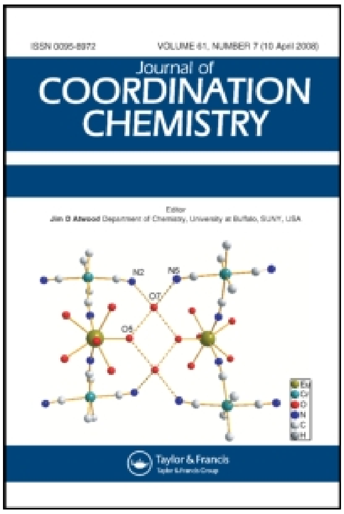

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Preparation of cobalt and nickel complexes of 8-hydroxyquinoline with nanobelt structure *via* one-step, low-heating, solid-state reactions

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Preparation of cobalt and nickel complexes of 8-hydroxyquinoline with nanobelt structure *via* one-step, low-heating, solid-state reactions

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Two nano-structural complexes, *bis*-(8-hydroxyquinoline) cobalt and *bis*-(8-hydroxyquinoline) nickel, have been prepared by one-step, low-heating, solid-state reaction, a simple, safe, economical and environmentally-friendly method. TEM and SEM images show that the complexes are composed of nanobelts with width ranging from 100 to 300 nm and a length of up to 1 μm. The technique offers a new way for fabricating coordination compounds with one-dimensional nanostructure.

Keywords: Low-heating solid-state reaction; 8-Hydroxyquinoline; Nanobelt; Complex

1. Introduction

8-hydroxyquinoline (8-HQ) and its derivatives are good chelating agents due to their strong coordination ability to metal ions [1–3] and are widely applied for extractive industry and analytical chemistry [4, 5]. Complexes of 8-HQ have been extensively studied from both applied and theoretical viewpoints [6–8]; copper(II), cobalt(II) and zinc(II) complexes have been used in industrial applications because of their ability to protect wood and textiles from rot-producing fungi [9, 10]. Some complexes of 8-HQ have been used as the emitting elements in electroluminescent (EL) devices [11–14]. EL devices with AlQ_3, ZnQ_2 and BeQ_2 as emitters have a high external quantum efficiency and brightness at a driving voltage below 10V. Generally, complexes of 8-HQ have been synthesized in solution, and the formation of the coordination complexes in solution is well understood. Synthesis of complexes of HQ has been replaced by solid-state coordination chemistry reactions [15–18].

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One-dimensional (1D) materials including nanotubes, nanowires, nanorods and nanobelts have attracted attention owing to their low dimensionality, high aspect ratio, unique physical and chemical properties [19–21]. Various syntheses of 1D nanomaterials including template-assisted synthesis, chemical vapor deposition, molecular beam epitaxy, laser ablation, etc. have been exploited [22–24]. To accomplish highly oriented growth of 1D nanomaterials, solid templates such as porous alumina, polymer, nanotubes, etc. are used. Furthermore, special conditions, tedious procedures or complex apparatus may be required. The main challenge for chemists and material scientists is to develop a simple, mild and template-free method to synthesize 1D nanomaterials. Only a few 1D metal complex nanomaterials have been synthesized [25–27], although there have been increasing reports on various metallic semiconductors and other kinds of inorganic nanostructures.

In the present work, we prepared Co(II) and Ni(II) complexes with nanobelt structure *via* low-heating, solid-state chemical reaction based on 8-HQ and $Co(CH_3COO)_2 \cdot 4H_2O$ or $Ni(CH_3COO)_2 \cdot 4H_2O$. This method requires neither complex apparatus and sophisticated techniques, nor solvent, template or catalyst. Consequently, it is a simple, safe, economical and environmentally-friendly method to synthesize metal complex nanomaterials, offering a new way to fabricate coordination compounds with 1D nanostructures.

2. Experimental

2.1. *Synthesis*

The procedure for synthesizing *bis*-(8-hydroxyquinoline) cobalt nanobelts is as follows. Cobalt acetate and 8-hydroxyquinoline were weighed accurately in a 1 : 2 molar ratio and ground separately at room temperature for about 5 min in an agate mortar, and then mixed. The mixture was ground at room temperature for 30 min and heated at 50°C in a water bath for 2 h and stored in a glass tube for 24 h to ensure complete reaction. After further grinding at room temperature for 5 min, the mixture was washed with water and alcohol, respectively. Finally, the product was dried at room temperature in air. Elemental analysis calculated for $CoC_{18}H_{12}N_2O_2[Co(HQ)_2]$; C 62.24, H 3.49, N 8.07; found: C 61.96, H 3.62, N 7.98. *Bis*-(8-hydroxyquinoline) nickel nanobelts were synthesized by the same procedure. Elemental analysis calculated for $NiC_{18}H_{16}N_2O_4[Ni(HQ)_2 \cdot 2H_2O]$; C 56.54, H 4.22, N 7.33; found: C 56.12, H 3.90, N 7.35.

2.2. *Characterization*

Elemental analyses of carbon, hydrogen and nitrogen were carried out with a 2400 Perkin–Elmer analyzer. Infrared spectra were measured on a Bio-RAD FTS-40 spectrophotometer on KBr pellets. TG-DTA measurements were carried out on a Netzsch STA 449C thermal analyzer. X-ray powder diffraction studies were performed on a MAC Science MXP18AHF diffractometer with Cu-Kα radiation ($\lambda = 1.054056$ Å). Transmission electron microscope (TEM) images were obtained on a Hitachi H-600

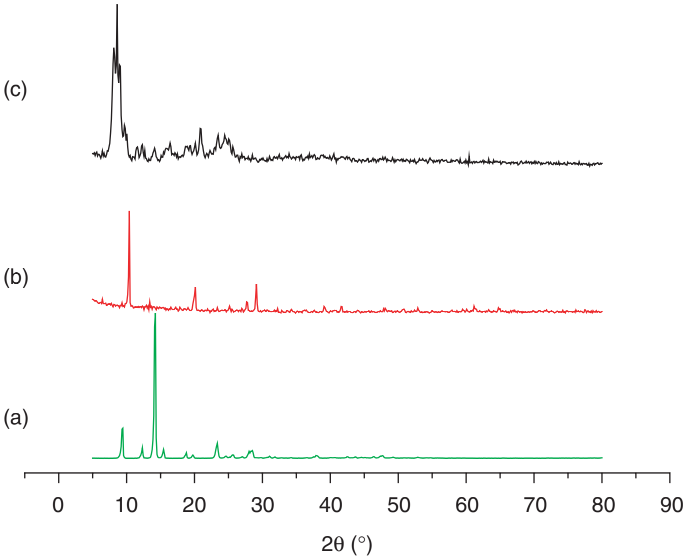

Figure 1. XRD patterns of (a) 8-hydroxyquinoline; (b) $Co(CH_3COO)_2 \cdot 4H_2O$; (c) $Co(HQ)_2$.

TEM with an accelerating voltage of 100 kV. Scanning electron microscope (SEM) images were obtained on a LEO1430 VP SEM.

3. Results and discussion

Figures 1 and 2 show X-ray diffraction patterns of $Co(CH_3COO)_2 \cdot 4H_2O$/8-HQ and $Ni(CH_3COO)_2 \cdot 4H_2O$/8-HQ reaction systems, respectively. From figure 1, 8-HQ has typical diffraction peaks located at 9.2, 12.3, 14.3, 15.6, 19.1, 19.8, 23.4, 24.9, 25.6, and 28.5°, and diffraction peaks located at 10.3, 20.3, 27.8, and 29.2° are in the pattern of $Co(CH_3COO)_2 \cdot 4H_2O$. However, in the pattern of the product $Co(HQ)_2$, the above diffraction peaks disappear and new diffraction peaks appear, located at 8.1, 8.7, 21.1, 23.4, 24.5 and 25.2°. Similarly, from figure 2, $Ni(CH_3COO)_2 \cdot 4H_2O$ has diffraction peaks located at 12.8, 18.5, 21.0, 22.3, and 28.3°. However, in the pattern of the product $Ni(HQ)_2 \cdot 2H_2O$, the diffraction peaks of 8-HQ and $Ni(CH_3COO)_2 \cdot 4H_2O$ disappear and new diffraction peaks appear, located at 6.9, 8.8, 16.8, 18.3, 20.9, 23.2, 25.0, and 29.4°. The results indicate that the solid-state product is a new species, not a mixture of reactants, in accord with results reported by Dubey [16].

Comparing IR spectral data of complexes with that of 8-HQ, the C–OH stretching band of 8-HQ at 1276 cm^{-1} disappears in the spectra of the complexes and new absorption bands attributed to $\upsilon(C\text{–}O^-)$ are observed at 1107 [$Co(HQ)_2$] and 1110 cm^{-1} [$Ni(HQ_2) \cdot 2H_2O$], respectively [29–31]. These spectral results imply that 8-HQ coordinates with metal ions through a deprotonated oxygen. Moreover, the $\upsilon(C\text{–}N)$ of benzene at 1255 cm^{-1} shifts to lower wave number (1239 cm^{-1}), indicating

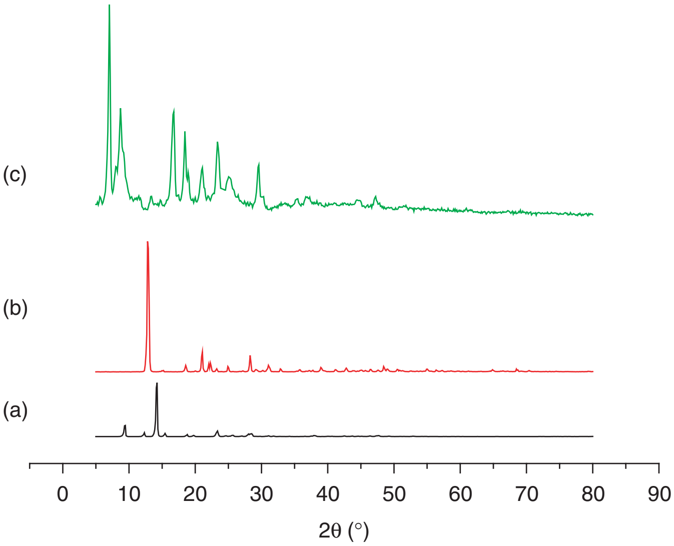

Figure 2. XRD patterns of (a) 8-hydroxyquinoline; (b) $Ni(CH_3COO)_2 \cdot 4H_2O$; (c) $Ni(HQ)_2 \cdot 2H_2O$.

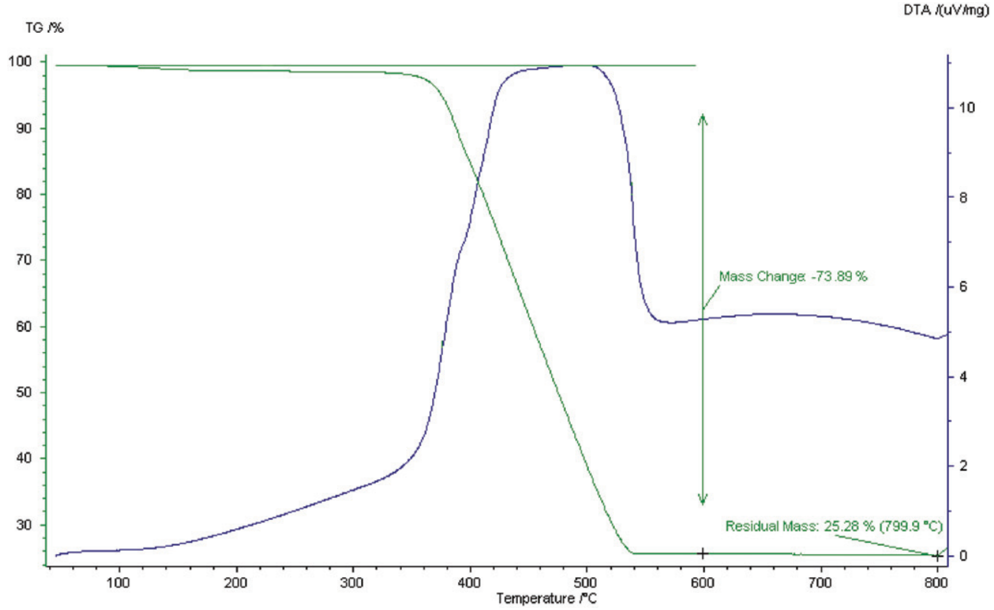

Figure 3. TG-DTA curves of $Co(HQ)_2$.

coordination of azomethine. All of these data confirm that 8-HQ is a mononegative bidentate ligand.

Figures 3 and 4 show TG-DTA curves of the solid complexes, which are obviously different. There is no weight loss until 340°C in the TG curve of *bis*-(8-hydroxyquinoline) cobalt, ruling out the possibility of lattice or coordinated water. Up to 550°C, the final

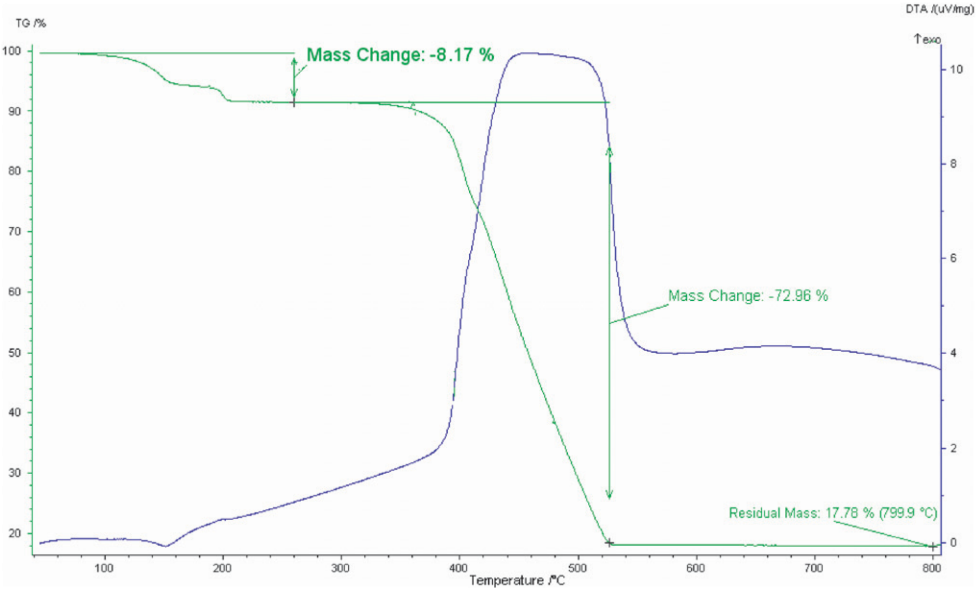

Figure 4. TG-DTA curves of $Ni(HQ)_2 \cdot 2H_2O$.

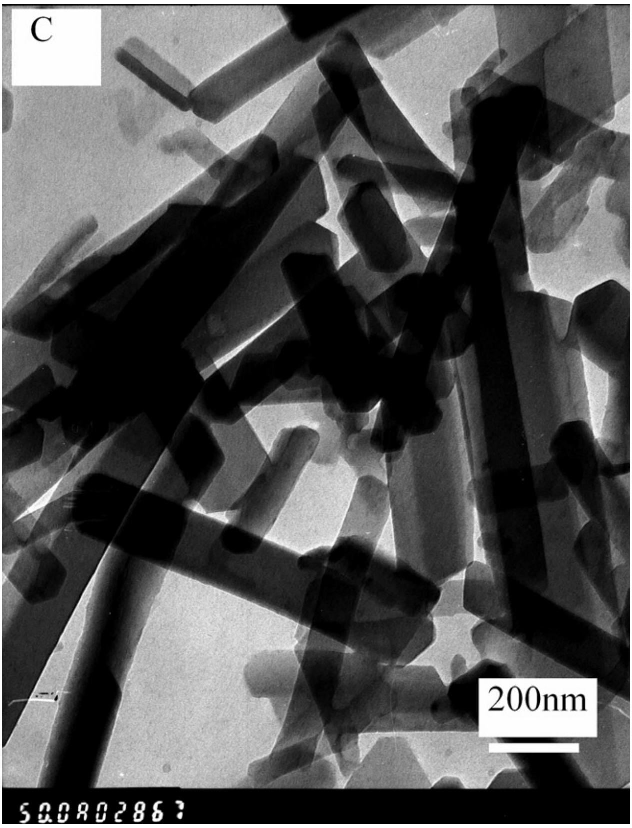

Figure 5. TEM image of $Co(HQ)_2$.

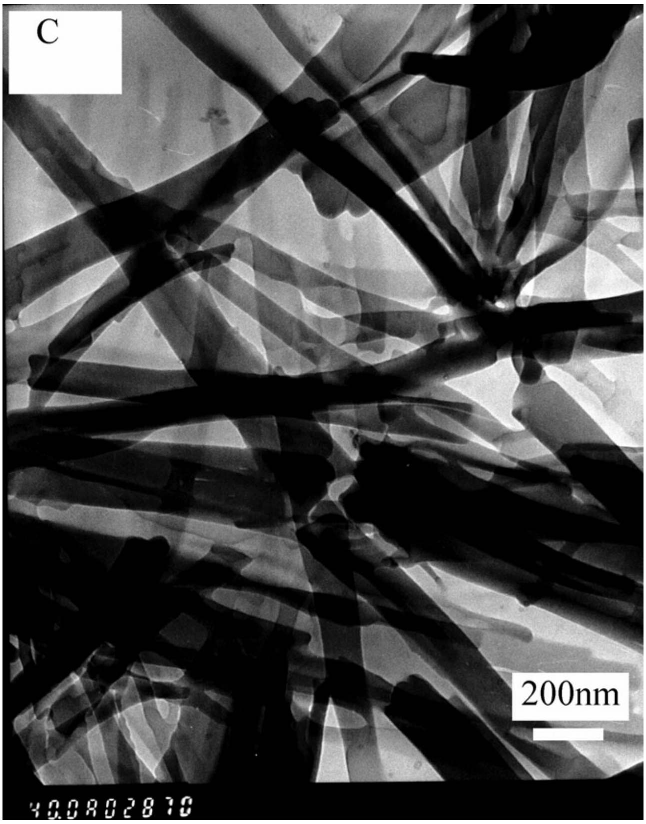

Figure 6. TEM image of $Ni(HQ)_2 \cdot 2H_2O$.

product Co_2O_3 (25.28%, Calcd 23.89%) is obtained after CoQ_2 decomposes completely. However, *bis*-(8-hydroxyquinoline) nickel follows a two-step decomposition pattern. In the first stage, loss (8.17%) of two water molecules takes place in the temperature range 60–260°C, which is in agreement with the calculated value (9.42%). The second stage of decomposition leads to the formation of NiO (17.78%, Calcd 19.52%). These results agree with elemental analysis data and further confirm that anhydrous *trans* *bis*-(8-hydroxyquinoline) cobalt and hydrated *bis*-(8-hydroxyquinoline) nickel have been obtained by one-step, low-heating, solid-state reaction.

Figures 5 and 6 illustrate typical TEM images of *bis*-(8-hydroxyquinoline) cobalt and *bis*-(8-hydroxyquinoline) nickel, respectively. The products consist of nanobelts with width from 100 to 300 nm and a length of up to 1 μm. The SEM image of $Ni(HQ)_2 \cdot 2H_2O$ (shown in figure 7) indicates only nanobelts, but from figure 8 it is obvious that $Co(HQ)_2$ has 1D structures with various sizes and aspect ratios, and some nanobelts agglomerated together. It is well known that the morphology of products from solid-state reactions depends on the rate of nucleation and growth of the reaction product. Usually, the rate of nucleation of the product is faster than that of growth of the products, so nanoparticles can be easily obtained during solid-state reactions. In nickel acetate/8-HQ and cobalt acetate/8-HQ reaction systems, the structures of nickel acetate and cobalt acetate are very similar, with

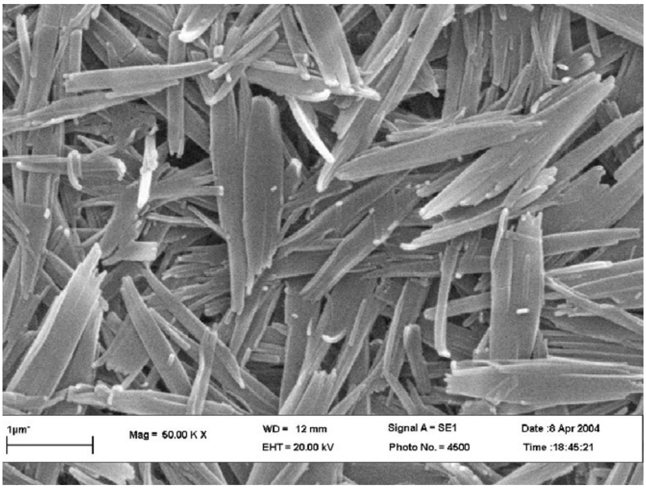

Figure 7. SEM image of $Ni(HQ)_2 \cdot 2H_2O$.

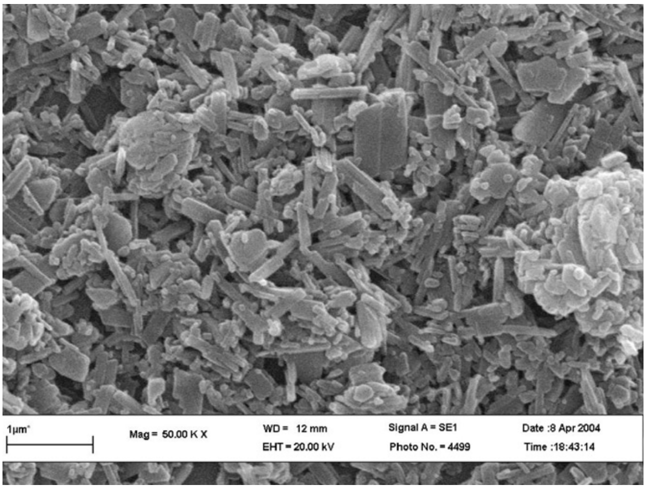

Figure 8. SEM image of $Co(HQ)_2$.

octahedral metals coordinated by four water molecules and two oxygens of two acetates [32]. Nickel acetate and cobalt acetate are so stable that reaction with 8-HQ at room temperature is difficult [30]; however, we accelerate the reaction by heating. Subsequently, the rate of growth of the products is faster than that of nucleation, leading to formation of nanobelts.

In conclusion, two nano-structural complexes, *bis*-(8-hydroxyquinoline) cobalt and *bis*-(8-hydroxyquinoline) nickel, have been prepared by a one-step, low-heating, solid-state reaction. It is expected that the present synthesis method can be extended to prepare other one-dimensional complexes.

Acknowledgements

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