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Synthesize and crystal structure of a novel complex $[Co(dipic)_2Mn)OH_2(5].2H_2O$ prepared by different methods

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In this research, a new complex of [Co(dipic)2Mn)OH2(5].2H2O, where dipic is pyridine-2,6-dicarboxylic acid synthesized by sonochemistry (1) and reflux (2). The crystals of this complex, were prepared by reflux and characterized by single crystal X-ray diffraction)SC-XRD). The crystal structure of this complex was found to be a binuclear coordination complex. The structure of complex 2 was compared to that of the structure complex prepared by sonochemistry (1), using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), x-ray powder diffraction (XRD).

Keywords: Sonochemical method; Reflux; Crystal structure; Binuclear complex.

1.INTRODUCTION

Ultrasound has been used for diverse purposes in many different areas. In terms of frequency, ultrasound can be categorized into two main strands:(1) high frequency (2-10 MHz)-low power diagnostic ultrasound, involving medical imaging, nondestructive testing, and (2) low to medium frequency (20-1000 KHz), frequency-high power ultrasound, involving other application in industry, nanotechnology, ultrasonic therapy, and sonochemistry [1]. 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 [2-6]. Recent advances in nanostructured materials have been led by the development of new synthetic methods that provide control over size, morphology, and nano/microstructure. The utilization of high intensity ultrasound offers a facile, versatile synthetic tool for nanostructured materials that are often unavailable by conventional methods. The chemical effect of ultrasound has been explored for many years, practically in water [7-10]. Ultrasonic irradiation of aqueous liquids generates free radicals, and the formation of free radicals by sonolysis of water has been particularly well-studied. Sonolysis products in water are H and OH. Radicals. These radicals can recombine to return to their original form or combine to produce H2 and H2O2. They can also produce HO2 by combining with O2. These strong oxidants and reductants are utilized for various sonochemical reactions in aqueous solutions [11]. In the recent past, it has been recognized that sonochemistry is one of the new techniques for the synthesis of functional nanoparticles and nanostructured materials, because a unique reaction can be induced by the irradiation of a liquid at approximately room temperature [12]. By decreasing the size of coordination, supramolecular compounds as polymers in nanosize, surface area will increase. Hence, the production of supramolecular coordination compounds in any form in nanoscale is certainly a major step forward in the technological application of these new materials [13]. Bimetallic clusters are known to exhibit specific reactivity. Their catalytic efficiency is also controlled by their size. One of the most important factors controlling the reactivity of metal clusters is the nucleation and growth mechanism of the clusters [14-17]. It seems that most of the features presented by the final clusters depend on the synthetic conditions under which clusters are formed during the early steps of the metal ion reduction. Therefore, it is of interest to develop new and effective preparation methods. Various methods of preparation have been reported: chemical reduction, photolytic reduction, radiolytic reduction and metal evaporation [18-21]. The sonochemical synthesis of nanometric materials has been found to be unique due to the unusual experimental conditions generated during acoustic cavitation [22-25].

In this investigation, a novel complex of [Co(dipic)2Mn(OH2)5].2H2O, was prepared by two methods, reflux and sonochemistry and confirmed by various techniques.

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2. EXPERIMENTAL

Materials and method

All synthetic work was done at room temperature. Co(NO3)2.6H2O, Mn(NO3)2.4H2O, pyridine 2,6-dicarboxylic acid, and sodium hydroxide were obtained and used as received from Aldrich Chemical. FT-IR spectra were recorded as KBr pellets on a FT-IR JASCO 460 spectrophotometer. Measurements of C, H and N were applied using a Pakin-Elmer 2400 CHN elemental analyzer. The morphology of complex was studied by scanning electron microscopy technique (SEM) using a VEGA\\TESCAN-XMU equipment. Phase analysis for sample prepared by sonochemistry was evaluated by X-ray diffraction (XRD) using Cu-Kα radiation between 0°-50° (2θ) with step size 0.02 °s-1 was recorded on a diffractometer model X Pert MPD. The XRD graph for single crystal 2 was prepared using Mercury software.

Sonochemical Synthesis of [Co(dipic)$_2$ Mn)OH$_2$(5] 2H$_2$O (1)

For preparation of [Co(dipic)$_2$Mn)OH$_2$(5].2H$_2$O, to 10 mL aqueous solution of cobalt (II) nitrate hexahydrate (0.1 M) and manganese (II) nitrate tetrahydrate (0.1 M) under ultrasonic irradiation, were added gutty (10 mL) aqueous solution of pyridine-2,6-dicarboxylic acid (0.2 M) and (10 mL) of sodium hydroxide (0.4 M) under high-density ultrasonic probe, operating at 20 KHz with a maximum power output of 300 W for 1 hour. The obtained red crystals were filtered off and then dried in air. Analytical calculation for C14H20CoMnN2O15: C, 29.46; H, 3.50; N, 4.90 Found: C, 28.23; H, 3.12; N, 4.70.

Synthesis single crystal of [Co(dipic)$_2$Mn)OH$_2$(5.2H$_2$O by reflux (2)

The equivalent molar ratios of two metal nitrates, 5.0 mL of Co(NO3)2 (0.50 mmol) and 5mL of Mn(NO3)2 (0.50 mmol) were dissolved in 10.0 mL of distilled water. Next, pyridine-2,6-dicarboxylic acid (167mg, 1.00 mmol) and an aqua solution (2.0 mL) of NaOH (80 mg, 2.0 mmol) were added gutty to this solution. The mixture was stirred at room temperature. Solution filtered off and left to evaporate at room temperature. After 5 days, red crystals of [Co(dipic)2Mn)OH2(5].2H2O, were formed 62% yield based on metal nitrates. Analytical calculation for C14H20CoMnN2O15: C, 29.46; H, 3.50; N, 4.90; Found: C, 28.94; H, 3.25; N, 4.73.

3. RESULT AND DISCUSSION

The crystallography data collections and structure refinement of [Co(dipic)$_2$Mn)OH$_2$(5].2H$_2$O (2) are listed in Table 1. Bond lengths and bond angles for single crystal (2) are listed in Table 2 and hydrogen bonds are listed in Table 3. Fig. 1, shows the ORTEP diagram of [Co(dipic)$_2$Mn)OH$_2$(5].2H2O. In the structure of complex [Mn(H$_2$O)$_5$Co(dipic)2].2H2O, the coordination number for Mn and Co is six and [Mn(H2O)5]2+ is formed by hexacoordinated Mn(II) center with five aqua ligands and one oxygen from the carbonyl group of pyridine-2,6-dicarboxylic acid of [Co(dipic)$_2$]$_2$ and forming octahedron. The cobalt ion achieves six coordination by coordinating with two deprotonated dipicolinate groups, acting as tridentate chelating ligands. As shown in Fig.2 the coordination geometry around Co(II) is a distorted octahedron, because as shown in Table.2 bond distances around Co is different. The title complex crystallized in the monoclinic space group P21/c. The linkage of [Mn(H$_2$O)$_5$]$^{2+}$ 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 (Fig. 3).

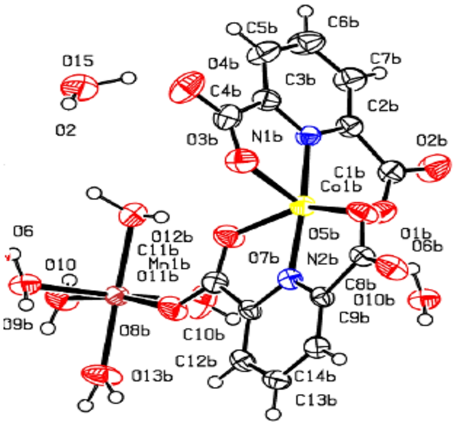

Fig. 1.ORTEP representation of [Mn(H2O)5Co(dipic)2].2H2O

Table 1. Crystal data and structure refinement details for complex [Co(dipic)2Mn(OH2)5].2H2O

Empirical formula	$C_{14}H_{20}CoMnN_2O_{15}$
Formula weight	570.19
Temperature (K)	293(2)
Wavelength (A$^{\circ}$)	0.71073
Crystal system	Monoclinic
Space group	P21/c
a (A$^{\circ}$)	8.4425(17)
b (A$^{\circ}$)	27.340(5)
c. (A$^{\circ}$)	9.7050(19)
α (^{o})	90
β (^{o})	98.33(3)
λ (^{o})	90
V (A$^{\circ}$)	2216.5(8)
Z	4
ρ_{calc} (Mg/m^3)	1.709
μ(Mo Kα) (mm^{-1})	1.395
F(000)	1160
Theta range for data collection	2.6 to 25.0
R(int)	0.078
R_1, wR2	0.0346, 0.0594
Largest difference in peak and hole	0.44, -0.73

Table 2. Selected bond lengths (A^{o}) and angles(^{o})for complex $[Co(dipic)_2Mn(OH_2)_5].2H_2O$

Bond lenghts			
Co1-O1	2.185(2)	Co1-O3	2.119(2)
Co1-O5	2.183(2)	Co1-O7	2.212(2)
Co1-N1	2.010(3)	Co1-N2	2.028(3)
Mn1-O8	2.133(2)	Mn1-O9	2.135(2)
Mn1-O11	2.115(3)	Mn1-O12	2.147(2)
Bond angles		Bond angles	
O9-Mn1-O12	101.61(9)	O9-Mn1-O11	90.77(9)
O11-Mn1-O10a	86.31(9)	O9-Mn1-O13	89.89(9)
O11-Mn1-O13	97.40(10)	O11-Mn1-O12	89.08(10)
O1-Co1-N1	75.47(10)	O10a-Mn1-O11	175.49(10)
O3-Co1-O5	86.32(9)	O1-Co1-N2	103.83(10)
O3-Co1-N1	76.67(10)	O3-Co1-O7	96.67(9)
O5-Co1-N2	75.28(9)	O5-Co1-N1	112.53(9)

Table 3.Hydrogen bond geometry (A^{o}) in complex $[Co(dipic)_2Mn(OH_2)_5].2H_2O$

D-H….A	d(D…A)	(D-H…A)
O9-H4…O5	2.759(3)	166
O9-H5…O15	2.661(4)	161
O10-H6…O1	2.799(3)	168
O10-H7…O6	2.691(3)	168
O11-H8…O14	2.822(4)	160
O11-H9…O4	2.720(4)	170
O12-H10…O7	2.834(3)	168
O12-H11…O2	2.707(3)	173
O13-H12…O6	2.662(3)	154
O13-H13…O14	2.964(3)	162
O14-H17…O10	2.949(3)	167
O14-H18…O3	3.070(3)	145
O14-H18…O3	2.780(5)	166
O15-H21…O2	2.797(4)	158

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

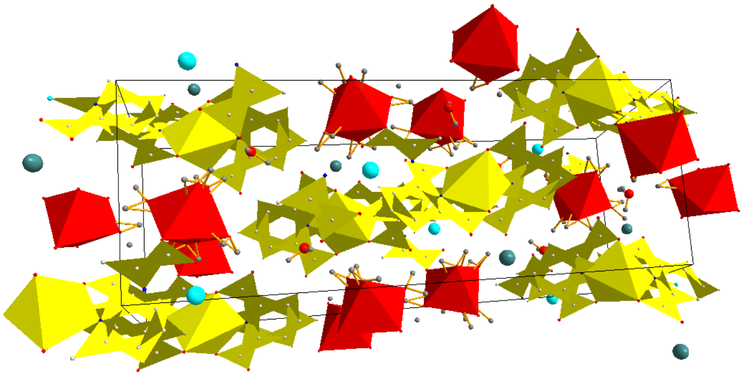

Fig. 2. Octahedral geometry around Co (yellow) and Mn (red) for [Mn(H2O)5Co(dipic)2].2H2O complex.

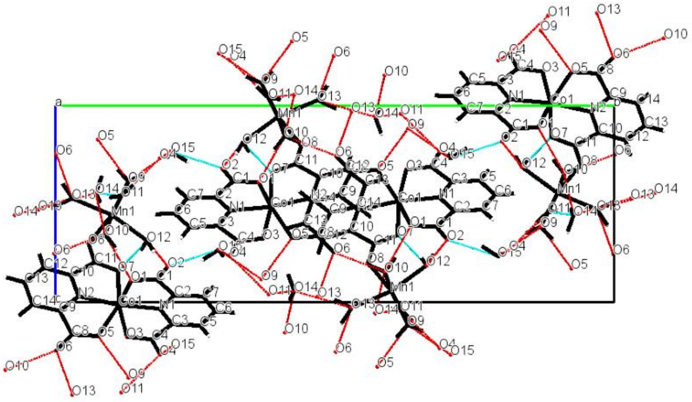

Fig. 3. Inter and intra molecular hydrogen bonds for [Mn(H2O)5Co(dipic)2].2H2O complex

The FT-IR spectrum of $[Co(dipic)_2Mn)OH_2(5].2H_2O$ prepared by reflux (2) (Fig. 4a), show broad absorption bonds at 3484-3239 cm-1, assigned to the asymmetric and symmetric υ(H2O) stretching vibration of coordinated and lattice water molecules. The stretching vibrations of dipicolinate carboxylate groups were observed at 1614, 1588 cm-1 for υas(COO), and 1469, 1429 and 1383 cm-1, for υs(COO), respectively. The FT-IR spectrum of complex 1 (Fig. 4b) is the same with FT-IR of single crystal 2 (Fig. 4a).

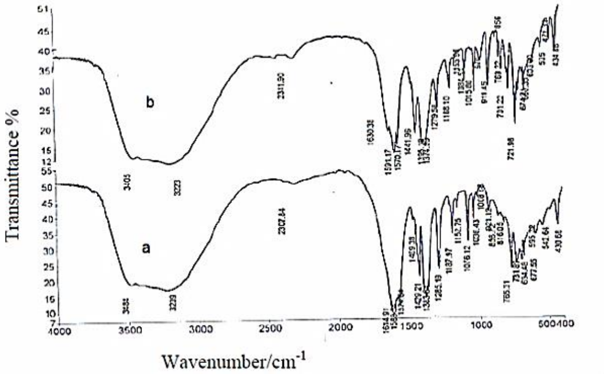

Fig. 4. FT-IR spectra of $[Mn(H_2O)_5Co(dipic)_2]$. $2H_2O$. (a) prepared by reflux, (b) produced sonochemically.

The morphology of complexes synthesized by sonochemistry (1) and reflux (2) characterized by scanning electron microscopy (SEM). Fig. 5, shows the SEM of these complexes. Images show that, the particles size of complex was prepared by reflux is bigger than in grain size of complex was prepared by sonochemical method with the same concentration, owing to preparation methods are different for these complexes and in sonochemistry, usage of high intensity ultrasound is a good synthetic method for preparation nanostructured materials that are often unavailable by other method [13].

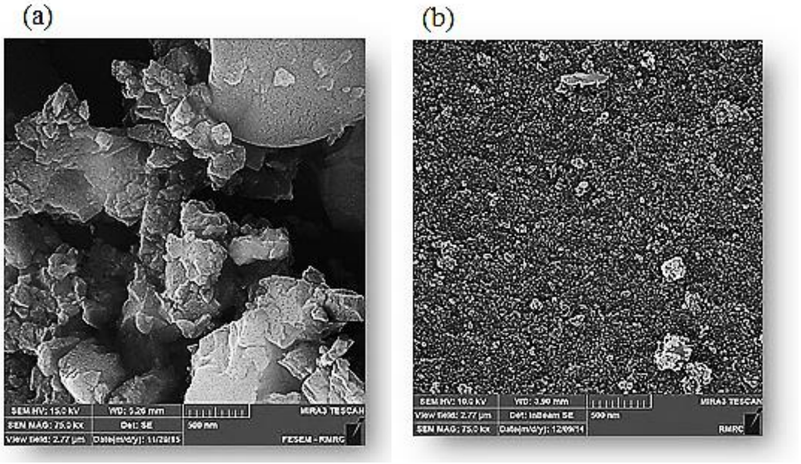

Fig. 5. SEM images of [Mn(H2O)5Co(dipic)2].2H2O (a) prepared by reflux (b) prepared by sonochemistry.

The structural comparison of these complexes was performed by X-ray powder diffraction analysis (XRD). Fig. 6a shows the XRD graph of the typical sample of this complex was prepared by sonochemical process. Fig. 6b shows the XRD graph from single crystal 2, this pattern was obtained using Mercury software.

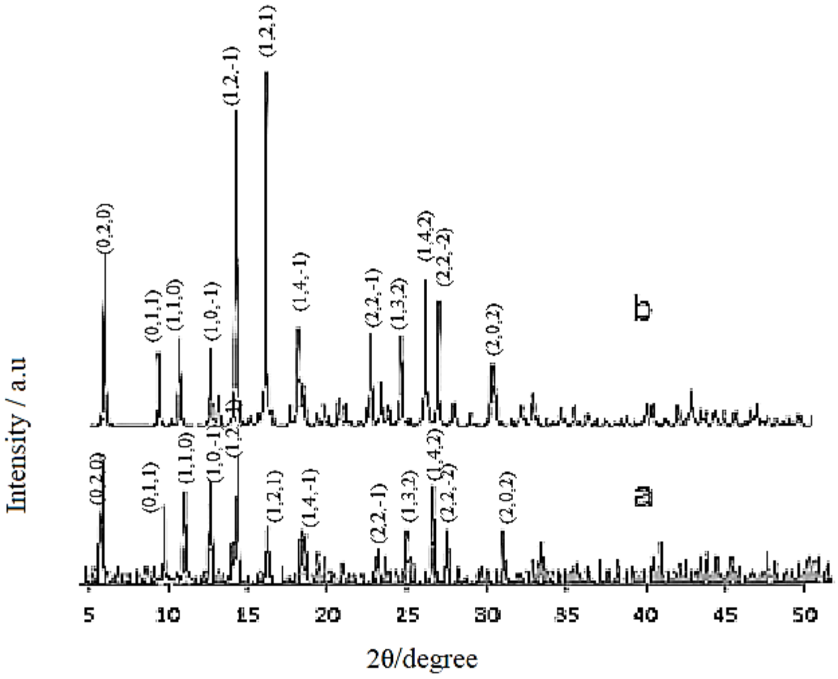

Fig. 6. XRD pattern of [Mn(H2O)5Co(dipic)2].2H2O (a) prepared by sonochemical process, (b) prepared by reflux.

4. CONCLUSION

In this work, new complex of [Co(dipic)2Mn)OH2(5].2H2O synthesized by reflux and characterized by SC-XRD and elemental analysis. In different method, this complex was prepared by sonochemistry, next these structures compared by, FT-IR spectroscopy, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The results confirmed that, these structures are the same but complex 1 has smaller particles size than complex 2.

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-1423365. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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