(8)–O(37)	2.438(17)
W(9)–O(9)	1.67(2)	W(9)–O(14)	1.977(18)
W(9)–O(23)	1.88(2)	W(9)–O(13)	1.98(2)
W(9)–O(20)	1.886(17)	W(9)–O(37)	2.430(17)
W(10)–O(10)	1.707(19)	W(10)–O(24)	1.942(17)
W(10)–O(22)	1.886(18)	W(10)–O(31)	1.981(17)
W(10)–O(28)	1.896(18)	W(10)–O(38)	2.374(19)
W(11)–O(11)	1.673(19)	W(11)–O(22)	1.940(19)
W(11)–O(12)	1.88(2)	W(11)–O(23)	1.94(2)
W(11)–O(19)	1.885(16)	W(11)–O(38)	2.488(18)
W(12)–O(2)#1	1.845(18)	W(12)–O(38)	2.413(18)
W(12)–O(29)	1.933(19)	P(1)–O(38)	1.531(19)
W(12)–O(28)	1.955(18)	P(1)–O(37)	1.550(19)
W(12)–O(12)	1.98(2)	P(1)–O(39)	1.559(17)
W(12)–O(34)	1.975(18)	P(1)–O(36)	1.569(18)
O(2)–W(12)#2	1.845(18)	O(2)–Co(2)#2	1.845(18)
O(38)–P(1)–O(39)	109.1(10)	O(2)–W(2)–O(20)	101.0(8)
O(37)–P(1)–O(39)	107.8(10)	O(2)–W(2)–O(19)	99.7(7)
O(38)–P(1)–O(36)	109.5(10)	O(20)–W(2)–O(19)	86.7(7)
O(37)–P(1)–O(36)	109.8(10)	O(2)–W(2)–O(18)	99.5(7)
O(39)–P(1)–O(36)	108.3(10)	O(20)–W(2)–O(18)	89.2(8)
O(38)–P(1)–O(37)	112.3(10)	O(19)–W(2)–O(18)	160.6(7)
O(18)–W(2)–O(15)	86.1(8)	O(2)–W(2)–O(15)	99.2(8)
O(2)–W(2)–O(36)	170.7(7)	O(20)–W(2)–O(36)	85.8(7)
O(19)–W(2)–O(36)	86.7(6)	O(18)–W(2)–O(36)	74.1(7)
O(15)–W(2)–O(36)	73.9(7)	O(20)–W(2)–O(15)	159.8(8)
O(19)–W(2)–O(15)	91.3(8)	O(28)–W(12)–O(12)	88.7(9)
O(2)#1–W(12)–O(29)	101.3(8)	O(2)#1–W(12)–O(34)	100.0(8)
O(2)#1–W(12)–O(28)	97.0(8)	O(29)–W(12)–O(34)	85.0(8)
O(29)–W(12)–O(28)	161.2(7)	O(28)–W(12)–O(34)	87.5(7)
O(2)#1–W(12)–O(12)	100.8(9)	O(12)–W(12)–O(34)	159.2(8)
O(29)–W(12)–O(12)	92.1(9)	O(2)#1–W(12)–O(38)	170.2(7)
O(29)–W(12)–O(38)	87.7(7)	O(12)–W(12)–O(38)	74.7(8)
O(28)–W(12)–O(38)	74.4(7)	O(34)–W(12)–O(38)	84.6(7)

#1: x + 1/2, −y + 1/2, z + 1/2; #2: x−1/2, −y + 1/2, z−1/2.

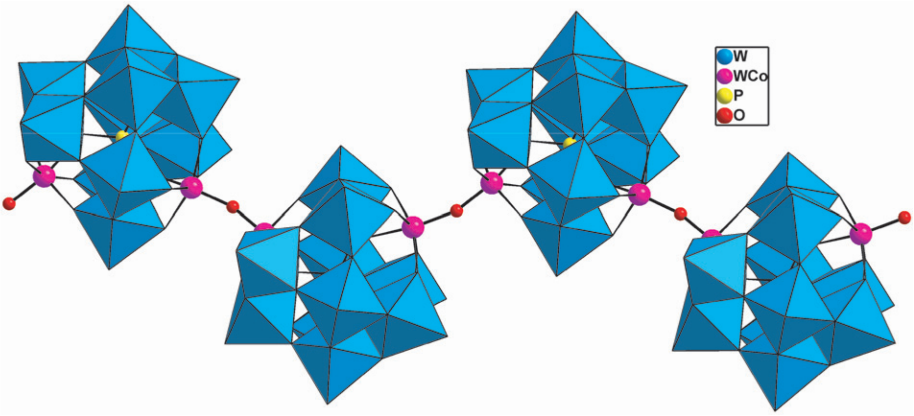

Figure 2. 1D chain-like structure of the title compound.

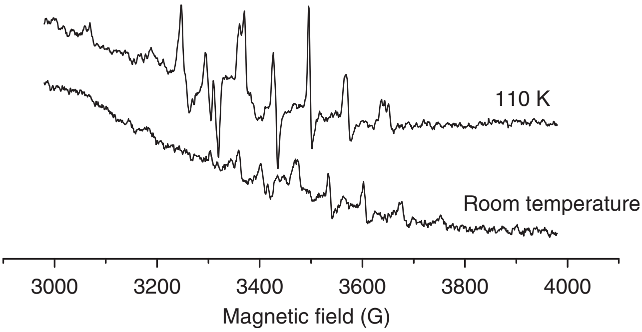

Figure 3. Room temperature (300 K) ESR spectrum of the title compound using $\nu = 9.7745$ GHz, $g = 2.11$–1.90, and low temperature (110 K) using $\nu = 9.4849$ GHz, $g = 2.08$–1.86.

1.94, 1.90 at room temperature (300 K) and $g = 2.08$, 2.06, 2.05, 2.00, 1.98, 1.94, 1.92, 1.90, 1.86 at low temperature (110 K), concentrated around 2.00, are attributed to low spin Co(III). Compared with the signal at low temperature, the signal at room temperature grows weaker (figure 3).

3.4. *Thermal analysis*

The TG curves of compound **2** exhibited one distinct step in the whole progress. The whole weight loss (15.50%) in the range of 15 ~ 631°C corresponds to the loss of lattice water and 4,4′-bipy molecules, in good agreement with the calculated value (15.45%). The DTG curves show that one very strong exothermal peak at 553°C probably results from the oxidation and combustion of organic groups and the framework decomposition of the title polyoxoanion (figure 4).

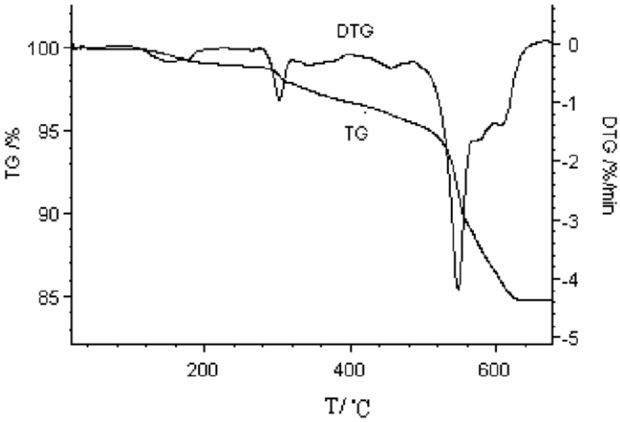

Figure 4. Thermal analytical curves (TG-DTG) of the title compound in flowing N_2 with a heating rate of 20°C min^{-1} at the temperature scope of 15 and 700°C.

Supplementary material

Crystallographic data for structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Center with the deposited numbers CCDC Number 295616. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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