

A Heterometallic MOC Assembled from Cobalt-bisupported Keggin Subunits

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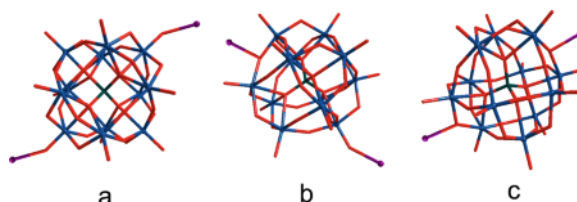
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A heterometallic metal-organic complex (MOC), $\text{K}[\text{Co}(1,10\text{-phen})_2(\text{H}_2\text{O})_2]_2[\text{BW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$ (phen = 1,10-phenanthroline) (**1**), has been synthesized hydrothermally and characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. The complex exhibits cobalt-bisupported tungstoborate units and potassium cations. The luminescence of the title complex has been investigated.

Key words: Polyoxometalate, Tungstoborates, Cobalt

Introduction

The design and assembly of metal-organic complexes (MOCs) have attracted considerable attention, because of their diverse topologies and potential applications in areas such as catalysis and materials science [1–6]. Polyoxometalates (POMs), as a unique class of inorganic metal oxide clusters, have been regarded as excellent candidates to obtain MOCs due to their controllable shapes and sizes, and their high negative charges [7–18]. As important members of the POM family, the classical Keggin polyanions have been extensively studied [19–22]. Many Keggin polyanions have been modified by cationic metal complexes to obtain novel MOCs. The cationic metal complexes can play several roles: (i) charge compensation, (ii) covalent binding to subunits of the POM framework, and (iii) linking of polyanions into infinite extended networks. The bisupporting Keggin subunits are the most common examples [23–28], which can be roughly divided into three types regarding the coordinating oxygen atoms that connect the cationic metal complexes as shown in Scheme 1. As reported herein, we synthesized and characterized a new one-dimensional (1D) heterometallic MOC that



Scheme 1. View of the three types of bisupported Keggin subunits.

is assembled from *in-situ* formed cobalt-bisupported Keggin subunits and potassium cations: $\text{K}[\text{Co}(1,10\text{-phen})_2(\text{H}_2\text{O})_2]_2[\text{BW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$ (**1**). The structural pattern of **1** is similar to that of the compound $\text{K}[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2]_2[\text{HCoW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$ previously reported by Chen [29], but the two compounds possess different composition. The luminescence properties of compound **1** have been investigated.

Experimental

Materials and methods

All reagents were purchased commercially and used without further purification. The IR spectrum was recorded in the

range 4000–400 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets. Fluorescence spectra were recorded with a Perkin Elmer LS55 luminescence spectrometer using a 150 W xenon lamp as excitation source.

Synthesis of

$K[\text{Co}(1,10\text{-phen})_2(\text{H}_2\text{O})]_2[\text{BW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$ (**1**)

Complex **1** was prepared under hydrothermal conditions. A mixture of $\text{K}_5\text{BW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$ (0.3 g, 0.1 mmol), phen (0.04 g, 0.2 mmol), $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.58 g, 2.5 mmol), and H_2O (10 mL) was stirred for 30 min in air, and the pH was adjusted by HCl (3 M) to 2.4. Then the mixture was sealed in a 23 mL Teflon-lined stainless-steel container, which was heated to 165 °C under autogenous pressure for 6 d. After slow cooling to room temperature at a rate of 10 °C h^{-1} , saffron crystals were collected, washed with distilled water, and dried at room temperature (36% yield based on W). – Elemental analysis: $\text{C}_{48}\text{H}_{40}\text{BCo}_2\text{KN}_8\text{O}_{44}\text{W}_{12}$ (3802.70): calcd. C 15.16, H 1.06, N 2.95; found C 15.09, H 1.12, N 3.02 (%). – IR (KBr pellet): see table supplied as Supporting Information available online. See note at the end of the paper for availability.

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1**.

Empirical formula	$\text{C}_{48}\text{H}_{40}\text{BCo}_2\text{KN}_8\text{O}_{44}\text{W}_{12}$
M_r	3802.70
Crystal color, habit	saffron, block
Crystal size, mm^3	$0.22 \times 0.16 \times 0.14$
Crystal system	triclinic
Space group	$P\bar{1}$
a , Å	10.8680(7)
b , Å	13.3219(8)
c , Å	13.5855(8)
α , deg	69.509(1)
β , deg	71.608(1)
γ , deg	78.405(1)
V , Å ³	1739.28(18)
Z	1
$D_{\text{calcd.}}$, g cm^{-3}	3.63
$\mu(\text{MoK}\alpha)$, mm^{-1}	20.4
$F(000)$, e	1698.0
hkl range	$\pm 13, -16 \rightarrow 15, \pm 16$
Refl. measured / unique / R_{int}	14 876 / 8214 / 0.0313
Data / ref. parameters	6541 / 544
R_1 / wR_2 [$I > 2\sigma(I)$] ^{a,b}	0.0496 / 0.0930
R_1 / wR_2 (all data)	0.0611 / 0.0979
GoF (F^2) ^c	1.050
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	1.91 / -1.55

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

X-Ray crystallography

A single crystal of **1** was selected for X-ray diffraction analysis. Data collection was performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). The data were collected at 293 K. The data processing was accomplished with the program PROCESS-AUTO. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 crystallographic software package [30]. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The phen hydrogen atoms were generated geometrically. The water hydrogen atoms could not be refined but were included in the structure factor calculations. The crystal data and data collection and structure refinement details are summarized in Table 1.

CCDC 783480 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

Description of the structure of **1**

Single-crystal X-ray diffraction analysis has revealed that **1** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $Z = 1$. It consists of $[\text{BW}_{12}\text{O}_{40}]^{5-}$ anions (abbreviated as BW_{12}), Co^{2+} cations and phen ligands (Fig. 1). The BW_{12} POM shows the well-known α -Keggin-type structure, consisting of a central BO_4 tetrahedron corner-sharing with four triad $\{\text{W}_3\text{O}_{13}\}$ clusters. The W–O distances vary between 1.670 and 2.460 Å. All these bond lengths are within the normal ranges and in close agreement with those described in the literature [31, 32]. The selected bond lengths and

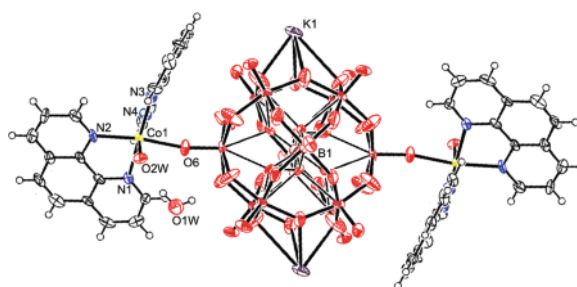


Fig. 1. ORTEP drawing of the formula unit in **1** including the bridging K atoms exhibiting crystallographic inversion symmetry (displacement ellipsoids set at 50% probability; H atoms as spheres with arbitrary radii).

angles of **1** are listed in Table 2. Each Co^{2+} ion is hexacoordinated by two oxygen atoms from BW_{12} anions, four nitrogen atoms from two phen ligands and one water molecule. The Co center adopts an elongated octa-

hedral geometry with bond lengths and angles in the range of 2.076–2.136 Å for Co–O, 2.109–2.130 Å for Co–N, 87.2° for O–Co–O, and 78.8–102.7° for N–Co–N.

Co(1)–O(2W)	2.076(11)	Co(1)–O(6)	2.126(11)
Co(1)–N(1)	2.130(13)	Co(1)–N(2)	2.109(13)
Co(1)–N(3)	2.124(12)	Co(1)–N(4)	2.129(14)
O(2W)–Co(1)–N(2)	93.9(5)	O(2W)–Co(1)–O(6)	87.2(4)
N(2)–Co(1)–N(4)	95.1(5)	O(6)–Co(1)–N(4)	85.0(5)
O(19)#1–W(1)–K(1)#2	43.0(4)	O(11)–W(1)–K(1)#2	89.9(4)

Table 2. Selected bond lengths (Å) and angles (deg) for **1**^a.

^a Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+1$; #2 $x-1, y, z$.

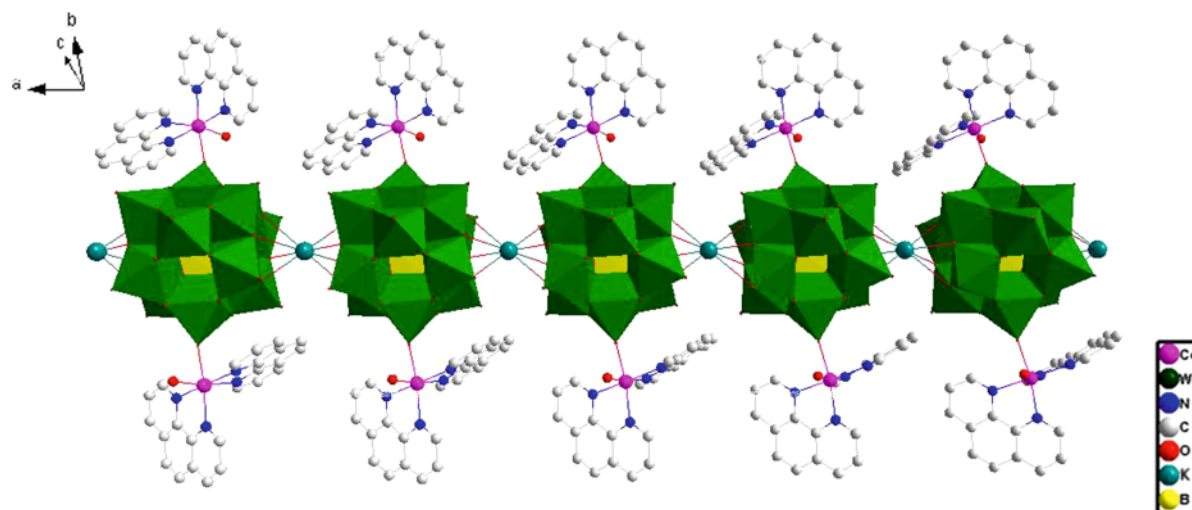


Fig. 2. View of the chain formed by cobalt-bisupported tungstoborates and potassium cations.

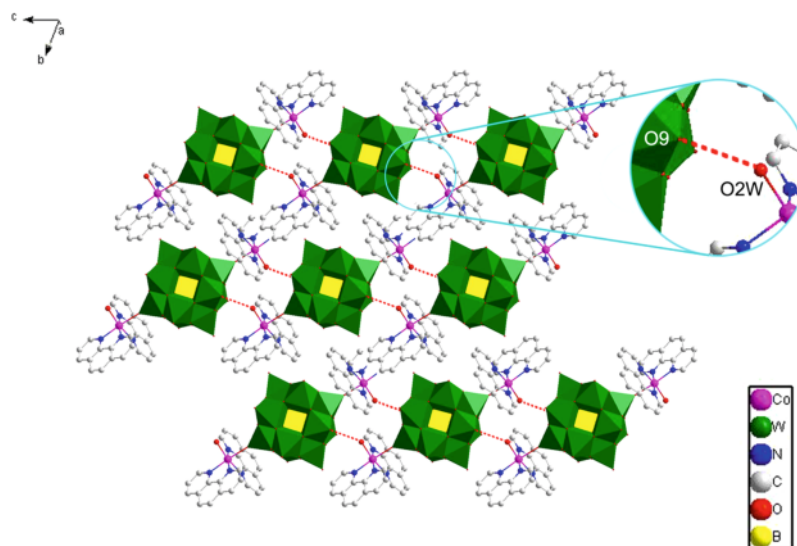


Fig. 3. Hydrogen bonding interactions in the layer structure of **1**. H bonds are shown as broken lines.

Each BW_{12} anion is linked to two $\text{phen}_2\text{Co}^{2+}$ cations *via* its two terminal oxygen atoms to form a cobalt-bisupporting subunit. Each cobalt-bisupported subunit has contacts to two potassium cations *via* 2×4 bridging oxygen atoms of its BW_{12} anion to form a chain along the *a* axis (Fig. 2). These chains are connected by hydrogen bonding between the coordinated water molecules and oxygen atoms of the Keggin anion [$(\text{O}(8) \cdots \text{O}2\text{W} = 2.826 \text{ \AA})$] to form a layer on the *ab* plane (Fig. 3).

IR spectrum

The IR spectrum of **1** exhibits four strong bands at 954 , 897 , 823 , and 725 cm^{-1} , attributed to $\nu(\text{W}=\text{O}_a)$, $\nu(\text{W}-\text{O}_b)$, $\nu(\text{W}-\text{O}_c)$, and $\nu(\text{W}-\text{O}_d)$ of the BW_{12} anions, respectively [33]. The bands at 1625 , 1516 and 1426 cm^{-1} are associated with the phen ligands. The broad band at 3392 cm^{-1} is associated with the water molecules [34].

Luminescence properties

Recently, inorganic-organic hybrid coordination polymers, especially those comprising a d^{10} metal center and aromatic systems have been intensively investigated for attractive fluorescence properties and potential applications as new luminescent materials [35, 36]. In this work, the photoluminescence of **1** was investigated in the solid state at room temperature. Upon excitation at 215 nm , **1** shows strong emission at 375 nm (Fig. 4). The emission peak of free phen is located at 383 nm .

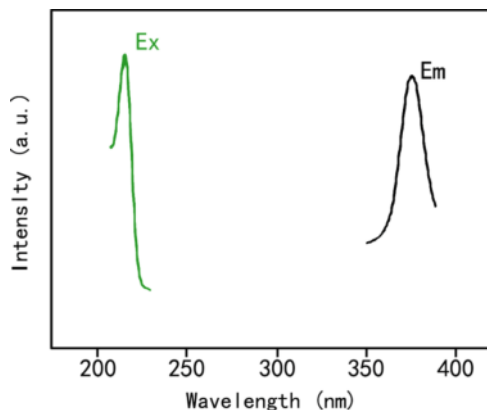


Fig. 4. Luminescence of **1** in the solid state at room temperature (Ex = excitation, Em = emission).

Conclusion

In summary, a new heterometallic metal-organic complex has been synthesized hydrothermally. It shows a chain structure built of cobalt-bisupported tungstoborates anions and potassium cations.

Supporting information

The IR spectrum of **1** in tabular form is given as Supporting Information available online (DOI: [10.5560/ZNB.2013-3124](https://doi.org/10.5560/ZNB.2013-3124)).

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