Journal of Solid State Chemistry 184 (2011) 1339–1345

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Two new frameworks of potassium saccharate obtained from acidic and alkaline solution

Yao-Kang Lv, Yun-Long Feng*, Ji-Wei Liu, Zhan-Guo Jiang

Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, China

ARTICLE INFO

Article history:
Received 28 October 2010
Received in revised form
22 March 2011
Accepted 27 March 2011
Available online 5 April 2011

Keywords:
K(I) complexes
D-saccharic acid
Topology
Cyclic voltammetry
Nickel hydroxide electrode
Discharge curves

ABSTRACT

Two chiral K(I) complexes based on D-saccharic acid (H_2sac), $[K(Hsac)]_n$ (**1**) and $[K_2(sac)]_n$ (**2**) were obtained from acidic and alkaline solution. The 3D framework of **1** includes K(I) polyhedral rods and typical pairwise coaxial right- and left-handed helical chains, and displays binodal 6-connected pcu topology. **2** contains 2D polyhedral sheets consisting of left-handed helical chains, and generates 3D network with an unprecedented (7,11)-connected net. Cyclic voltammetry tests and charge–discharge tests indicate that the addition of complex **2** to the electrolyte could improve the electrochemical properties of the nickel hydroxide electrode.

1. Introduction

Helical assemblies are prevalent in biological systems and play key roles in molecular recognition, replication, and catalysis [1]. These facts have aroused the interests to design and synthesize coordination complexes containing helix. Several approaches have been developed for constructing helical complexes of potential applications [2], to date, the self-assembly of helical structure is still a challenging subject to chemists for the difficulty of selection of optimal components. Inspired by the aforementioned considerations, we aimed to couple our interest in obtaining new helical complexes via linking metal centers with chiral flexible ligands [3]. D-saccharic acid (H_2sac) (Scheme 1), which can be obtained from the oxidation of D-glucose, is a chiral flexible multidentate ligand and attractive as an excellent building blocks for the construction of metal coordination networks [4]. Due to the variable coordinate modes of this ligand, chemically similar complexes with diverse structure could be obtained from different experimental condition. In 1977, Taga et al. [5] reported a crystal structure of monopotassium saccharate K(Hsac), and in 2002, Styron et al. [6] reported another crystal structure of dipotassium saccharate monohydrate $K_2(sac) \cdot H_2O$. In this work, we reported two new K(I) complexes based on D-saccharic acid, $[K(Hsac)]_n$ (**1**) and $[K_2(sac)]_n$ (**2**) with novel helical chains.

In recent years, considerable attention has been paid to Ni/MH batteries for their high discharge capacity, high charge/recharge rate, environmental friendliness, reasonable price, etc. [7]. Up to now, most of the studies of Ni/MH batteries focus on electrode materials composition, molecular structure, morphology, kinetic property and so on [8]. But the effect of electrolyte additive on the electrochemical properties of electrode is also important, and now few concerns. Zhu et al. [9] demonstrated the effects of the redox additive such as $K_4Fe(CN)_6$ on the charge–discharge performances and internal pressure of the Ni/MH batteries. Shen et al. [10] reported the influence about the addition of $Cu(OH)_2$ to the KOH alkaline electrolyte on the electrochemical properties of $La_{0.75}Mg_{0.25}Ni_{3.5}$ hydrogen storage alloy electrode. Herein the influence about the addition of complex **2** to the KOH alkaline electrolyte on the electrochemical properties of nickel hydroxide electrode was further investigated.

2. Experiment section

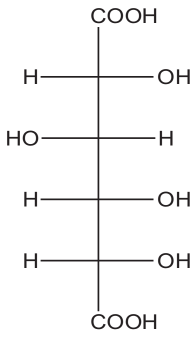
2.1. Materials and measurements

Spherical β-$Ni(OH)_2$ particles coated with 5 wt% $Co(OH)_2$ were purchased from Changsha Xinye Industrial Co., Ltd. (China). All other starting reagents were purchased commercially and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. IR spectra were measured in KBr pellets on a Nicolet 5DX FT-IR spectrometer.

---

* Corresponding author. Fax: +86 579 82282269.
E-mail address: sky37@zjnu.edu.cn (Y.-L. Feng).

0022-4596/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2011.03.042



Scheme 1. D-saccharic acid (H_2sac).

2.2. Synthesis of $[K(Hsac)]_n$ (**1**)

D-saccharic acid potassium salt ([K(Hsac)]) purchased commercially were recrystallized from 25% of acetic acid, and colorless prism crystals suitable for X-ray diffraction studies were obtained. Elemental analysis calcd (%) for $C_6H_9KO_8$: C, 29.08; H, 3.70. Found: C, 29.03; H, 3.65. IR (KBr cm^{-1}): 3380(vs), 3264(vs), 2947(m), 1745(s), 1451(m), 1407(m), 1331(w), 1260(m), 1220(m), 1110(s), 1050(m), 945(w), 856(m), 656(s), 494(w).

2.3. Synthesis of $[K_2(sac)]_n$ (**2**)

Dissolve 0.124 g of **1** in 20 mL 7 mol L^{-1} KOH solution. The colorless microcrystalline powder was separated from the filtrate in three weeks. Crystals suitable for X-ray diffraction studies were recrystallized from N,N-dimethylformamide (DMF). The yield was about 57%. Elemental analysis calcd (%) for $C_6H_8K_2O_8$ (%): C, 25.20; H, 2.88. Found: C, 25.17; H2.82. IR (KBr cm^{-1}): 3420(vs), 3030(m), 2920(m), 2850(m), 1960(w), 1870(w), 1740(w), 1670(m), 1610(s), 1560(m), 1500(m), 1420(s), 1380(m), 1220(s), 1070(m), 1010(s), 802(m), 609(s), 513(m).

2.4. Single-crystal structure determination

The data collection of complexes **1** and **2** was performed on a Bruker APEX II diffractometer equipped with a graphite-monochromatized Mo-$K\alpha$ radiation (λ=0.71073 Å) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by direct methods and expanded with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Except the hydrogen atoms on oxygen atoms were located from the difference Fourier maps, the other hydrogen atoms were generated geometrically. All calculations were performed using SHELXS-97 and SHELXL-97 [11]. Further details for structural analyses are summarized in Table 1, selected bond lengths and angles are listed in Table S1 and Table S2, the hydrogen bond distances and bond angles are listed in Table S3 and S4, respectively. CCDC−689246 and 703535 contains the crystallographic data in CIF format.

2.5. Electrochemical evaluation

Nickel hydroxide electrodes were prepared by inserting an active paste into a nickel foam substrate. A paste containing 85 wt% active materials (5 wt% $Co(OH)_2$-coated nickel hydroxide spherical powder), 10 wt% carbon black and 5 wt% poly(tetrafluoroethylene) (PTFE) was used. The electrode was dried at 80 °C for 1 h and cut into a disk ($1.0 \times 2.0\ cm^2$), which was pressed at a pressure of 100 kg cm^{-2} to a thickness of 0.4 mm. Then the electrode was spot-welded to a nickel sheet for electrical connection. Cyclic voltammetry tests were carried out in a classical three-electrode cell with an electrochemistry work station (CHI650C, Chenhua instrument Ltd., Shanghai). The working electrode was the as-prepared nickel hydroxide electrode, the counter electrode was a nickel foil, and the reference electrode was an Hg/HgO electrode. For comparing, four kinds of electrolyte were used, 7 mol L^{-1} KOH solution, 7 mol L^{-1} KOH solution with the addition of 0.01 mol L^{-1} complex **2**, 7 mol L^{-1} KOH solution with the addition of 0.02 mol L^{-1} complex **2** and 7 mol L^{-1} KOH solution with the addition of 0.05 mol L^{-1} complex **2**. Using a Neware battery program-controlled test system, the charge–discharge tests were performed at 20 °C in a half-cell consisting of a working electrode (as-prepared nickel hydroxide electrode) and a counter electrode (a metal hydride electrode with excess capacity). There were four kinds of electrolyte: 7 mol L^{-1} KOH solution, 7 mol L^{-1} KOH solution with the addition of 0.01 mol L^{-1} complex **2**, 7 mol L^{-1} KOH solution with the addition of 0.03 mol L^{-1} complex **2** and 7 mol L^{-1} KOH solution with the addition of 0.05 mol L^{-1} complex **2**. The nickel hydroxide electrodes were charged at a rate of 0.2 C for 7.5 h, standed for 1 h and discharged at a 0.2 C rate to 0.9 V. Morphology of nickel hydroxide electrodes were also detected by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

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

Complexes	**1**	**2**
Empirical formula	$C_6H_9KO_8$	$C_6H_8K_2O_8$
Formula weight	248.23	286.32
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a (Å)	4.8417 (2)	7.06520 (10)
b (Å)	10.8136 (6)	8.26060 (10)
c (Å)	8.4630 (5)	16.2660 (3)
β (deg.)	91.413 (4)	
V (Å^3)	442.96 (4)	949.33 (2)
Z	2	4
D/g (cm^{-3})	1.861	2.003
μ (mm^{-1})	0.63	1.03
GOF on F^2	1.000	1.000
$R1$, w$R2$ [$I > 2\alpha(I)$]	0.0238, 0.0642	0.0183, 0.0474
$R1$, w$R2$ (all data)	0.0248, 0.0657	0.0190, 0.0481

$R1=[\Sigma|F_o|-|F_c|]/[\Sigma|F_c|]$. $wR2=\{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

3. Results and discussion

3.1. Crystal structure

Single-crystal X-ray diffraction analysis shows that complex **1** is monoclinic with chiral space group $P2_1$ with absolute structure Flack factors of 0.01(4). The asymmetric unit consists of one K(I) center and one $Hsac^-$ ligand. The K(I) cation is coordinated by nine oxygen atoms from six $Hsac^-$ ligands, forming a distorted monocapped square antiprism geometry (Fig. 1). All of the bond lengths of K–O vary considerably from 2.747(6) to 3.327(7) Å (Table S1), which are in agreement with those in the previously reported complexes [12]. The neighboring K(I) polyhedral share an edge to form an infinite rod-shaped chain, in which the adjacent K···K distance is 4.842(3) Å. Each $Hsac^-$ ligand adopts the unusual μ_6, η^2:η^2:η^1:η^1:η^1:η^1:η^1 coordination mode and binds to six K(I) cations through seven oxygen atoms from two bidentate carboxyl groups, one α-hydroxyl group and two β-hydroxyl group to generate two-dimensional (2D) wavy sheets around bc plane. The sheets are further interconnected by the K(I) polyhedral rods which stacked in parallel along a-axis, and complete the construction of the three-dimensional (3D) framework (Fig. 2). It is worth noting that K(I) is bridged by two bidentate carboxyl groups [O1–C1–O2] and