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## Solid–solid synthesis, characterization and thermal decomposition of a homodinuclear cobalt(II) complex

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**Abstract:** The homodinuclear cobalt(II) complex  $[\text{Co}_2(\text{dipic})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  was synthesized using pyridine-2,6-dicarboxylic acid ( $\text{H}_2\text{dipic}$ ) and cobalt(II) acetate as raw materials by room temperature solid–solid reaction. The complex was characterized by elemental analyses, single crystal X-ray diffraction, X-ray powder diffraction, Fourier transform infrared spectroscopy, UV spectroscopy, thermogravimetry and differential scanning calorimetry. Its crystal structure belongs to monoclinic system and space group  $P2(1)/c$ . There are two types of six-coordinated Co(II) ions, one Co(II) is coordinated by four carboxyl O atoms and two pyridine N atoms from two  $\text{dipic}^{2-}$  anions, and another Co(II) is coordinated by five O atoms from five  $\text{H}_2\text{O}$  molecules and one bridged carboxyl O atom from the  $\text{dipic}^{2-}$  anion. The possible pyrolysis reactions in the thermal decomposition processes of the complex, the experimental and calculated percentage mass loss are also given.

**Keywords:** cobalt(II) complex; pyridine-2,6-dicarboxylic acid; room temperature solid–solid reaction; crystal structure; thermal analysis.

### INTRODUCTION

In the past several years, coordination frameworks with transition metal and organic functional ligands have been rapidly developing. However, it still remains one of the most active areas in chemistry and materials science, not only due to their highly fascinating structures and topologically diverse architectures, but also because they have potential applications in gas storage, molecular separations, drug delivery, heterogeneous catalysis, ion exchange, nonlinear optics, and other biomedical applications.<sup>1–5</sup> The complexes of pyridinecarboxylic acids and their derivatives were successfully used as model systems for the design of new metallo-pharmaceutical compounds.<sup>6</sup> Investigations on metalloproteins

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revealed that the carboxylate group plays an important role for structural folding and proton transfer *via* hydrogen bonding interactions in proteins.<sup>7</sup>

Pyridine-2,6-dicarboxylic acid (abbreviated as H<sub>2</sub>dipic) can partly or fully deprotonate, the three coordination sites can undergo chelate or bridge coordination to form diverse structures.<sup>8–10</sup> Furthermore, H<sub>2</sub>dipic is usually found in the decomposition products of vitamins, coenzymes and alkaloids, which also have potential pharmacological activity.<sup>10,11</sup> Cobalt is an essential trace element for humans and animals, which has potential applications in medicine and bio-inorganic chemistry, such as blood pressure regulation and proper thyroid function.<sup>12,13</sup>

The method of room temperature solid–solid reaction is a simple and convenient method for the preparation of complexes. This method is energy-saving and environmentally friendly. In this article, cobalt acetate and the biologically functional ligand H<sub>2</sub>dipic were chosen to synthesize a homodinuclear complex, using the room temperature solid–solid reaction method.

## EXPERIMENTAL

### *Materials and physical measurements*

H<sub>2</sub>dipic was purchased from Alfa Aesar, while cobalt acetate was obtained from Merck. All chemicals were of analytical reagent grade and used without further purification.

Elemental analysis data were obtained using a Vario EL CUBE elemental analyzer, and cobalt was determined using a Thermo X-II inductively coupled plasma mass spectrometer. The XRD pattern was recorded on a D/max-II X-ray diffractometer in the diffraction angle range of 3–80°. The IR spectra were recorded from KBr pellets in the range of 400–4000 cm<sup>-1</sup> on a Perkin-Elmer Spectrum One spectrometer. The thermal analysis was realized using a SDT Q600 thermogravimetric analyzer, and the measurement was recorded from 30 to 800 °C at a heating rate of 10 °C min<sup>-1</sup> under air flow of 50 mL min<sup>-1</sup>. The UV spectra in aqueous solution (1.0×10<sup>-4</sup> mol L<sup>-1</sup>) were recorded on a Shimadzu UV-2450 spectrophotometer.

### *Synthesis of complex*

A mixture of H<sub>2</sub>dipic (0.84 g, 5 mmol) and cobalt acetate (1.25 g, 5 mmol) was carefully ground in an agate mortar at room temperature, whereby a strong irritant gas was released. The released gas was tested with moist pH paper, and the result indicated that the gas was slightly acid due to the release of acetic acid during the reaction process. When the evolution of the irritant gas ceased, the reaction was complete. The reaction was conducted by grinding at room temperature for 4–5 h, and the mixture turned into loose pink powder. After obtaining the XRD data, the powder was dissolved in a small amount of distilled water and the solution was filtered and concentrated. When the concentrated solution was kept at room temperature for about 24 h, red–brown block-shaped crystals were obtained. Yield: 84 %; Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>O<sub>15</sub>N<sub>2</sub>: C, 29.28; H, 3.51; N, 4.88; Co, 20.53 %. Found: C, 29.12; H, 3.65; N, 4.71; Co, 20.68 %.

### *X-Ray crystal structure determination*

X-Ray diffraction data for a single crystal of the complex were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated MoK<sub>α</sub> radiation using the  $\omega$  and  $\phi$  scan mode. A crystal with dimensions 0.40 mm×0.38

mm×0.34 mm was mounted on a glass fiber. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL program package.<sup>14</sup> All of the non-hydrogen atoms were refined with anisotropic displacement parameters and all of the hydrogen atoms were found objectively from difference Fourier syntheses. The crystallographic data for the complex are given in Table S-I of the Supplementary material to this paper, the selected bond distances and angles are listed in Table S-II, hydrogen bond lengths and angles are given in Table S-III of the Supplementary material, and the crystallographic data are deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 1028718.

## RESULTS AND DISCUSSION

### *X-Ray crystal structure analysis*

A view of the key fragments of the structure and the atom numbering of the complex are shown in Fig. 1. The complex crystallizes in the monoclinic system and space group  $P2(1)/c$  with cell parameters of  $a = 8.3680 \text{ \AA}$ ,  $b = 27.2976 \text{ \AA}$ ,  $c = 9.5826 \text{ \AA}$  and  $\beta = 98.276^\circ$ . The asymmetrical unit consists of the neutral complex  $[\text{Co}_2(\text{dipic})_2(\text{H}_2\text{O})_5]$  and two lattice water molecules. The unit of the neutral complex is composed of two Co(II) ions, two  $\text{dipic}^{2-}$  anions and five coordinated water molecules. There are two different coordination environments that form two octahedral cobalt cations, one  $\text{dipic}^{2-}$  anion ligand utilizes the carboxyl bridged coordination mode to link Co1 and Co2. The Co1 contains a bridged carboxyl oxygen atom (O2) from one  $\text{dipic}^{2-}$  anion and five oxygen atoms (O9, O10, O11, O12 and O13) from water molecules. The Co1 bridges the carboxyl oxygen (O2) of  $\text{dipic}^{2-}$ , and is surrounded by water molecules, forming an octahedral geometry. The Co2 exhibits a distorted octahedral coordination with two  $\text{dipic}^{2-}$ , which has two anionic tridentate chelating modes. Therefore, its molecular structure could be written as  $[(\text{H}_2\text{O})_5\text{Co}(\mu\text{-OCO-dipic})\text{Co}(\text{dipic})] \cdot 2\text{H}_2\text{O}$ . The molecular structure shown in Fig. S-1 of the Supplementary material to this paper may indicate weak face-to-face  $\pi\text{-}\pi$  stacking interactions, because the distances

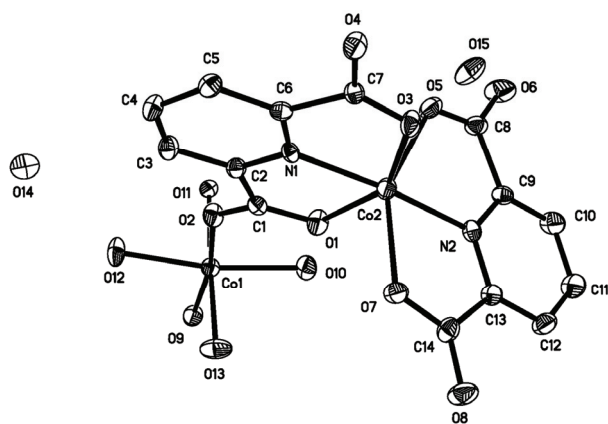


Fig. 1. Molecular structure of the title complex.

between the pyridine rings of situated in neighboring mirror planes are 3.703 and 3.791 Å.<sup>15</sup>

Crystal packing diagram of the title complex is presented in Fig. 2, which shows that the molecule of the complex is held together by intermolecular hydrogen bonds. There are three types of hydrogen bonds in the complex, the hydrogen bonds between coordinated water molecules and the O atoms of carbonyl groups, the coordinated water and lattice water molecules, and the O atoms of carboxylate groups with the lattice water molecules. The adjacent asymmetrical molecular units are interconnected through the hydrogen bond interactions between the coordinated water molecules (O13 and O9) and the carboxylic oxygen atoms (O5 and O6) of the  $\text{dipic}^{2-}$  ligand forming an extended 1D supramolecular chain. The chains of the 1D supramolecular chain are further combined with each other by means of hydrogen bond interactions between the lattice water or coordinated water molecules and other carboxylic oxygen atoms of the  $\text{dipic}^{2-}$  ligand, giving rise to the final extended 3D supramolecular network.

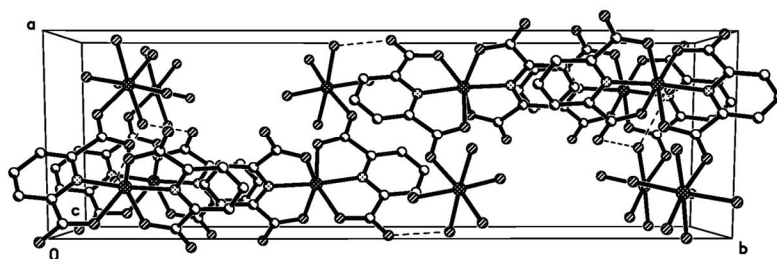


Fig. 2. Crystal packing diagram of the title complex.

#### *X-Ray powder diffraction*

The XRD pattern of the complex is shown in Fig. S-2a of the Supplementary material, from which it could be seen that the main diffraction peaks appeared at  $2\theta$  14.60, 16.45 and 26.38°. The index was calculated from the XRD database on the computer program by the least squares method,<sup>16</sup> and the results are shown in Table S-IV of the Supplementary material. The calculated spacing  $d_{hkl}$  is consistent with the experimental ones, and the maximum relative deviation between the experimental and calculated spacing  $d_{hkl}$  was less than 0.15 %. This indicates that the obtained powder was a single-phase compound. The crystal structure of the complex belongs to monoclinic system with the cell parameters  $a = 8.397$  Å,  $b = 27.409$  Å,  $c = 9.609$  Å and  $\beta = 98.22^\circ$ . The results of indexes to the XRD data are consistent with the results of the single crystal structure. The experimental XRD pattern agrees well with the simulated pattern generated based on the single crystal analysis for the complex (Fig. S-2b of the Supplementary material).

### FT-IR and UV spectra

The FT-IR spectrum of the complex is shown in Fig. S-3 of the Supplementary material. An intense broad absorption band in the region of 3200–3500  $\text{cm}^{-1}$ , which can be assigned to stretching vibration of water molecules, could be seen.<sup>17</sup> The presence of carboxyl groups was evidenced by the occurrence of strong absorption bands at 1618  $\text{cm}^{-1}$ , attributed to  $\nu_{\text{as}}(\text{COO}^-)$ , and at 1395  $\text{cm}^{-1}$ , attributed to  $\nu_{\text{s}}(\text{COO}^-)$ . The difference ( $\Delta\nu = 223 \text{ cm}^{-1}$ ) between  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  suggests monodentate or bridged coordination mode of the carboxylate group to Co(II).<sup>18</sup> The bands at 1576 and 1430  $\text{cm}^{-1}$  were assigned to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$ , respectively. In addition, the bands at 594 and 544  $\text{cm}^{-1}$  are attributed to  $\nu(\text{Cu}-\text{N})$  and  $\nu(\text{Cu}-\text{O})$ , respectively.

UV spectra of the ligand and the complex (Fig. S-4 of the Supplementary material) have only one absorption band, which was attributed to a  $\pi-\pi^*$  transition of the ligand. Compared with those of the ligand (273 nm), the maximum absorption peak of the complex was shifted to 265 nm. The coordination bonds formed stabilize the structure, which led to the blue shift of the absorption peak.

### Thermal analysis

Studying the thermal decomposition process of complexes is helpful to understanding of the coordination structure and the mechanism of thermal decomposition.<sup>19,20</sup> The TG–DSC curves of the complex are shown in Fig. S-5 of the Supplementary material. The possible pyrolysis reaction, and the experimental and calculated mass losses in the thermal decomposition process are summarized in Table S-V of the Supplementary material. The first mass loss occurs about 102 °C, corresponding to the release of two crystalline water molecules, then the composition of the complex corresponds to be  $[\text{Co}_2(\text{dipic})_2(\text{H}_2\text{O})_5]$ . The second step in the mass loss of 14.61 % (calcd. 15.69 %) occurred at 150 °C, which shows the loss of five coordinated water molecules. The residue of  $[\text{Co}_2(\text{dipic})_2]$  was stable between 180 to 320 °C. Thereafter, the exothermic peak at 469 °C corresponded to the decomposition of the ligand. In this step, two pyridine free radicals and two  $\text{CO}_2$  molecules were lost, and the decomposition products were cobalt oxalate and Co atoms.<sup>12</sup> The cobalt oxalate decomposed at between 470 to 600 °C, and the result shows that the thermal decomposed product of cobalt oxalate is metallic cobalt<sup>21</sup> at about 576 °C. Due to the oxidation of cobalt, a mass increase was observed (found 5.28 %, calcd. 5.57 %) in the TG curve. The final residue was CoO.

### CONCLUSIONS

The homodinuclear complex  $[\text{Co}_2(\text{dipic})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  was synthesized by room temperature solid–solid reaction, and characterized by EA, single crystal X-ray diffraction, XRD, FT-IR, UV and TG–DSC. The crystal structure of the

complex belongs to monoclinic system and space group  $P2(1)/c$ . The two Co(II) ions are both six-coordinated, and the octahedral Co(II) cations show different coordination environments. The  $\text{dipic}^{2-}$  ligands utilize the carboxyl bridged coordination mode to link the two Co(II) ions. The 3D supramolecular architecture of the complex is constructed by means of hydrogen bond interactions between water molecules and carboxyl oxygen atoms of the ligands. The thermal decomposition processes of the complex include dehydration and pyrolysis of the ligand, and the residue is cobalt oxide.

#### SUPPLEMENTARY MATERIAL

The crystal data, bond lengths and angles, the results of indexes to XRD data, thermal decomposition data, XRD patterns, FT-IR and UV spectra, and TG–DSC curves of the complex are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request. The crystallographic data are deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 1028718.

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#### ИЗВОД

#### СИНТЕЗА У ЧВРСТОМ СТАЊУ, КАРАКТЕРИЗАЦИЈА И ТЕРМИЧКО РАЗЛАГАЊЕ ХОМОДИНУКЛЕАРНОГ КОБАЛТ(II)-КОМПЛЕКСА

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Полазећи од пиридин-2,6-дикарбоксилне киселине и кобалт(II)-ацетата у чврстом стању на собној температури синтетисан је хомодинуклеарни  $[\text{Co}_2(\text{dipic})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$  комплекс. Комплекс је окарактерисан помоћу елементарне микроанализе, методом дифракције X-зрака са кристала и праха, Фуријеровом трансформационом инфрацрвеном и електронском апсорпционом спектроскопском методом, као и на основу термогравиметријских и диференцијалних калориметријских метода. Нађено је да комплекс представља моноклинични кристални систем са просторном групом  $P2(1)/c$ . У структури комплекса постоје два хексакоординована Co(II) јона. Један Co(II) јон је координован за четири карбоксилна атома кисеоника и два атома азота из  $\text{dipic}^{2-}$ , док је други јон овог метала координован за пет молекула воде и један  $\text{dipic}^{2-}$  преко моста. Приказане су могуће реакције пиролизе и термичког разлагања комплекса, док су експериментално одређене масе продуката ових реакција.

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