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THERMOLYSIS PREPARATION OF CADMIUM(II) OXIDE NANOPARTICLES FROM A NEW THREE-DIMENSIONAL CADMIUM(II) SUPRAMOLECULAR COMPOUND

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The reaction of cadmium(II) chloride and 4-pyridine carboxylic acid (4-Hpyc) produces a new three-dimensional supramolecular compound $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ (**1**). Compound **1** is characterized by IR spectroscopy and elemental analyses. The single crystal X-ray data show an infinite three-dimensional structure formed by the hydrogen bonding and π—π stacking interactions. The CdO nanoparticles are obtained by direct calcination at 400 °C, 500 °C and 600 °C in the air atmosphere as well as by thermolysis in oleic acid at 200 °C. The obtained cadmium(II) oxide nanoparticles are characterized by X-ray diffraction and scanning electron microscopy. This study demonstrates another potential application of cadmium(II) supramolecular compounds in the preparation of nanoscale cadmium(II) oxide materials with a specific size and morphologies.

Keywords: supramolecular, cadmium(II) oxide, nanoparticle, thermolysis.

INTRODUCTION

During the last two decades, supramolecular compounds and especially coordination polymers have received great attention and the number of their synthesized compounds is still growing, which is mainly due to their potential application in various fields such as microelectronics, nonlinear optics, ion exchange, catalysis, gas storage, separation and luminescence [1—6]. In modern coordination chemistry the role of most metals as clustering centers for ligands appears to be predictable and the coordination number and the coordination geometry can be extrapolated for most of the common metal/ligand combinations with quite high certainty.

As a d^{10} metal ion Cd(II) is particularly suited for the construction of coordination polymers and networks. The spherical d^{10} configuration is associated with a flexible coordination environment so that geometries of these complexes can vary from tetrahedral (CN = 4) to dodecahedral (CN = 8) and severe distortions in the ideal polyhedron easily occur. Furthermore, due to the general lability of Cd complexes, the formation of coordination bonds is reversible, which enables metal ions and ligands to rearrange during the process of polymerization to give highly ordered network structures. Consequently, Cd(II) can readily accommodate all kinds of architectures and a selection of topological types of 1D, 2D and 3D polymers is given [7—17].

Cadmium(II) oxide based transparent conductive oxides have been of interest because of their relatively simple crystal structures, high carrier mobility, and sometimes nearly metallic conductivities. Cadmium(II) oxide have been extensively used as transparent conducting oxide (TCO) materials. Bulk cadmium(II) oxide (CdO) is an *n*-type semiconductor, with a wide direct band gap of 2.27 eV and a narrow indirect band gap of 0.55 eV [18—20]. In this paper, we report a new three-dimensional supramolecular compound $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ (**1**). This compound was used as a precursor for the

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preparation of cadmium(II) oxide nanoparticles. Two different methods were described for the synthesis of cadmium(II) oxide nanoparticles: direct calcination at three different temperatures and decomposition in oleic acid of compound **1**.

EXPERIMENTAL

Materials and physical techniques. All reagents for the synthesis and analysis were commercially available and used as received. Microanalyses were carried out using a Heraeus CHN—O—Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromataed MoK_α radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Structure solution and refinement were accomplished using SHELXL-97 program packages [21]. The molecular structure plot and the simulated XRD powder pattern based on single crystal data were prepared using the Mercury software [22]. X-ray powder diffraction (XRD) measurements were performed using a Philips X′pert diffractometer with monochromatized CuK_α radiation. The samples were characterized with a scanning electron microscope (SEM) with gold coating.

Synthesis of $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ (1). Compound **1** was prepared using the branched tube method: 4-pyridine carboxylic acid (0.117 g, 1 mmol) and cadmium(II) chloride (0.114 g, 0.5 mmol) were placed in the main arm to be heated. Water was carefully added to fill both arms, and then the arm to be heated was placed in a bath at 60 °C. After 10 days, colorless crystals were deposited in the cooler arm, which were filtered off, washed with water and air dried. (0.104 g, yield 55.8 %), m.p. > 300 °C. (Anal. calc. for $C_3H_4Cd_{0.25}N_{0.50}O_2$: C, 33.59; H, 3.73; N, 6.53 %; found; C, 32.80; H, 3.79; N, 6.44 %). IR (cm^{-1}) selected bands: 684(vs), 776(s), 853(m), 1007(m), 1392(vs), 1538(vs), 1584(vs) and 3350 (br).

Synthesis of cadmium(II) oxide nanoparticles by direct calcination of compound 1. Nanostructures of CdO have been generated by the thermal decomposition of compound **1**. The final product upon the calcination of compound **1** at three different temperatures, based on their IR and XRD patterns, is CdO in all three cases.

Synthesis of cadmium(II) oxide nanoparticles by thermal decomposition in oleic acid as a surfactant. To prepare cadmium(II) oxide nanoparticles by surfactant, a small amount of compound **1** (446 mg, 2.0 mmol) was dispersed in oleic acid (OA), (16 ml, 50 mmol) to form a homogenous emulsion solution. This solution was degassed for 1 h and then heated to 200 °C for 2 h under an air atomsphere in an electric furnace. At the end of the reaction, a black precipitate was formed. A small amount of toluene and a large excess of EtOH were added to the reaction solution; finally, CdO nanoparticles were separated by centrifugation. The solid was washed with EtOH and dried; neither d.p. nor IR bands were observed.

RESULTS AND DISCUSSION

A reaction between 4-pyridine carboxylic acid (4-Hpyc) with cadmium(II) chloride leads to the formation of a new 3D Cd(II) supramolecular compound $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ (**1**). The crystal data for **1** indicate a triclinic space group P1 (Tables 1 and 2). The IR absorption bands in the frequency range 1405—1607 cm^{-1} correspond to vibrations of the pyridine rings. The vibrations ν(COO) are found at *ca* 1392 cm^{-1} and 1538 cm^{-1}. The broad band at 3350 cm^{-1} shows the existence of water in compound **1** [23]. Single crystal XRD analysis of compound **1** reveals that Cd(II) atoms are coordinated by water molecules and 4-pyridine carboxylate ligands resulting in a six-coordinate complex. The structure consists of $Cd(H_2O)_4$ units coordinated by 4-pyc$^-$ ligands, thus forming a mononuclear complex (Fig. 1). The carboxylate moieties of the 4-pyc$^-$ ligands act both as bidentate groups, where two oxygen atoms of the carboxylate group are bidentate toward the Cd(II) ion to create a four-membered chelate ring. The monomeric units are grown into a 3D framework through the hydrogen bonding and π—π stacking [24, 25] interactions (Fig. 2).

Table 1

Crystal data and structure refinement for [Cd(4-pyc)$_2$(H$_2$O)$_4$]$_n$ **1**

Empirical formula	$C_3H_4Cd_{0.25}N_{0.5}O_2$
Formula weight	107.17
Temperature	273(2)
Wavelength	0.71073
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions a, b, c, Å	6.4435(9), 6.9763(10), 9.4241(13)
α, β, γ, deg.	94.862(4), 104.682(4), 112.058(4)
V, Å^3	372.074
Z	4
Density (calculated), g·cm^{-3}	1.91305
Absorption coefficient, mm^{-1}	1.512
Crystal size, mm	0.21×0.18×0.15
θ range for data collection, deg.	2.28 to 25.24
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 7$, $-11 \le l \le 11$
Reflections collected	3231
Independent reflections	2056
Max. and min. transmission	0.7418 and 0.8049
Refinement method	Full-matrix Least-squares on F^2
Data / restraints / parameters	2056 / 12 / 216
Goodness-of-fit on F^2	1.131
Final R indices [I > 2σ(I)]	$R_1 = 0.0194$, $wR_2 = 0.0515$
R Indices (all data)	$R_1 = 0.0194$, $wR_2 = 0.0515$
Largest diff. Peak, hole, e/Å^{-3}	0.358 and –0.421

Table 2

Bond lengths (Å) *and angles* (deg.) *for* [Cd(4-pyc)$_2$(H$_2$O)$_4$]$_n$ **1**

Cd1—O5	2.288(8)
Cd1—O7	2.304(8)
Cd1—O8	2.308(10)
Cd1—N1	2.329(3)
Cd1—N2	2.331(3)
Cd1—O6	2.366(8)
O5—Cd1—O6	86.7(3)
O7—Cd1—O8	85.4(3)
O5—Cd1—N1	94.4(3)
O7—Cd1—N2	90.6(3)

In the solid state the [Cd(4-pyc)$_2$(H$_2$O)$_4$] moieties are bound through O—H···N hydrogen bonding involving one proton of the coordinated water molecules (the hydrogen-bond donor) and a heterocyclic nitrogen atom of py (the hydrogen-bond acceptor). Consequently the self-complementary hydrogen bonds system grows into a two-dimensional network by packing via the hydrogen-bonding interactions (Fig. 2). There are π—π stacking [11, 12] interactions between the aromatic rings belonging to 4-pyc$^-$ ligands in compound **1**. The py groups of 4-pyc$^-$ ligands are almost parallel and this parallel array of the planes of the aromatic moieties indicates that these interactions are of the face-to-face ″π-stacking″ type (Fig. 2) [25, 26].

The XRD pattern of the residue obtained from calcination of compound **1** matches with the standard pattern of monteponite cadmium(II) oxide with the lattice parameters (a = 4.6953 Å, space group $Fm3m$ and Z = 4), which is the same as the reported values (JCPDS card number 05-0640). SEM images of the residue obtained from the direct calcination of compound **1** show the formation of cadmium(II) oxide nanoparticles with a diameter distribution of 50—95 nm and an average diameter of about 77 nm at 400 °C (Fig. 3). The SEM images of CdO nanostructures produced by the calcination of compound **1** at 500 °C and 600 °C show that the particles are different in the three samples obtained at three different temperatures. This point shows the effect of the calcination temperature on the size of nanomaterials produced by calcination. At higher temperatures, agglomeration occurs and the particles formed have a larger size at 500 °C and 600 °C with an average particle diameter of about 83 nm and 92 nm respectively. Since the calcination process was successful for the preparation of cadmium(II) oxide nanopartic-

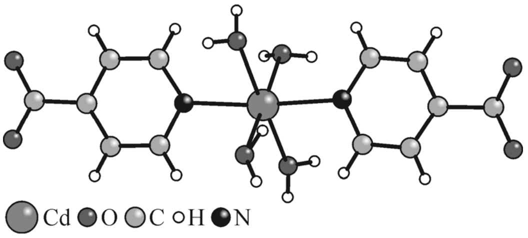

Fig. 1. Molecular structure and coordination environment of the [Cd(4-pyc)$_2$(H$_2$O)$_4$]$_n$ compound **1**

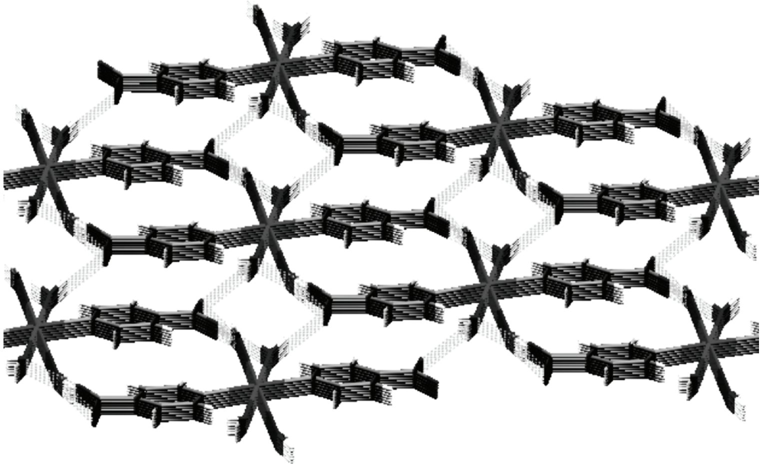

Fig. 2. A fragment of the 3D framework in the $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ compound **1** showing the hydrogen bonding and π—π stacking interactions

les, these experiments indicate that the calcination temperature correlates to the particle size of the formed cadmium(II) oxide nanoparticles and that the low temperature produces smaller particles of cadmium(II) oxide.

Surfactants are often used to synthesize nanostructures in order to change the morphology and particle size. To investigate the role of a surfactant on the particle size of cadmium(II) oxide nanostructures, the calcination of compound **1** was performed in the presence of oleic acid as a surfactant at 200 °C. As shown in Fig. 4, nanoparticles have been grown separately, which leads to the production of a suitable size of cadmium(II) oxide with an average particle diameter of about 70 nm. Again, the XRD pattern of the residue shows that the resulting residue was cadmium(II) oxide with the lattice parameters mentioned above.

CONCLUSIONS

A new Cd(II) three-coordination polymer $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ (**1**) (4-Hpyc = 4-pyridinecarboxylic acid) has been synthesized using a thermal gradient approach. Compound **1** was structurally characterized by single crystal XRD and consists of a 3D supramolecular compound. This polymer precursor has been thermally decomposed in a suitable surfactant to obtain nanosized CdO. Calcination of compound **1** at different temperatures without and with the surfactant produced nanoparticles of cadmium(II) oxide. Sizes of the CdO nanoparticles depend on the calcination temperature.

Supplementary material. Appendix A. Supplementary data CCDC 830644 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via

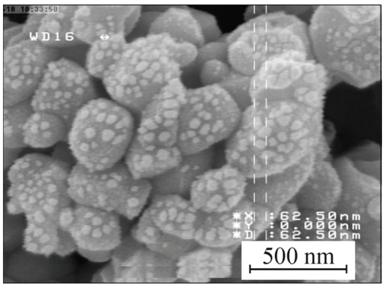

Fig. 3. SEM image of agglomerated CdO nanoparticles prepared by thermolyses of the $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ compound **1** at 400 °C

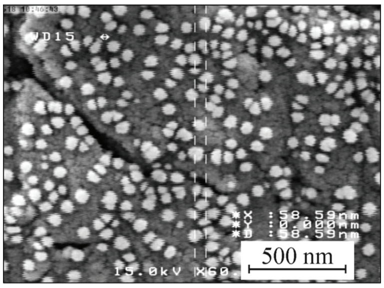

Fig. 4. SEM image of the nanostructures of the $[Cd(4\text{-pyc})_2(H_2O)_4]_n$ compound **1** prepared by treatment with oleic acid as a surfactant at 200 °C

http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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