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Synthesis, structures and properties of new hybrid solids containing ruthenium complexes and polyoxometalates

Bangbo Yan *, Samantha A. Hodsdon, Yan-Fen Li, Christopher N. Carmichael, Yan Cao, Wei-Ping Pan

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101, USA

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ABSTRACT

Two new organic–inorganic hybrid solids containing Keggin ions and ruthenium complexes have been synthesized and characterized by FT-IR, UV–vis, luminescence, X-ray, and TG analysis. In $KNa[Ru(bpy)_3]_2[H_2W_{12}O_{40}]\cdot 8H_2O$ (**1**), the $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) complex ions are located in between the infinite one-dimensional double-chains formed by adjacent Keggin anions $[H_2W_{12}O_{40}]^{6-}$ linked through $\{KO_7\}$ and $\{NaO_6\}$ polyhedra, while in $K_6[Ru(pzc)_3]_2[SiW_{12}O_{40}]\bullet 12H_2O$ (**2**), the $[Ru(pzc)_3]^-$ (pzc=pyrazine-2-carboxylate) complex anions are confined by layered networks of the $[SiW_{12}O_{40}]^{4-}$ clusters connected by potassium ions. Both compounds exhibit three-dimensional frameworks through noncovalent interactions such as hydrogen bonds and anion$\cdots\pi$ interactions. Additionally, compound 1 shows strong luminescence at 604 nm in solid state at room temperature.

1. Introduction

Polyoxometalates are attracting increasing interest as building blocks of hybrid materials due to their large variety of applications such as catalysts [1], medicine[2], optoelectronics [3] and magnetism [4]. In the last decade, the chemistry of organic–inorganic hybrid solids containing polyoxotungstates has expanded rapidly [5,6]. On the other hand, ruthenium polypyridyl complexes have been extensively studied for their applications as photosensitizer in solar energy conversion and photoelectronic materials [7–10]. Recently, ruthenium heterocyclic ligand complex-based building blocks have been used for the synthesis of metal organic frameworks through the self-assembly [11]. However, the research on the interaction of polyoxotungstate anions with ruthenium complexes is rarely explored, except for a few reports on the interaction of polyoxotungstate anions with sensitizer $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) in solutions in the last few years [12–16]. The fundamental structural study on the single-phase crystalline hybrid solid materials containing both Ru complex ions and polyoxotungstate anions remains particularly challenging, although thin films containing $[Ru(bpy)_3]^{2+}$ and polyoxotungstate anions [17], or solid compounds that built from the $[Ru(bpy)_3]^{2+}$ and polyoxotungstate anion building units have been reported [18]. It is clear that coordination or covalent bonds have played a significant role in the self-assembly of solid materials. However, in recent years, noncovalent interactions such as hydrogen bonding, π–π stacking, and anion–π interactions have been recognized as important bonding forces in forming supramolecular systems or metal organic framework materials. We are interested in the synthesis and structural study of transition metal complexes connected to polyoxotungstate anions through different ways such as coordination bonds, hydrogen bonds and ionic bonds [19]. In this study, we report the synthesis and characterization of two new hybrid solids $KNa[Ru(bpy)_3]_2[H_2W_{12}O_{40}]\cdot 8H_2O$ (**1**), and $K_6[Ru(pzc)_3]_2[SiW_{12}O_{40}]\cdot 12H_2O$ (**2**) (pzc=pyrazine-2-carboxylate), in which ruthenium heterocyclic ligand complexes are confined in space formed by one-/two-dimensional networks of polyoxometalates.

2. Material and methods

The reactions were carried out under hydrothermal/solvothermal autogenous pressure conditions using 3″ × 4″ Teflon bags in Teflon-lined stainless steel autoclave reactors. All chemicals were obtained from commercial sources and used without purification. No hazards were encountered in the experimental work reported. Reagents used were purchased from Alfa Aesar and used without further purification. Ultraviolet–visible (UV–vis) diffuse reflectance spectra were obtained using a Varian Cary 100 UV–vis spectrophotometer equipped with the DRA-CA-30 diffuse reflectance accessory. The infrared spectra were recorded from 400 to 4000 cm^{-1} on a Perkin Elmer Spectrum One FTIR spectrometer using KBr pellets. The thermogravimetric data were collected on a TA Q5000 TGA

* Corresponding author. Fax: +1 270 745 5361.
E-mail address: bangbo.yan@wku.edu (B. Yan).

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instrument at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in an air atmosphere. Powder X-ray analysis was performed on an ARL Thermo X-ray Diffraction instrument, and there are good matches between simulated powder pattern and experimental data. Fluorescence spectra were obtained by a Perkin Elmer LS55 fluorescence spectrophotometer. The emission spectra were obtained using an excitation wavelength of 450 nm.

2.1. Syntheses

$KNa[Ru(bpy)_3]_2[H_2W_{12}O_{40}]\cdot 8H_2O$ (**1**) was synthesized from a mixture of bpy, $3Na_2WO_4\cdot 9WO_3\cdot H_2O$, $RuCl_3\cdot xH_2O$ and H_2O. A typical synthesis is as follows: 1.0 mL aqueous solution containing 0.020 g $RuCl_3\cdot xH_2O$ was mixed thoroughly with 1.0 mL methanol solution containing bpy (0.029 g). Then, $3Na_2WO_4\cdot 9WO_3\cdot H_2O$ (0.141 g) was added and the pH of the resulting mixture was adjusted with 0.5 M KOH to approximately 10. The reaction mixtures were transferred to a Teflon bag, sealed and placed in a 45 mL reaction vessel, and heated in an oven at 90 °C for 48 h. Orange crystals were filtered and dried in air (yield: 0.034 g). FT-IR spectrum (KBr, cm^{-1}): 3492 (broad), 1624 (*m*), 1600 (*m*), 1445 (*m*), 1320 (*w*), 929 (*s*), 871 (*s*), 786 (*s*).

$K_6[Ru(pzc)_3]_2[SiW_{12}O_{40}]\cdot 12H_2O$ (**2**) was synthesized as follows: $H_4SiO_4\cdot 12WO_3\cdot xH_2O$ (0.103 g), and 1.0 mL methanol solution of pzc (0.027 g) were added to 1.0 mL aqueous solution containing 0.013 g $RuCl_3\cdot xH_2O$. The pH of this mixture was adjusted with 0.5 M KOH to approximately 8.5. The reaction mixtures were transferred to a Teflon bag, sealed and placed in a 45 mL reaction vessel, and heated in an oven at 105 °C for 48 h. Purple plate crystals were filtered and dried in air (yield: 0.053 g). FT-IR spectrum (KBr, cm^{-1}): 3457 (*s*), 1627 (*s*), 1606 (*s*), 1457 (*w*), 920 (*s*), 778 (*s*).

2.2. Crystallography

X-ray diffraction data for compounds **1** and **2** were collected on a Nonius kappa CCD diffractometer. Raw data were integrated, scaled, merged and corrected for Lorentz-polarization effects using the HKL-SMN package [20]. The structure was solved by direct methods and was refined against F^2 by weighted full-matrix least-squares calculations [21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography [22]. Crystal data and relevant details of the structure determinations are summarized in Table 1 and selected geometrical parameters are given in Table 2. The CCDC reference numbers are 838,475 and 838,476.

3. Results and discussions

3.1. Crystal structure

3.1.1. Crystal structure of compound 1

The structure of **1** consists of Keggin cluster anion $[H_2W_{12}O_{40}]^{6-}$, water molecules, and charge balancing cations $[Ru(bpy)_3]^{2+}$, K^+ and Na^+. The classic $[H_2W_{12}O_{40}]^{6-}$ Keggin cluster ion [23] consists of twelve WO_6 octahedra with the four types of W–O bond lengths in normal ranges (Table 2). The bond valence sum calculations indicate oxygen atoms in the polyoxoanion have values between 1.60 and 2.06, normal for oxo groups, except that the triply bridging

Table 2
Selected bond lengths (Å) in **1** and **2.**

1		**2**	
W–O_t	1.704–1.744(6)	1.666–1.680(7)	
W–$O_{b/c}$	1.842–2.016(5)	1.780–2.061(7)	
W–O_a	2.126–2.302(5)	2.345–2.434(7)	
Si–O		1.60–1.66(1)	
Ru(1)–N(2)	2.052(7)	Ru(1)–N(3)	2.003(8)
Ru(1)–N(5)	2.057(7)	Ru(1)–N(1)	2.007(8)
Ru(1)–N(1)	2.059(7)	Ru(1)–N(5)	2.010(8)
Ru(1)–N(6)	2.061(7)	Ru(1)–O(27)	2.085(7)
Ru(1)–N(4)	2.062(7)	Ru(1)–O(23)	2.085(7)
Ru(1)–N(3)	2.067(6)	Ru(1)–O(25)	2.091(7)
Ru(2)–N(9)	2.046(7)		
Ru(2)–N(7)	2.050(7)		
Ru(2)–N(8)	2.059(7)		
Ru(2)–N(10)	2.059(7)		
Ru(2)–N(11)	2.061(7)		
Ru(2)–N(12)	2.067(7)		

Table 1
Crystal data and structure refinements for **1** and **2**

	1	2
Formula	$C_{60}H_{66}KN_{12}NaO_{48}Ru_2W_{12}$	$C_{15}H_{21}N_6K_3O_{32}RuSiW_6$
Mol. wt.	4193.68	2146.9
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	13.5339(1)	11.886(2)
b (Å)	26.9360(1)	12.206(2)
c (Å)	23.7255(1)	16.128(3)
α (deg.)		74.40(3)
β (deg.)	92.3155(2)	89.43(3)
γ (deg.)		61.46(3)
V (Å^3)	8642.05(8)	1960.2(7)
Z	4	2
ρ (Mg/m^3)	3.223	3.657
Abs. coeff. (mm^{-1})	16.39	18.36
Abs. correction	Multi-scan	Multi-scan
Wavelength (Å)	0.7103	0.7103
Temperature (K)	92.0(2)	92.0(2)
Reflections collected/unique [R_{int}]	19840 [0.125]	38,993[0.0467]
Goodness-of-fit (F^2)	1.068	1.060
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0346$, w$R_2=0.0778$	$R_1=0.0424$, w$R_2=0.115$
R indices (all data)	$R_1=0.0507$, w$R_2=0.0856$	$R_1=0.0508$, w$R_2=0.120$