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Research Article

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Synthesis and characterization of new nanostructure complex $[Co(dipic)_2Ni(OH_2)_6]$, as a precursor for the synthesis of $NiCo_2O_4$ nanoparticles

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ABSTRACT

In this research, nano-structure and single crystals(bulk)of, $[Co(dipic)_2Ni(OH_2)_5].2H_2O$ where dipic is pyridine -2,6-dicarboxylic acid, was synthesized using the reaction of cobalt (II) nitrate hexahydrate, nickel (II) nitrate hexahydrate, NaOH andpyridine-2,6-dicarboxylic using sonochemical process and reflux approach respectively. The nano-structured of complex was characterized using scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and FT-IR spectroscopy and compared with bulk of this complex. The crystal structure(bulk) of this complex, which was synthesized using a reflux approach, was found to be a binuclear coordination complex and was determined using single-crystal X-ray diffraction. The cobalt center in $Co(dipic)_2^{-2}$ achieves hexacoordination by coordinating with two deprotonated dipicolinate groups, which acting as tridentate chelating ligands. In this structure $Ni(OH_2)_5(O)^{+2}$ part is formed by a hexacoordinated Ni center with five water ligands and one μ -carboxylate oxygen O from the $Co(dipic)_2^{-2}$ part. Pure phase $NiCo_2O_4$ nanoparticles were obtained by thermal decomposition of nano-sized complex at 500 °C under air atmosphere.

Keywords: Sonochemical method, Pure-phase NiCo₂O₄,. Binuclear complex., Crystal structure .Thermal decomposition.,

INTRODUCTION

Nanoscience and nanotechnology have grown at an enormous rate for the last three decades, and recent advances nanostructured materials have opened up new opportunities for diverse applications in electronics, catalysis, energy, materials chemistry and even biology. Materials in the nanometer-size regime often exhibit properties distinct from their bulk counterparts, in part because clusters that small have electronic structures that have a high density of states, but not yet continuous bands.

Nanomaterials can be produced by different methods: mechanical, chemical, hydrothermal, sol-gel, chemical deposition in vacuum, pyrolysis, combustion, chemical coprecipitation, etc. By each of these methods particles defined by a certain dimensional morphology and distribution can be obtained. The characteristics of nanoparticles can be modified by the action of additional external factors, such as microwave heating, ultrasonic treatment, etc. [1-5]. Ultrasounds have a wide range of uses, like applications in development of nanoparticles using solutions of different chemical compounds. The production facility consists of a thermostatic chamber where the solution of salts or other compounds is introduced and a high power ultrasonic generator. The last one produces a powerful stream of ultrasonic energy that breaks the chemical bonds of compounds [5-12].

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Many researchers have investigated the effect of ultrasound on chemical reactions, and most theories imply that the physical or chemical effects of ultrasound originate from acoustic cavitation within collapsing bubbles, which generates extremely localized hot spots having pressures of about1,000 bar, temperatures of roughly 5,000 K, and heating and cooling rates of about 1010 Ks-1. Between the microbubble and the bulk solution, the interfacial region around the bubble has very large gradients of pressure, temperature, and the rapid motion of molecules leading to the production of excited states, bond breakage, the formation of free radicals, mechanical shocks, and high shear gradients [13]. The use of high-intensity ultrasound to enhance the reactivity of metals as a stoichiometric reagent has become a synthetic technique for many heterogeneous organic and organometallic reactions [14-18]. The physical effects of ultrasound (e.g., ultrasound-induced shockwaves and microjets at the liquid-solid interface) are primarily responsible for unusual sonochemical effects such as generation of surface damage, high-speed interparticle collisions, and fragmentation of friable solids[19]. The impact of shock waves and microjets on solid particles suspended in liquids was demonstrated in the early works of the Suslick research group[20-23]. The physical effects of ultrasound have often been utilized to deposit nanoparticles onto the surface of substrates. Gedanken and coworkers reported sonochemical deposition of in-situ generated noble metal nanoparticles on various substrates (e.g., silica, carbon, or polymer). This sonochemical process significantly reduces the reaction time, achieving uniform coating of nanoparticles on substrates. Also, noble metal nanoparticles can be easily anchored on various substrates without tailoring surface properties (e.g., attaching thiols to the surface of a substrate) via this procedure.

EXPERIMENTAL SECTION

Materials and physical techniques

All synthetic work was performed at room temperature. The water was distilled and deionized. $Co(NO_3)_2.6H_2O$, Ni(NO₃)₂.6H₂O, Pyridine 2,6-dicarboxylic acid and sodium hydroxide were obtained and used as received from Aldrich Chemical Co. Atomic absorption spectroscopy on metals was performed via Varian AA50 equipment. FT-IR spectra were recorded as KBr pellets on a FT-IR JASCO 460 spectrophotometer. X-ray data were collected on an STOE-IPDS 2T diffractometer, equipped with a graphite monochromator and using Mo K_a radiation (λ =0.71073). The morphology of bulk and nanostructured complex was studied by scanning electron microscopy technique (SEM) using a VEGA\\TESCAN-XMU. Phase analysis of the products was evaluated by X-ray diffraction (XRD) using Cu-K_a radiation between 0°-90° (20) with step size 0.02°/s recorded on a diffractometer model X Pert MPD. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software. Ultrasonic generators were carried out on ultrasonic equipment, (maximum 300 W at 20 kHz).

Synthesis of $[Ni(H_2O)_5Co(dipic)_2]$.2H₂O as single crystal

To an aqueous solution, containing an equimolar mixture of two metal nitrates [5.0 ml of $Co(NO_3)_2$ (0.50 mmol) + 5.0 ml of $Ni(NO_3)_2$ (0.50 mmol)] were added pyridine 2,6-dicarboxylic acid (167mg,1.00 mmol) and dropwise an aqueous solution (2.0ml) of NaOH (80 mg, 2.0 mmol) with continuous stirring at room temperature. Solution filtered off and left to evaporate in beaker in air at room temperature, After 5 days, black crystals of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$ were formed.

Synthesis of $[Ni(H_2O)_5Co(dipic)_2]$.2H₂O nanostructured by a sonochemical process

To prepare the nano-sized of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$, 40 ml solution of cobalt (II) nitrate hexa-hydrate (0.1 mol L⁻¹) and nickel(II) nitrate hexa-hydrate (0.1 mol L⁻¹) in water were positioned in a high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 300 W. Into this aqueous solution a 20 ml solution of the pyridine 2,6-dicarboxylic acid (0.2 mol L⁻¹) and an aqueous solution (20 ml) of NaOH (0.4 mol L⁻¹) were added dropwise. Solution filtered off and left to evaporate in beaker in air at room temperature, After 5 days, black crystals of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$ were formed.

Preparation of NiCo₂O₄nanoparticlesby thermal decomposition of $[Ni(H_2O)_5Co(dipic)_2]$. 2H₂O

For provide of NiCo₂O₄ nanoparticles, thermal decomposition of nanostructured[Ni(H₂O)₅Co(dipic)₂]. 2H₂O was done at 500 °C with heating rate 10 °C/min in static atmosphere of air for 4 h. After cooling, black precipitate was obtained. FT-IR spectrum and powder XRD diffraction shows that decomposition was complete.

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RESULTS AND DISCUSSION

The reaction of pyridine 2,6-dicarboxylic acid as ligand and aqueous solution of NaOH with cobalt (II) nitrate hexahydrate and nickel(II) nitrate hexahydrate results in the formation of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$. The nano-structured of this complex were synthesized using the ultrasonic method at an ambient temperature and atmospheric pressure. The single crystals (bulk) of this complex, which are suitable for X-ray crystallography, were synthesized according to section of 2, 2. The nano-structured of complex was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and FT-IR spectroscopy. The crystal structure of this complex, which synthesized using a reflux approach was found to be a binuclear coordination complex and was determined by single-crystal X-ray diffraction.

The FT-IR spectra of the bulk material of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$ (Figure. 1a) and that of the nano-structure produced using the sonochemical method (Figure. 1b), show broad absorption bonds at 3484-3323 cm⁻¹ for a single crystal assigned to the asymmetric and symmetric $v(H_2O)$ stretching vibration of coordinated and lattice water molecules. In asymmetric $v_{as}(COO)$ and symmetric $v_s(COO)$, the stretching vibrations of the dipicolinate carboxylate groups were observed at 1614, 1577 cm⁻¹ for $v_{as}(COO)$, and 1431, 1395 and 1383 cm⁻¹, for $v_s(COO)$ respectively. This complex as nanostructure shows broad absorption bonds at 3486-3241 cm⁻¹, for $v(H_2O)$ and 1614, 1578 cm⁻¹ of $v_{as}(COO)$ and 1432,1395 and 1384 cm⁻¹ for $v_s(COO)$ respectively.



Fig. 1. FT-IR spectra of [Ni(H₂O)₅Co(dipic)₂]. 2H₂O as (a) bulk, (b) nano-particles produced by sonochemical method

The Crystallographic data collections and structure refinements are listed in Table 1. The bond lengths, bond angles and hydrogen bond geometry of the complex are listed in Table 2 and 3. Figure2 shows the ORTEP diagram of. $[Ni(H_2O)_5Co(dipic)_2].2H_2O$. The X-ray single crystal, showed, in the structure of complex $[Ni(H_2O)_5Co(dipic)_2].2H_2O$, the coordination number for Ni and Co is six and $[Ni(H_2O)_5(O)]^{2+}$ part, is formed by a hexacoordinated Ni center with five water ligands and one μ -carboxylate oxygen O from the $[Co(dipic)_2]^2$ part. The cobalt ion accede six coordination by coordinating with two deprotonated dipicolinate groups, acting as tridentate chelating ligands. The complex, crystallizes in the monoclinic space group P21/c. The linkage of $[Ni(H_2O)_5(O)]^{2+}$ and $[Co(dipic)_2]^{2-}$ and inter molecular hydrogen bonds between coordinated water molecule and oxygen of dipicolinate and intra molecular hydrogen bonds between two crystallization water molecules and oxygen of dipicolinate leading to the stabilization of layers of bulk structure (Table 3)

Empirical formula	C14H20CoNiN2O15	
Formula weight	573.96	
Temperature (K)	298(2)	
Wavelength (A ^o)	0.71069	
Crystal system	Monoclinic	
Space group	P2(1)	
a (A°)	8.4548(17)	
b (A°)	27.170(5)	
c. (A°)	9.7380(19)	
α (°)	90	
β (°)	98.50(3)	
λ (°)	90	
V (A°)	2212.4(8)	
Z	4	
ρ_{calc} (Mg/m ³)	1.723	
$\mu(Mo K\alpha) (mm^{-1})$	1.678	
F(000)	1172	
Theta range for data collection	2.55 to 28.00	
R(int)	0.0183	
R ₁ , wR2	0.0458, 0.1177	
Largest difference in peak and hole	0.827 and -1.234	

 $Table \ 1 \ Crystal \ data \ and \ structure \ refinement \ details \ for \ complex \ [Ni(H_2O)_5 Co(dipic)_2]. \ 2H_2O(dipic)_2] \ data \ and \ structure \ refinement \ details \ for \ complex \ [Ni(H_2O)_5 Co(dipic)_2]. \ and \ and \ structure \ refinement \ data \ and \ structure \ refinement \ and \ structure \ refinement \ and \ structure \ refinement \ and \ structure \ s$

Table 2 Selected bond lengths (A $^{\circ}$) and angles($^{\circ}$) for [Ni(H₂O)₅Co(dipic)₂]. 2H₂O

1.977(2)	Co(1)-O(7)	2.107(2)
1.979(2)	Co(1)-O(5)	2.165(2)
2.172(2)	Co(1)-O(1)	2.175(2)
2.098(3)	Ni-O(9)	2.105(3)
2.123(2)	Ni-O(11)	2.127(2)
2.127(3)	Ni-O(15)	2.228(2)
	Bond angles	
97.21(9)	N(1)-Co(1)-O(5)	102.10(9)
96.45(13)	O(7)-Co(1)-O(5)	154.19(9)
88.98(10)	N(2)-Co(1)-O(3)	108.61(9)
88.98(10)	N(1)-Co(1)-O(3)	76.69(8)
175.86(10)	O(7)-Co(1)-O(3)	87.29(10)
85.95(9)	O(2)-Ni-O(11)	170.30(9)
116(3)	O(12)-Ni-O(10)	167.63(10)
77.55(9)	O(9)-Ni-O(11)	90.96(11)
153.96(8)	O(12)-Ni-O(11)	90.62(9)
103.42(9)	O(9)-Ni-O(2)	87.22(10)
78.01(9)	O(12)-Ni-O(2)	80.13(9)
94.10(9)	O(12)-Ni-O(15)	86.35(11)
100.51(10)	O(2)-Ni-O(15)	96.28(9)
96.28(9)	Ni-O(15)-H(15B)	113(3)
	$\begin{array}{c} 1.977(2)\\ 1.977(2)\\ 2.197(2)\\ 2.098(3)\\ 2.123(2)\\ 2.127(3)\\ 97.21(9)\\ 96.45(13)\\ 88.98(10)\\ 88.98(10)\\ 175.86(10)\\ 85.95(9)\\ 116(3)\\ 77.55(9)\\ 116(3)\\ 77.55(9)\\ 153.96(8)\\ 103.42(9)\\ 78.01(9)\\ 94.10(9)\\ 100.51(10)\\ 96.28(9)\\ \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$



Fig. 2.ORTEP representation of [Ni(H₂O)₅Co(dipic)₂].2H₂O complex

D-HA	d(DA)	(D-HA)
O9-H9AO7	3.29	124.46 (iii)
O9-H9BO2	2.89	78.89 (i)
O10-H10AO	15 4.43	89.08 (i)
O10-H10BO	1 3.37	152.40 (i)
011-H11A09	9 3.40	87.67 (i)
O11-H11BO	12 3.07	81.52 (i)
012-H12A0	14 2.62	171.96 (ii)
O12-H12BO	11 3.39	83.61 (i)
O13-H13AO	5 2.5	197.83 (iv)
O13-H13CO	6.16	106.23 (v)
O14-H14BO	12 4.22	83.25 (ii)
O14-H14AO3	2.32	128.80(i)
O15-H15BO	12 2.45	84.21(i)

Table 3Hydrogen bond geometry (A°) in complex [Ni(H₂O)₅Co(dipic)₂]. 2H₂O

Symmetry transformations used to generate equivalent atoms

:(i) x, y, z, (ii) -x+1,-y,-z+1 (iii) x,+y,+z-1(iv) x-1,+y,+z, (v) x,-y+1/2,+z-1/2

The reaction between pyridine 2,6-dicarboxylic acid and aqueous solution of NaOH with cobalt (II) nitrate hexahydrate and nickel tetrahydrate, leads to formation of $[Ni(H_2O)_5Co(dipic)_2].2H_2O$. The morphology of complex prepared by the sonochemical method and single crystal synthesized by reflux was characterized by scanning electron microscopy (SEM). Figure 3a shows the SEM of this complex prepared using ultrasonic. Figure3b shows the SEM image of the bulk powder sample. This images show, the particles size of bulk complex is bigger than the nano-structured sample, synthesis using ultrasonic method.

Figure4b shows the XRD graph from single crystal (bulk)in comparison with the XRD graph of nano structure complex (Figure4a). Acceptable matches, with slight differences in 2θ , were observed between the simulated and experimental powder X-ray diffraction graph. This indicates that the compound obtained by the sonochemical method as nanoparticles is similar to that synthesis by single crystal.



Fig. 3. SEM images of complex: (a) of nano-sized complex prepared by ultrasonic, (b) of bulkpowder prepared via simple mixing of precursors



Fig. 4. XRD pattern: (a) nano-structure of [Ni(H₂O)₅Co(dipic)₂].2H₂O prepared by sonochemical process, (b) simulated pattern based on single-crystal of this complex

To study, the compound of the final thermal decomposition, XRD was carried out. Figure 5 shows the XRD graph of nano-sized[Ni(H₂O)₅Co(dipic)₂].2H₂O at 500 °C under atmosphere monitoring for 4h. The obtained graph, relevant with the standard pattern of NiCo₂O₄ with the lattice parameters (a=8.1140 Ű, b=8.1140 Ű, c=8.1140 Ű, S.G = Fd-3m and z = 8) observed to be the same as the reported values (JCPDS card number.01-073-1702). An SEM image of the residue, which was obtained from the thermal decomposition of nano-structure of this complex at 500 °C shows the formation of NiCo₂O₄ anoparticles (Figure 6).



Fig. 5. XRD pattern of the residue obtained from calcination of nanostructured complex at 500°C



Fig. 6. SEM image of NiCo₂O₄nanoparticles prepared by calcination of [Ni(H₂O)₅Co(dipic)₂].2H₂O at 500°C

CONCLUSION

A new nano-sized complex of $[Mn(H_2O)_5Co(dipic)_2].2H_2O$, was synthesized using sonochemical irradiation and its crystalline structure(bulk) was synthesized using reflux apparatus, and compared by, FT-IR spectroscopy, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM), The crystal structure of the compound was found to be a hetero binuclear coordination compound and shows that the coordination number for Ni(II) and Co(II) ions is six. In this structure, cationic part is formed by a hexa-coordinated Ni center with five water ligands and one μ -carboxylate oxygen O from the Co(dipic)₂⁻² part. The cobalt ion accede hexa-coordination by coordinating with two deprotonated dipicolinate groups, function as tridentate chelating ligands. The nano-structured complex of[Ni(H₂O)₅Co(dipic)₂]. 2H₂O was decomposed at 500 °C under air atmosphere to produce NiCo₂O₄nanoparticles and characterized by SEM and XRD techniques.

Supplementary material

Crystallographic data for the structure reported in the paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-1423364. Copies of the data can be obtained on application to CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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