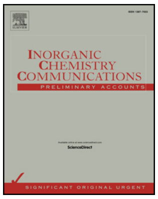
Inorganic Chemistry Communications 93 (2018) 15–19

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Short communication

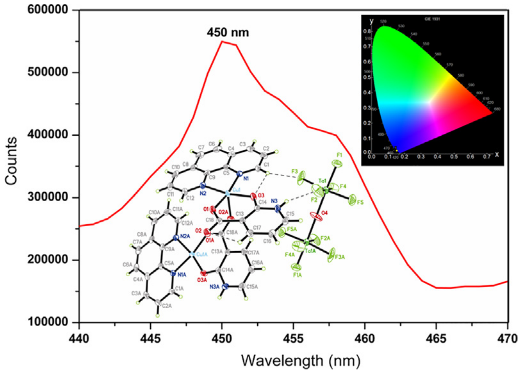
A new Cu(II) coordination polymer constructed from two kinds of ligands and rare $[Ta_2OF_{10}]^{2-}$ anion: synthesis, crystal structure and fluorescent properties

Yuquan Feng[a,*], Lu Wang[a], Zhengzheng Xing[a], Qunzeng Huang[a], Pengtao Ma[b,*]

[a] College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, PR China
[b] Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, PR China.

GRAPHIC ABSTRACT

A new 1-D zigzag chain coordination polymer $\{[Cu_2(opdc)_2(phen)_2][Ta_2OF_{10}]\}_n$ containing rare $[Ta_2OF_{10}]^{2-}$ anion has been synthesized by the two-step hydrothermal method. The luminescence properties reveal that it exhibits blue fluorescent emission with the quantum yield of 2.09 % and the short decay lifetime of 0.72 ns.



ARTICLE INFO

Keywords:
Two-step hydrothermal method
Linear $[Ta_2OF_{10}]^{2-}$ anion
Zigzag chain
XPS spectrum
Fluorescent properties

ABSTRACT

A new zigzag chain coordination polymer $\{[Cu_2(opdc)_2(phen)_2][Ta_2OF_{10}]\}_n$ [(opdc): 2-oxidopyridinium-3-carboxylate, phen: 1, 10-phenanthroline] has been synthesized by a two-step hydrothermal method and characterized by elemental analysis, energy-dispersive X-ray spectroscopy (EDS), infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray single-crystal diffraction studies. In its structure, each Cu(II) cation is coordinated by two N atoms from one phen ligand and three O atoms from two different $opdc^-$ anions to furnish a distorted square pyramidal configuration. Neighboring two copper cations are bridged by one carboxylate group from opdc ligand in an anti-anti bridging mode, leading to a 1-D infinite zigzag chain. The linear dinuclear $[Ta_2OF_{10}]^{2-}$ anions are further linked to the zigzag chain through intermolecular N—H···F and C—H···F hydrogen bonds. Moreover, the fluorescence emission, quantum yield and decay lifetime of the compound were also investigated.

Currently, great efforts have been contributed to the construction of metal coordination polymers containing carboxylate groups because of their interesting structural features and luminescent properties as well as other potential applications in molecular magnetism, catalysis,

---

[*] Corresponding authors.
E-mail addresses: yqfeng2008@126.com (Y. Feng), mpt@henu.edu.cn (P. Ma).

https://doi.org/10.1016/j.inoche.2018.04.029
Received 27 March 2018; Received in revised form 25 April 2018; Accepted 26 April 2018

electrical conductivity and so on [1–4]. A regular and significant synthetic strategy is that connects various metal cations with carboxylate groups utilized as flexible linkers. Carboxylate groups can be regarded as excellent bridging or chelating ligands in the formation of different dimensional (chain, layer, or framework) coordination polymers [5,6]. In addition, these ligands containing carboxylate groups always possess multiple proton acceptor or donor sites which can involve hydrogen bonds during the synthesis of supra-molecular complexes. These hydrogen bonds not only enhance their crystal structural stabilities, but also enrich the family of metal coordination polymers. Depending on the above considerations, we selected two types of ligands as linkers to build metal coordination polymers with novel structural features. As we know, multi-dentate ligand 2-oxidopyridinium-3-carboxylic acid owns three potential coordination sites (carboxylate O site, hydroxyl group and N site) and it often exhibits superior coordination capacities. Meanwhile, we choose phen (1, 10-phenanthroline) as the second ligand to furnish the structure of metal coordination polymers. Phen ligand exhibits low π-anti-bonding orbital energy and it can be regarded as a rigid conjugated chelating ligand. Also, it can easily form MLCT electronic transition and can act as a kind of superior optically active ligand.

Most importantly, $[Ta_2OF_{10}]^{2-}$ anion-containing tantalum-oxyfluorides have become more attractive in recent years due to their unique structure-related properties including ferro-electricity, piezoelectricity and second-order nonlinear (NLO) optical properties [7]. Up to the present, only a few complexes containing $[Ta_2OF_{10}]^{2-}$ anion were reported, such as $(C_{10}H_{22}NO_4)_2[Ta_2OF_{10}]$ and $(C_{12}H_{12}N_2)[Ta_2OF_{10}]$ [8,9]. Therefore, using rare $[Ta_2OF_{10}]^{2-}$ anion as a building block to obtain tantalum-oxyfluorides with new structural features and practical applications is a meaningful work.

We expected that the combination of linear $[Ta_2OF_{10}]^{2-}$ anion and metal coordination cationic fragments would obtain a new coordination polymer. As part of our continual work [10–16], herein, with the aid of two types of ligands, (opdc: 2-oxidopyridinium-3-carboxylate, phen: 1, 10-phenanthroline) and linear $[Ta_2OF_{10}]^{2-}$ anion, we obtained an infinite chain coordination polymer $\{[Cu_2(opdc)_2(phen)_2][Ta_2OF_{10}]\}_n$ (**1**). The compound displays interesting zigzag chain and adds a new member into the family of Cu (II) coordination polymer containing rare linear $[Ta_2OF_{10}]^{2-}$ anion.

Compound **1** was obtained by means of a two-step hydrothermal method [17]. X-ray diffraction determination [18] indicates that **1** belongs to monoclinic system with the space group of $P2_1/c$. The results reveal that its molecular structure contains two Cu^{2+} cations, two $opdc^-$ anions, two phen ligands and one linear $[Ta_2OF_{10}]^{2-}$ anion. In order to determine the valence of Cu and Ta sites, the bond valence sum (BVS) calculations were applied. Results of BVS calculations reveal that the Cu and Ta sites are in their normal valences of +II and +V, respectively (Table 1). The molecular structure of **1** is shown in Fig. 1. In the structure of $[Ta_2OF_{10}]^{2-}$ anion, each Ta^{5+} cation adopts firstly five F atoms to form a $\{TaF_5\}$ square pyramid, then the two$\{TaF_5\}$ square pyramids are linked into a linear dinuclear $[Ta_2OF_{10}]^{2-}$ anion through the bridging O atom (O4). The Ta—O bond length is 1.8868(8) Å and Ta—F bond lengths span in the range of 1.876(7)–1.911(7) Å. These bond lengths agree well with previously reported results for related compounds [8,9,15,16]. Within the structure of the dinuclear Cu fragment, each Cu(II) cation is coordinated by two N atoms from one phen ligand and three O atoms from two different $opdc^-$ anions to furnish a slightly distorted square pyramidal configuration. The N1, N2, O1, O3 atoms are located on the equatorial positions and O2 atom is laid on the position of vertex. The bond distances of Cu—N and Cu—O fall in the scope of 1.915(5)–2.291(6) Å and 2.000(6)–2.023(6) Å, respectively, which are comparable with the corresponding bond distances observed in known Cu(II) coordination polymers [19]. Two adjacent Cu(II) cations are connected by two bridging O atoms from the same carboxylate group in an anti-anti linking mode with the Cu···Cu distance of 5.799 Å. It is noting that the $opdc^-$ anion, phen ligand and Cu^{2+} cation are nearly coplanar. In the dinuclear fragment, the dihedral angle between adjacent two planars is 4.3°. The dinuclear Cu fragments are further bridged through μ_2-O atom (O2), leading to an infinite zigzag chain (Fig. 2). In the zigzag chain, each $opdc^-$ anion can be viewed as a tridentate ligand bridging two Cu^{2+} cations and each Cu^{2+} cation is arranged by two $opdc^-$ anions and one phen ligand. Interestingly, the linear dinuclear $[Ta_2OF_{10}]^{2-}$ anions are bonded to the infinite zigzag chain via intermolecular N—H···F and C—H···F hydrogen bonds.

Moreover, three kinds of hydrogen bonds involving N—H···F, C—H···F and C—H···O are observed in the packing structure of compound **1**. Related parameters of hydrogen bonds are shown in Table S1. Under the interactions of hydrogen bonds, the zigzag chains and neighboring $[Ta_2OF_{10}]^{2-}$ anions are interconnected into a three-dimensional supra-molecular network, as shown in Fig. 3. In its packing structure, the zigzag chains and $[Ta_2OF_{10}]^{2-}$ anions are arranged alternately in a –ABAB– mode along the *c* axis. To the best of our knowledge, the bridging mode between $[Ta_2OF_{10}]^{2-}$ anions and zigzag chains has never been observed in the series of tantalum-oxyfluorides. Besides the existence of hydrogen bonds, there are also three types of π-π stacking interactions in the 3-D network: the adjacent pyridine rings (N1/C1–C5) are parallel to each other, with the centroid-to-centroid distances of 3.280(5) Å (type I) and 3.397(6) Å (type II), respectively; the adjacent benzene rings (C4–C9) are parallel to each other, with a centroid-to-centroid distance of 3.404(9) Å (type III). These multi-types of hydrogen bonds and π-π stacking interactions play key roles for enhancing the structural stability of compound **1**.

The chemical component of 1 was determined by the EDS spectroscopy, the results confirmed that compound **1** contains the elements of Ta, Cu, F, O, C and N. The powder XRD pattern is in agreement with the simulated one originating from crystal structural data, which proves the phase purity of the as-synthesized product as given in Fig. S1. The IR spectrum of **1** shows that three characteristic vibrations at 858, 783 and 542 cm^{-1} can be attributed to the ν_{asym}(Ta-O), ν_{asym}(Ta-O-Ta) and ν_{asym}(Ta-F) belonging to the $[Ta_2OF_{10}]^{2-}$ anion [9]. Peaks at 1643 and 1436 cm^{-1} can be attributed to the $\nu_{asym}(OCO^-)$ and $\nu_{sym}(OCO^-)$, respectively. Compared with the values of two peaks, 207 cm^{-1} $[\Delta(OCO^-)]$ can be observed, which reveals that the opdc ligand should be coordinated to the Cu(II) cation by means of a bidentate coordinated fashion [19]. The peak 2869 cm^{-1} in the high-frequency region should be ascribed to the C—H vibration originated from the aromatic groups. In the low-frequency region, while a series of absorptions in the scope

Table 1
The BVS values of Cu^{2+} and Ta^{5+} cations in 1 (symmetry code: A: $-x$, $1-y$, $1-z$).

Bonds	Distances (Å)	BVS value
Cu(1)—O(1)	1.915 (3)	0.528
Cu(1)—O(3)	1.915 (8)	0.527
Cu(1)—O(2A)	2.291 (1)	0.191
Cu(1)—N(1)	2.000 (3)	0.510
Cu(2)—N(4)	2.023 (2)	0.479
Total		2.236
Ta(1)—F(1)	1.906 (1)	0.932
Ta(1)—F(2)	1.911 (2)	0.919
Ta(1)—F(3)	1.898 (3)	0.952
Ta(1)—F(4)	1.876 (3)	1.010
Ta(1)—F(5)	1.879 (8)	1.001
Ta(1)—O(4)	1.886 (8)	0.547
Total		5.360