Synthesis, Crystal Structure, and Thermal Decomposition of the Cobalt(II) Complex with 2-Picolinic Acid

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The cobalt(II) complex of 2-picolinic acid (Hpic), namely, \([\text{Co} (\text{pic})_2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\), was synthesized with the reaction of cobalt acetate and 2-picolinic acid as the reactants by solid-solid reaction at room temperature. The composition and structure of the complex were characterized by elemental analysis, infrared spectroscopy, single crystal X-ray diffraction, and thermogravimetry-differential scanning calorimetry (TG-DSC). The crystal structure of the complex belongs to monoclinic system and space group \(P2(1)/n\), with cell parameters of \(a = 9.8468(7) \text{ Å}, b = 5.2013(4) \text{ Å}, c = 14.6041(15) \text{ Å}, \beta = 111.745(6)^\circ, V = 747.96(11) \text{ Å}^3, Z = 2, D_\text{c} = 1.666 \text{ g cm}^{-3}, R_1 = 0.0297, \text{ and } wR_2 = 0.0831.\) In the title complex, the Co(II) ion is six-coordinated by two pyridine N atoms and two carboxyl O atoms from two 2-picolinic acid anions, and two O atoms from two H2O molecules, forming a slightly distorted octahedral geometry. The thermal decomposition processes of the complex under nitrogen include dehydration and pyrolysis of the ligand, and the final residue is cobalt oxalate at about 450°C.

1. Introduction

In recent years, chemists have tended to design and synthesise metal-organic frameworks, which are undergoing accelerated and sustained growth because of their fascinating structures and potential applications, such as molecular adsorption, catalysis, gas storage, multifunctional materials, and chemical separation [1–10]. The transition metal carboxylates have the diversity of coordination modes for carboxyl group, which tend to form cluster or polymer structures [11], and it is significant to synthesis of some specific structure and function complexes in future. It is known that 2-picolinic acid is terminal tryptophan metabolite, and its anion has been used as a valuable chelating ligand, and the pyridine N atom and the carboxylate oxygen atoms are capable of coordinating various metal ions. Besides, 2-picolinic acid is not only a potential proton acceptor but also proton donor depending on deprotonated groups [12]. To the best of our knowledge, the crystal structures of 2-picolinic acid with Ni(II), Zn(II), Co(III), and Cu(II) derivations have been reported [11–14].

The method of room temperature solid-solid synthesis is a simple and convenient method for the preparation of metal complexes, and many complexes have been synthesized by this method [15–17]. Advantages of the solid-solid synthesis method are much higher yield, being inexpensive, faster reaction rate, easier operating, energy saving, and environmental friendly [18], and it is in accordance with the requirements of green chemistry. Cobalt is an essential trace element for human and all animals, and its complexes have been used in the fields of medicine, bioinorganic chemistry, functional materials, and so forth [19–24]. At the same time, the cobalt compounds are often used in chemical reactions as oxidation catalysts, such as typical catalysts that are the cobalt carboxylates, which are also used in paints, varnishes, and pigments industry [25]. We report herein the X-ray single crystal structure and thermal property of the cobalt(II) complex of 2-picolinic acid which is synthesized by solid-solid reaction at room temperature.

2. Experimental

2.1. Materials and Physical Measurements. All the chemicals used in the experiments were analytical reagents as received.
from commercial sources and without further purification. 2-Picolinic acid was purchased from Alfa Aesar, while cobalt(II) acetate tetrahydrate was purchased from Merck.

The contents of carbon, hydrogen, and nitrogen in the complex were measured by a Vario EL CUBE elemental analyzer, and the cobalt content was determined by EDTA complexometric titration. The FTIR spectra were obtained using a Perkin-Elmer Spectrum One-Spectrometer in the complexometric titration. The FTIR spectra were obtained using an analyzer, and the cobalt content was determined by EDTA

| Empirical formula | CoC_{12}H_{16}O_{5}N_{2} | F(000) | 386 |
|------------------|-------------------------|--------|-----|
| Formula weight   | 375.20 g mol⁻¹           | Crystal size | 0.42 mm × 0.35 mm × 0.25 mm |
| Temperature      | 298(2) K                 | Theta range for data collection | 2.50–25.02° |
| Wavelength       | 0.71073 Å                | Limiting indices | -11 ≤ h ≤ 8, -6 ≤ k ≤ 6, -15 ≤ l ≤ 17 |
| Crystal system   | Monoclinic              | Reflections collected/unique | 3424/1320 [R(int) = 0.0438] |
| Space group      | P2(1)/n                 | Completeness to theta = 25.02 | 99.6% |
| Unit cell dimensions |                      | Absorption correction | Semiempirical from equivalents |
| a                | 9.8468(7) Å             | Max. and min. transmission | 0.7549 and 0.6344 |
| b                | 5.2013(4) Å             | Refinement method | Full-matrix least squares on F² |
| c                | 14.6041(15) Å           | Data/restraints/parameters | 1320/10/107 |
| β                | 90.2310(10)°            | Goodness of fit on F² | 1.077 |
| Volume           | 74796(11) Å³            | Final R indices [I > 2σ(I)] | R₁ = 0.0297, wR₂ = 0.0831 |
| Z                | 2                       | R indices (all data) | R₁ = 0.0338, wR₂ = 0.0877 |
| Calcd. density   | 1.666 g cm⁻³            | Extinction coefficient | 0.222(10) |
| Absorption coefficient | 1.192 mm⁻¹             | Largest diff. peak and hole | 0.333 and -0.358 e Å⁻³ |

| Table 1: Crystal data and structure refinement parameters for the title complex. |

2.2. Synthesis of the Complex [Co(pic)$_2$(H$_2$O)$_2$] · 2H$_2$O. The synthesis reaction of the title complex is as follows:

$$2C_6H_2O_3N + Co(CH_3COO)_2 \cdot 4H_2O 
--> [Co(C_6H_4O_2N)_2(H_2O)_2] \cdot 2H_2O \quad (I)
+ 2CH_3COOH \uparrow$$

2-Picolinic acid and cobalt acetate of the two reactants were weighed and placed in an agate mortar, and the molar ratio of 2-picolinic acid to cobalt acetate was 2 : 1. Then, the mixture was grinded carefully at room temperature and released a strong irritant gas in the grinding process. The released gas was tested with moist pH paper, and the result indicated that the gas was faintly acid gas. The reason was that the acetic acid was released in the reaction process. When there was no irritant gas that escaped, the reaction was completed. The reaction was conducted in grinding at room temperature for 6 h, and the mixture became into loose pink powder. Afterwards the resultant was transferred to the beaker and stirred to dissolve with a little distilled water, and the solution was filtered and concentrated. The concentrated solution was placed at room temperature about 10 days, and the red-orange crystals of the cobalt(II) complex were obtained. The yield of the complex was about 82%. Anal. Calcd. for CoC$_{12}$H$_{16}$O$_{5}$N$_{2}$ (%): C, 38.40; H, 4.27; N, 7.47; Co, 15.71. Found (%): C, 38.26; H, 4.23; N, 7.41; Co, 15.53.

2.3. X-Ray Diffraction Crystallography. The appropriate crystal was cut from larger crystals and mounted on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Cu K$_{α}$ radiation (λ = 0.71073 Å). The data were collected at 298(2) K using multiscan modes. A red-orange crystal with dimensions 0.42 mm × 0.35 mm × 0.25 mm was mounted on a glass fiber. Diffraction data were collected in ω mode in the ranges of 2.50°–25.02°. The programs SHELXS-97 and SHELXL-97 were used for the structure determination and refinement [26, 27]. The structure was solved by direct methods, and all nonhydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F². All nonhydrogen atoms were refined anisotropically.

The structure refinement parameters for the title complex are given in Table 1, and the crystallographic data are deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 913361.

3. Results and Discussion

3.1. X-Ray Crystal Structure Analysis. Figure 1 shows the key fragments of the structures and the atom numbering in the title complex. Crystallographic data and structure refinement parameters for the title complex are given in Table 1, and the selected bond distances and angles are shown in Table 2. The unit of the complex is composed of one Co(II) ion, two 2-picolinic acid anions, and four water molecules. The Co(II) ion occupies the center of symmetry, which is six-coordinated through two nitrogen atoms and two hydroxy oxygen atoms.
Table 2: Selected bond lengths (Å) and angles (°) for the title complex.

| Bond/Angle Description | Value       |
|-------------------------|-------------|
| Co(1)–O(1)#1           | 2.0765(15)  |
| Co(1)–N(1)#1           | 2.1196(18)  |
| Co(1)–O(3)#1           | 2.1477(16)  |
| N(1)–C(6)              | 1.339(3)    |
| O(1)–C(1)              | 1.277(3)    |
| O(1)#1–Co(1)–O(1)      | 180.00(8)   |
| O(1)–Co(1)–N(1)#1      | 101.08(7)   |
| O(1)#1–Co(1)–O(3)#1    | 90.89(6)    |
| O(1)–Co(1)–O(3)        | 89.11(6)    |
| O(1)#1–Co(1)–O(3)      | 95.51(7)    |
| O(1)–Co(1)–N(1)        | 180.0       |
| O(1)–Co(1)–N(1)#1      | 112.10(15)  |
| C(1)–O(1)–Co(1)        | 116.23(14)  |
| N(1)–C(2)–C(1)         | 116.00(18)  |
| O(2)–C(2)–O(1)         | 124.8(2)    |

Symmetry transformations used to generate equivalent atoms: #1 – x + 1, –y + 1, –z + 1.

![Figure 1: Molecular structure of the title complex.](image1)

![Figure 2: Coordination environment of the Co(II) ion.](image2)

![Figure 3: Crystal packing diagram of the title complex.](image3)

of the carboxyl group [Co(1)–N(1), 2.1196(18) Å; Co(1)– N(1)#1, 2.1196(18) Å; and Co(1)–O(1), 2.0765(15) Å; Co(1)– O(1)#1, 2.0765(15) Å] from two 2-picolinic acid anions and two oxygen atoms from two H₂O molecules [Co(1)–O(3), 2.1477(16) Å; and Co(1)–O(3)#1, 2.1477(16) Å]. The complex is formed by 2-picolinic acid anion as bidentate ligand and the space group is P2(1)/n. The O or N atoms of coordination from the two 2-picolinic acid molecules are equivalent. Figure 2 shows that the four atoms of O(1), N(1), O(1)#1, and N(1)#1 are in the equatorial plane and form a parallelogram array, and the bond angle of O(3)#1–Co(1)– O(3) is 180° and the atoms of O(3)#1, Co(1), and O(3) are in a straight line; therefore the two atoms of O(3) and O(3)#1 from the coordinated water molecules are in the axial symmetry position, forming a slightly distorted octahedral geometry. In the complex, the bond length of Co(1)–O(1) is slightly shorter than the bond lengths of Co(1)–N(1) and Co(1)–O(3); this indicates that the coordination ability of the carboxyl O atom is stronger than that of the N atom from pyridine ring and the O atom from water molecule. The bond angles (O(1)–Co(1)– O(3) and O(1)#1–Co(1)–O(3)#1, 90.89(6)°; O(1)#1–Co(1)– O(3) and O(1)–Co(1)–O(3)#1, 95.51(7)°) in the complex are near to ideal 90° values. Because of the Jahn-Teller effect of the Co(II) ion with d⁷ electron configuration, the axial bond lengths of Co(1)–O(3) and Co(1)–O(3)#1 are stretched.

In Figures 3 and 4, the molecules of the complex [Co(pic)₂(H₂O)₂]·2H₂O are held together by intermolecular hydrogen bonds. Hydrogen bond length and bond angle for the title complex are given in Table 3. There are three
Table 3: Hydrogen bond lengths (Å) and bond angles (°) for the title complex.

| D–H   | d (D–H) | d (H⋯A) | ∠DHA  | d (D⋯A) | A                      |
|-------|---------|---------|-------|---------|------------------------|
| O3–H3C | 0.850   | 1.896   | 171.34| 2.739   | O1 [−x + 1, −y, −z + 1]|
| O3–H3D | 0.851   | 1.963   | 171.40| 2.808   | O4 [x − 1/2, −y + 3/2, z + 1/2]|
| O4–H4C | 0.850   | 1.852   | 175.51| 2.700   | O2 [x, y, z]           |
| O4–H4D,a| 0.850   | 2.095   | 175.29| 2.943   | O4 [−x + 3/2, y − 1/2, −z + 1/2]|
| O4–H4B,b| 0.849   | 2.203   | 145.57| 2.943   | O4 [−x + 3/2, y + 1/2, −z + 1/2]|

Figure 4: Packing diagram of the title complex showing H bonding.

Figure 5: Weak spatial π–π stacking interactions of the title complex.

3.2. FT-IR Spectra. The FT-IR spectra of 2-picolinic acid and the title complex are given in Figures 6 and 7. Comparison of IR spectra of the free ligand reveals that considerable changes
in frequencies have occurred which can determine the coordination sites in chelation. A wide intense absorption band around 3351 cm\(^{-1}\) can be assigned to stretching vibration of hydroxyl from the water molecules. The bands corresponding to the stretching vibration of the C–H and C=N are situated at 3153 cm\(^{-1}\) and 1630 cm\(^{-1}\), respectively. The vibration peak found in the 1569 cm\(^{-1}\) region is assigned to the stretching vibration of the C=C=C bond. The difference value of deformation vibration of the pyridine ring and compared to the C=O group of the Hpic monomer is situated at 1700–1769 cm\(^{-1}\)

Table 4: Thermal decomposition data of the title complex.

| Reaction | DSC/°C | \(W_{\text{exp}}\) | \(W_{\text{cal}}\) |
|----------|-------|-----------------|------------------|
| \([\text{Co(C}_5\text{H}_4\text{NCOO})_2(H_2\text{O})_2] \cdot 2\text{H}_2\text{O}\) | 96 (endo.) | 9.85 | 9.60 |
| \(-2\text{H}_2\text{O}\) | | | |
| \([\text{Co(C}_5\text{H}_4\text{NCOO})_2(H_2\text{O})_2]\) | 130 (endo.) | 9.45 | 9.60 |
| \(-2\text{H}_2\text{O}\) | | | |
| \([\text{Co(C}_5\text{H}_4\text{NCOO})_2]\) | 401 (endo.) | 42.17 | 41.63 |
| \(-\text{C}_6\text{H}_4\text{N} \cdot \text{C}_6\text{H}_4\text{N (2,2'-bipy)}\) | | | |
| \(\text{CoC}_2\text{O}_4\) | 38.53\(\ast\) | 39.17\(\ast\) |

\(\ast\) The experimental percentage mass of the residue in the sample.
\(\ast\) The calculated percentage mass of the residue in the sample.

3.3. Thermal Analysis. To study the thermal decomposition process of complexes is helpful to the understanding of the coordination structure of the complexes [33, 34]. The thermal stability of the title complex in nitrogen was investigated by TG-DSC analysis. The TG-DSC curves of the complex are shown in Figure 8, and the possible pyrolysis reaction and the experimental and calculated percentage mass losses in the thermal decomposition process of the complex are summarized in Table 4. As Figure 8 shows, there are three endothermic peaks at 96°C, 130°C, and 401°C in the DSC curve. The first mass loss of \([\text{Co(pic)}_2(H_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}\) occurs at about 96°C, corresponding to the release of two molecules of crystalline water. This is consistent with the single crystal structure. The experimental percentage mass loss (9.85%) is close to the calculated one (9.60%). The second mass loss of 9.45% (calcld. 9.60%) occurs between 100 and 140°C, which show loss of two water molecules from the complex. Because of the high dehydration temperature, this loss of the two water molecules should be coordinated water. After the four water molecules are lost, the complex become to be \([\text{Co(pic)}_2]\). The residue complex of \([\text{Co(pic)}_2]\) is relatively stable in nitrogen between 140 and 350°C. The next step mass loss in the temperature ranges of 350–450°C corresponds to the loss of two pyridine free radicals (\(\cdot \text{C}_6\text{H}_4\text{N}\)), and the two free radicals may eventually form 2,2'-bipyridine and then escape to volatile. This is just why there is an appreciable endothermic peak at 401°C in the DSC curve. The mass loss of 42.17% in the TG curve is in good agreement with the calculated result of 41.63%. The residual mass of the complex remains almost constant in nitrogen until 500°C. The composition of the final residue is cobalt oxalate, and the experimental result (39.17%) is in agreement with the result of theoretical calculation (38.53%).

The XRD pattern of the residue is shown in Figure 9, and the characteristic peaks of the residue are mostly consistent with the normative peaks according to the JCPDS cards number 25-0225 \((\text{CoC}_2\text{O}_4)\). The result of thermal analysis further ascertains that the molecule composition of the complex is \([\text{Co(pic)}_2(H_2\text{O})_2] \cdot 2\text{H}_2\text{O}\).
The complex \([\text{Co(pic)}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\) was synthesized with the reaction of cobalt acetate and 2-picolinic acid as the reactants. The composition and structure of the complex were characterized by EA, FTIR, single crystal X-ray diffraction, and TG-DSC. The crystal structure of the complex belongs to monoclinic system and space group \(P2(1)/n\), with cell parameters of \(a = 9.8468(7)\) Å, \(b = 5.2013(4)\) Å, \(c = 14.6041(15)\) Å, \(\beta = 111.745(6)\)^\circ, \(Z = 2\), and \(D_c = 1.666\) g cm\(^{-3}\). The cobalt ion is six-coordinated by two pyridyl N atoms and two carboxyl O atoms from two 2-picolinic anions and two O atoms from two \(\text{H}_2\text{O}\) molecules, forming a distorted octahedral geometry. The thermal decomposition processes of the complex under nitrogen include dehydration and pyrolysis of the ligand, and the final residue is cobalt oxalate at about 450°C.

Additional Material

Crystallographic data for the title complex \([\text{Co(pic)}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\) has been deposited with the Cambridge Crystallographic Data Centre. The deposition number is CCDC-913361. The data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, UK; fax: +44 1223 366 033; e-mail: deposit@ccdc.cam.ac.uk, or on the web http://www.ccdc.cam.ac.uk/pages/Home.aspx, or from the authors on request.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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