Spectrochimica Acta Part A 77 (2010) 749–754

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, crystal structure and photoelectric property of two new coordination polymers constructed by longer-spanning suberic acid and 4,4′-bipyridine ligands

Yan Xie[a,d], Feng Ying Bai[a], Jing Li[a], Yong Heng Xing[a,*], Zhuo Wang[a], Hai Yan Zhao[a], Zhi Feng Pu[b], Mao Fa Ge[b], Zhan Shi[c]

[a] College of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, PR China
[b] Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, PR China
[c] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China
[d] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, PR China

ARTICLE INFO

Article history:
Received 8 December 2009
Received in revised form 2 July 2010
Accepted 12 July 2010

Keywords:
Coordination polymer
Suberic acid
Synthesis
Crystal structure
Surface photovoltage spectrum

ABSTRACT

Two-dimensional coordination polymers, $[M(C_8H_{12}O_4)(C_{10}H_8N_2)]\cdot H_2O$ [M = Co (**1**), Cd (**2**); $C_{10}H_8N_2$ = 4,4-bipyridine, $C_8H_{14}O_4$ = subaric acid] were obtained from the reaction of the metal salts, bipy and subaric acid at 180 °C and characterized by elemental analysis, infrared spectrum, and single-crystal X-ray diffraction and surface photovoltage spectrum (SPS). The single-crystal X-ray diffraction showed that the subaric ligand in the two complexes exhibits two types of modes coordinating to transition metal ions, resulting in the formation of a 1D infinite chain along the *c*-axis. In addition, the results of SPS for complexes **1** and **2** indicate that these two complexes exhibit positive surface photovoltage responses in the range of 300–800 nm, which can be assigned to LMCT and MLCT, respectively. And the SPS of complex **1** also can be assigned to the d → d* electronic transition. The SPS spectra of the two complexes are consistent with their UV–vis spectra.

1. Introduction

Over the past decade, the construction of coordination polymers (CPs) has a rapid enormous expansion not only in supramolecular but also in material chemistry due to their fascinating molecular topologies and crystal-packing motifs along with potential applications as smart optoelectronic, magnetic, and porous materials [1–9]. Among all these CPs, it is found that α,ω-dicarboxylate anions exhibit versatile coordination fashions to interlink metal atoms to generate 1D chains, 2D layers and 3D networks [10–13]. As shown in Scheme 1 (see the supplementary materials), a large variety of chelating and/or bridging coordination fashions which are commonly used to combine with the coordination characteristics of the metal centers leads to a great number of high dimensional structures. To the best of my knowledge complexes constructed by such aliphatic α,ω-dicarboxylate ligands, such as oxalate; succinate; glutarate; adipate, have been extensively reported [14–20]. Besides, it is interesting to show that oxalic acid shows more complicated coordination modes because of the shorter distance between the two ending dicarboxylate groups [21]. It is clearly shown that self-assembly of metal cations with α,ω-dicarboxylate anions afforded a variety of supramolecular motifs, where the discrete metal-oxygen polyhedron could be interconnected by organic linkers into polymeric chains, layers and 3D frameworks. However, unfortunately, such 3D frameworks exhibit normally little porosity [20,22,23–26]. In order to overcome this issue, the rigid multicarboxylate containing ligands with aromatic rings have been used to control and adjust open and stable frameworks. At present, the auxiliary ligand (such as, 4,4′-bipy) seems to have a significant effect on the formation and structure of the metal N-containing polycarboxylate complexes [27–31]. Therefore, O-donors of α,ω-dicarboxylate and N-donors of 4,4′-bipy allow it to result in many different kinds of interesting structures of transition metal or lanthanide complexes. Some complexes, namely, $[Mn(bpy)(H_2O)(C_4H_4O_4)]\cdot 0.5bpy$, $Mn(bpy)(C_5H_6O_4)$ and $Mn(bpy)(C_6H_8O_4)$ have been successfully constructed in the past few years, possessing the characteristics of complexes with rigid and flexible ligands [32]. We have recently synthesized two new six-coordinated polymers, $[Ni(bpy)(C_{10}H_{16}O_4)H_2O]$ and $[Co(bpy)(C_{10}H_{16}O_4)H_2O]$, which exhibit positive surface photoelectric properties [33]. In order to further explore and understand well influence of longer-spanning aliphatic decarboxylate ligand on structural characterization and spectra properties of transition metal complexes, herein, we synthesized another two new complexes $[M(C_8H_{12}O_4)(C_{10}H_8N_2)]\cdot H_2O$[M = Co(**1**), Cd(**2**)] with three obvious characterizations: (i) the complexes are constructed by longer-spanning α,ω-dicarboxylate acid, suberic acid, and as we known, there are few examples of complexes constructed by the

---

* Corresponding author. Tel.: +86 0411 82156987.
E-mail address: yhxing2000@yahoo.com (Y.H. Xing).

1386-1425/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2010.07.009

mental irons with longer-spanning aliphatic decarboxylate ligand [34,35]; (ii) the complex **2** displays completely the flexible and variable coordination behavior of Cd with decahedral structure; (iii) analysis results show that the SPS of the two complexes are consistent with their UV–vis spectra.

2. Experimental

All chemicals purchased were of reagent grade or better and were used without further purification. C and H analyses were made on a PerkinElmer 240C automatic analyzer at the analysis center of Liaoning Normal University. Infrared (IR) spectra were recorded on JASCO FT/IR-480 PLUS Fourier Transform spectrophotometer with pressed KBr pellets in the range 200–4000 cm^{-1}. The powder X-ray diffraction (PXRD) data were collected on a Bruker Advance-D8 with Cu Kα radiation, in the range $5^\circ < 2\theta < 60^\circ$, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step. UV–vis spectra were obtained on a JASCO UV/vis/NIR UV-570 Spectrophotometer in the range of 200–800 nm using solid powder. SPS measurement was conducted with the light source-monochromator-lock-in detection technique. Thermogravimetric analysis of complexes **1–2** were carried out from room temperature to 1000 °C in flowing N_2 at 10 °C min^{-1}. All the measurements were performed under atmospheric pressure at ambient temperature.

2.1. *Preparation of Co($C_8H_{12}O_4$)($C_{10}H_8N_2$)]·H_2O (1) and Cd($C_8H_{12}O_4$)($C_{10}H_8N_2$)]·H_2O (2)*

Complex **1** was synthesized by the reaction, in which a mixture of $Co(CH_3COO)_2·4H_2O$ (0.12 g, 0.48 mmol), suberic acid (0.06 g, 0.35 mmol), 4,4′-bipy (0.07 g, 0.36 mmol) and 15 ml water was sealed into a bomb equipped with a Teflon liner (25 ml). The mixture was heated at 180 °C for 3 days and then cooled to room temperature at a rate of 10 °C h^{-1}. Light red crystals of complex **1** were obtained (yield: 71.53% based on Co(II)). Anal. Calcd for $C_{18}H_{22}N_2O_5Co$ (405.31): C, 53.29%; H, 5.43%; N, 6.91%, Found: C, 53.02%; H, 5.57%; N, 6.73%. IR spectrum (cm^{-1}): 3441, 922, 2851, 1603, 1585, 1551, 1488, 1430, 1411, 1312, 1217, 1175, 1128, 1072, 1046, 886, 817, 731, 630.

Complex **2** was synthesized by the reaction, in which a mixture of $CdCO_3·4H_2O$ (0.12 g, 0.40 mmol), suberic acid (0.05 g, 0.29 mmol), 4,4′-bipy (0.07 g, 0.36 mmol) and 15 ml water was sealed into a bomb equipped with a Teflon liner (25 ml). The mixture was heated at 180 °C for 3 days and then cooled to room temperature at a rate of 10 °C h^{-1}. Colorless crystals of complex **2** were obtained (yield: 51.23% based on Cd (II)). Anal. Calcd for $C_{18}H_{24}N_2O_5Cd$ (460.80): C, 46.86%; H, 5.21%; N, 6.10%, Found: C, 46.63%; H,5.42%; N, 6.00%. IR spectrum (cm^{-1}): 3442, 2943, 2919, 2848, 1605, 1577, 1549, 1482, 1438, 1422, 1311, 1215, 1172, 1125, 1073, 886, 818, 748, 632.

2.2. *X-ray data collection and refinement of the crystal structures*

Suitable single crystals of two complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Rigaku R-AXIS RAPID IP diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the basis of the difference Fourier map for all the complexes. All calculations were performed using the program SHELX-97 program [36]. The crystallographic data and experimental details of the data collection and the structure refinement are given in Table 1.

Table 1
Crystal and structure refinement data for **1** and **2**.

Complexes	1	2
Empirical formula	$C_{18}H_{22}N_2O_5Co$	$C_{18}H_{24}N_2O_5Cd$
Formula weight	405.31	460.80
Color and habit	Red, block	Colorless, block
Crystal size (mm^3)	0.488 × 0.260 × 0.035	0.205 × 0.142 × 0.028
Crystal system	*Triclinic*	*Triclinic*
Space group	*P*1	*P*1
a (Å)	9.647(5)	10.056(3)
b (Å)	9.884(5)	10.192(3)
c (Å)	10.623(5)	10.431(3)
α°	112.441(5)	110.429(4)
β°	92.153(7)	91.659(4)
γ°	107.869(6)	110.460(4)
V	877.2(8)	924.7(5)
Z	2	2
Dc ($g\,cm^{-3}$)	1.535	1.655
μ (mm^{-1})	1.011	1.212
Goodness of fit	1.061	1.001
R_1 [$I > 2\acute{o}(I)$]	0.0509	0.0445
wR_2	0.1251	0.0813

3. Results and discussion

3.1. *Synthesis*

By a hydrothermal method, complexes **1** and **2** were obtained at 180 °C under a similar reaction system. Originally, there was only much precipitation (IR spectra indicates that it is not the target production) to have been obtained when the pH value was adjusted to 6–7. Then, we tried to synthesize these complexes without adjusting the pH value, and well-shaped single crystals of the title complexes suitable for single-crystal X-ray diffraction were obtained. Similarly, we also tried to adopt different reagents to adjust the pH to 4–6, such as ethylenediamine, potassium hydroxide, and sodium hydroxide, the same structural complexes were obtained. On the basis of the results above, we thought that adjusting the pH value to 4–6 is not one of important factors for making good crystals of the complexes. Additionally, the compositions of **1** and **2** were confirmed by elementary analysis, IR spectra, and the phase purities of the bulk samples were identified by X-ray powder diffraction (Fig. S1).

3.2. *Crystal structures*

The single-crystal X-ray structural analysis shows that the structure of complex **1** is a two-dimensional coordination polymer, in which the asymmetric unit contains one Co atom, one suberic anion, one 4,4′-bipyridine and one water molecule. The Co atom is coordinated by four oxygen atoms [Co–O1, 2.197(3) Å; Co–O2, 2.169(4) Å; Co–O3B, 2.055(3); Co–O4A, 2.002(3) Å] of four suberic anions, two nitrogen atoms [Co–N1, 2.154(3) Å; Co–N3, 2.167(3) Å] of two 4,4′-bipyridine ligands, and one water molecule, showing an octahedral geometry (Fig. 1a). In complex **1**, suberic anion displays μ_3–η^2:η^1:η^1 coordination fashion (Fig. 2A), which links transition metal center atom (Co) and its corresponding centrosymmetric atom with bridging coordination mode to form a second building unit. Then the second building units are connected by chelating-bridging tetradentate suberic ligand to form a 1D chain along the *c*-axis. The chains are further connected by 4,4′-bipyridine ligands to generate a 2D layer in the bc plane (Fig. 3a). The average distance of Co–O is 2.105(3) Å, which is similar to 2.092(1) Å of the reported complex, $[Co(H_2O)_6][C_6H_2(COO)_2(COOH)_2]$ [37]. The average O–Co–O angle of $110.26(13)^\circ$ is lightly shorter than $118.70(3)^\circ$ of the reported complex, $[Co(H_2O)_6][C_6H_2(COO)_2(COOH)_2]$ [37]. The average dis-