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Cobalt(II) macrocycle complexes based synthesis of Co_3O_4 nanoparticles: structural and spectral characterization

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ABSTRACT: In this paper, macrocyclic cobalt(II) complexes $[CoL^1](NO_3)_2.4H_2O$ (1) and $[CoL^2](NO_3)_2.2H_2O$ (2) have been synthesized from the reaction of dialdehydes 1,2-bis(2-formylphenyl)ethane and 1,3-bis(2-formylphenyl)propane, $Co(NO_3)_2.6H_2O$ and 1,2-cyclohexanediamine with molar ration 1:1:1 in methanole and characterized by elemental analyses and FT-IR spectroscopy. Then used as precursors for preparation of Co_3O_4 nanoparticles via solid-state thermal decomposition without the need a catalyst, employing toxic solvent, template or surfactant and complicated equipment, which makes it efficient, one-step, simple and environment-friendly. The structure and morphology of the Co_3O_4 products were characterized by FT-IR spectroscopy, XRD and TEM. The XRD result shows that the Co_3O_4 products are pure, single phase and crystalline. The TEM result shows Co_3O_4 nanoparticles with the size between <100 nm. On the basis of the above results, other transition metal macrocyclic Schiff base complexes are therefore potentially capable of forming other transition metal oxide nanoparticles.

Keywords: *Co_3O_4; Cobalt(II) complexes; Characterized; Metal oxide; Nanoparticles; Thermal decomposition*

INTRODUCTION

The interest in exploring new macrocyclic Schiff base compounds containing nitrogen and oxygen donor atoms has been increasing (Borisova, *et al.*, 2007), because they play key role in the coordination chemistry of transition metals (Khandar, *et al.*, 2010, Ilhan, *et al.*, 2007a,b,c, Singh, *et al.*, 2011). Also, macrocyclic complexes have been received much attention because of their antibacterial properties (Keypour, et al, 2013, Khanmohammadi, *et al.*, 2009). Recently, Ilhan, *et al.* synthesized and characterized transition metal complexes with different size, number and donor atoms of macrocyclic Schiff base (Ilhan, *et al.*, 2007a,b,c, 2010, Ilhan, 2008).

Spinel Co_3O_4 is an important magnetic p-type semiconductor with a normal spinel structure, is an active metal oxides with wide applications and properties, such as catalytic oxidation of CO (Lv, *et al.*, 2013) and lithium ion batteries (Xu, *et al.*, 2009). Recently, several groups used cobalt complexes as new precursor for preparation of cobalt oxide nanoparticles by various methods (Hosseinian, *et al.*, 2012, Khalaji, *et al.*, 2014, Farhadi and Pourzare, 2012). Although considerable effort has been dedicated to control the shape- and

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size-controlled synthesized by different methods such as hydrothermal synthesis (Li, *et al.*, 2012, Teng, *et al.*, 2010), microwave (Kumar Meher and Rao, 2011, Chen *et al.*, 2013), chemical precipitation (Makhlouf, *et al.*, 2013) and the solid-state thermal decomposition (Farhadi, *et al.*, 2014a,b, Farhadi and Safabakhsh, 2012) methods. Among various techniques for preparation of cobalt oxide nanoparticles, solid-state thermal decomposition of transition metal complexes is one of the best method to preparation of Co_3O_4 (Hosseinian, *et al.*, 2012, Khalaji, *et al.*, 2014, Farhadi and Pourzare, 2012, Farhadi, *et al.*, 2014a,b, Farhadi and Safabakhsh, 2012), because it is inexpensive (economical) and doesn't use toxic solvent (pollution free) and surfactant route and is much faster where as process conditions, particle size and purity can be easily controlled. Up to now, many efforts have been made to develop a simple, economical and large scale synthetic method for the preparation of Co_3O_4 nanoparticles with different morphologies (Lv, *et al.*, 2013, Khalaji, *et al.*, 2015, Li, *et al.*, 2012).

Recently, we have been fascinated in the synthesis of Co_3O_4, utilizing new precursors (Khalaji, *et al.*, 2014 and 2015). Herein, we report the synthesis and characterization of Co_3O_4 nanoparticles by solid-state thermal decomposition of macrocyclic cobalt(II) complexes $[CoL^1](NO_3)_2.4H_2O$ (1) and $[CoL^2](NO_3)_2.2H_2O$ (2) (Scheme 1).

EXPERIMENTAL

Materials and characterization

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range 2θ = 100°–70°. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer. The transmission electron microscopy (TEM) images were obtained from a JEOL JEM 1400 transmission electron microscope with an accelerating voltage of 120 kV.

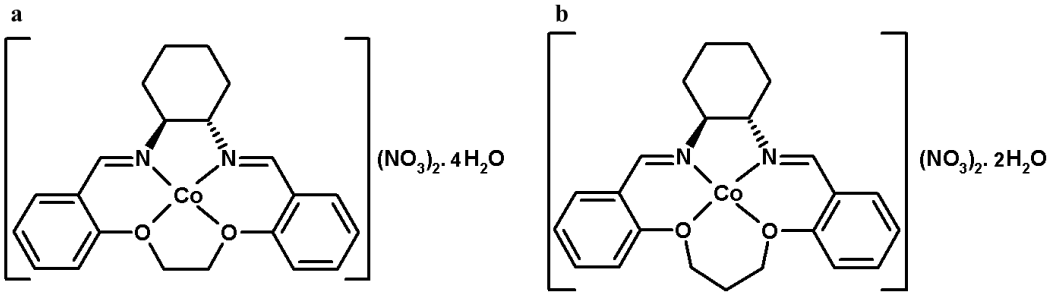
Preparation of Co(II) complexes

The macrocyclic cobalt(II) complexes 1 and 2 used in the paper were prepared according to the literature (Yilmaz, *et al.*, 2009). Anal. calcd for $C_{22}H_{24}N_4CoO_8.4H_2O$ (1): C, 43.78; H, 5.34; N, 9.28%; Found C, 43.89; H, 5.52; N, 9.57%. FT-IR (KBr, cm^{-1}): 1631 (C=N), 1384 (NO_3). Anal. calcd for $C_{23}H_{26}N_4CoO_8.2H_2O$: C, 47.51; H, 5.16; N, 9.63%; Found C, 47.66; H, 5.27; N, 9.51%. FT-IR (KBr, cm^{-1}): 1627 (C=N), 1383 (NO_3).

RESULTS AND DISCUSSION

Complexes

The macrocyclic cobalt(II) complexes (1) and (2) are insoluble in most common organic solvents such as methanol, chloroform, ethanol and acetonitrile. Then, the suitable crystals of the complexes could not be obtained for single-crystal X-ray structure determination. In the FT-IR spectra of the complexes a sharp band appear at 1631 and 1627 cm^{-1}, respectively, are corresponding to the frequency vibrations of C=N group of macrocyclic ligand indicating coordination



Scheme 1: The chemical structures of a) (1) and b) (2).

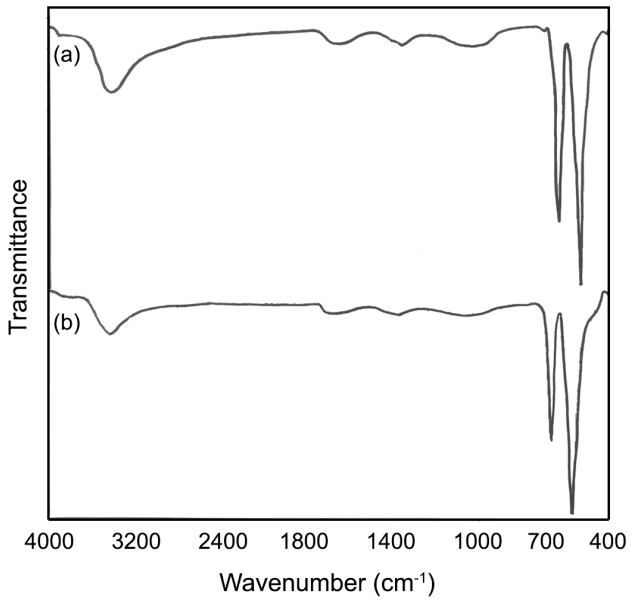


Fig. 1: FT-IR spectra of the Co_3O_4 nanoparticles prepared from a) (1) and b) (2).

of the azomethine nitrogen to cobalt ion. The stretching frequencies at 1384 and 1383 cm^{-1}, respectively, are corresponding to NO_3 counter ion (Yilmaz *et al.*, 2009).

Co_3O_4 nanoparticles

The Co_3O_4 nanoparticles were obtained by calcinations of complexes in an air atmosphere at 600°C for 3 h. The FT-IR spectra of the as-prepared Co_3O_4 nanoparticles are represented in Fig. 1 and shows two absorption bands at about 664 and 570 cm^{-1}, that are assigned to the CoIII-O and CoII-O vibration in octahedral and tetrahedral sites of Co_3O_4 lattice, respectively (Hosseinian, *et al.*, 2012, Farhadi and Pourzare, 2012).

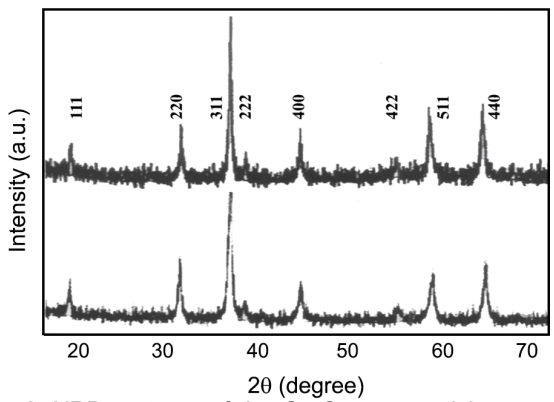


Fig. 2: XRD patterns of the Co_3O_4 nanoparticles prepared from a) 1 and b) 2.

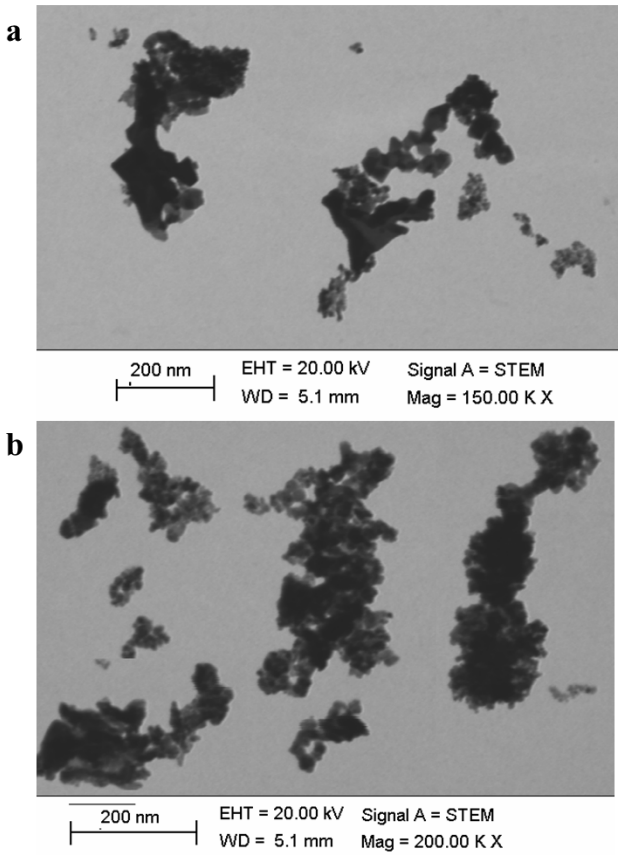


Fig. 3: TEM images of the Co_3O_4 nanoparticles prepared from a) 1 and b) 2.

The XRD patterns of Co_3O_4 nanoparticles prepared from 1 and 2 are shown in Fig. 2. The XRD patterns reveals diffraction peaks with 2 theta values of 19, 31, 37, 38, 45, 56, 59 and 65 that are assigned to the 111, 220, 311, 222, 400, 422, 511 and 440 crystal planes of the crystalline phase of Co_3O_4, respectively. All of the diffraction peaks are in good agreement with the cubic Co_3O_4 phase (Makhlouf, *et al.*, 2013), confirms that the macrocyclic cobalt(II) complexes 1 and 2 are decomposed completely into the cubic Co_3O_4 phase and is in good agreement with the FT-IR results. The crystal sizes of the Co_3O_4 nanoparticles based on the FWHM of the all diffraction peaks are in the range of 20 to 40 nm.

The morphology of the Co_3O_4 products was investigated by TEM (Fig. 3). The TEM samples were prepared by dispersing the powder in ethanol by ultrasonic vibration. From the TEM images, it was observed that the nanoparticles were approximately similar shapes and uniform sizes with weak agglomeration.

CONCLUSIONS

In this work, it was demonstrated that Co_3O_4 nanoparticles can be obtained by a simple solid-state thermal decomposition route of cobalt(II) macrocyclic Schiff base complexes, $[CoL^1](NO_3)_2.4H_2O$ (1) and $[CoL^2](NO_3)_2.2H_2O$ (2), as new precursors for the first time in air at 600ºC for 3 h. The synthesis method is simple, mild and can also be extended to other transition metal oxides.

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