研究简报

异核配合物 $K_2[Co(Dipc)_2]\cdot 7H_2O$ 的合成、性质、结构和热分解动力学研究

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Synthesis, Characterization, Structure and Kinetics of Thermal Decomposition of $K_2[Co(Dipc)_2]\cdot 7H_2O$

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A heteronuclear compound, $K_2[Co(Dipc)_2]\cdot 7H_2O$ (Dipc = pyridine-2, 6-dicarboxylic acid) has been synthesized and characterized by IR, elemental analysis, and X-ray diffraction. Crystal data: orthorhombic system with space group *Pnna* and unite cell parameters: $a = 2.0645(3)$ nm, $b = 1.3484(2)$ nm, $c = 0.8204(1)$ nm; $V = 2.2838(6)$ nm^3, $Z = 4$, $D_{calc} = 1.726$ g·cm^{-3}, $\mu = 1.193$ mm^{-1}, $F(000) = 1212$, Gof = 1.045, $\Delta\rho = 339 \sim -348$ e·nm^{-3}, the final R is 0.0295. In the molecule of the complex, Co(Ⅱ) ion is six-coordinate to form a distorted octahedron. The N atom and the carboxyl group of pyridine-2, 6-dicarboxylic acid are coordinated with the central ions. One of the carboxyl groups of the pyridine-2, 6-dicarboxylic acid connect K(Ⅰ) and Co(Ⅱ). The compound possesses approximate C_2 symmetry. The compounds form a three-dimensional network of infinite length connection with crystal waters, potassium ions and hydrogen bonds. The result of kinetics of thermal decomposition indicated that the compound decomposition takes place in two steps. CCDC: 207078.

Keywords: **pyridine-2, 6-dicarboxylic acid** **heteronuclear compound** **crystal structure** **kinetics of thermal decomposition**

0 Introduction

It is well known that cobalt(Ⅱ) can display various coordination polyhedron, the usual coordination number varying from four to six, while many reports on the crystal and molecular structure are of simple cobalt(Ⅱ)

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complex, relatively few cases concern heteronuclear complexes. Recently, some structures of heteronuclear compounds containing pyridine-2, 6-dicarboxylic acid have been determined[1~4], because of their important role in coordination chemistry, catalytic reactions, magnetic material and biological system.

We report here a novel structure of cobalt (II) complexes, which was synthesized with KOH , pyridine-2, 6-dicarboxylic acid and cobalt acetate. X-ray structure analysis and kinetics of thermal decomposition study of the title compound are reported here in.

1 Experimental

1.1 Synthesis of the Complex

$Co(Ac)_2 \cdot 4H_2O$ (4mmol) was added to a mixture of KOH (8mmol) and pyridine-2, 6- dicarboxylic acid (2mmol) in a mixed solvent of acetone(50mL) and water (50mL) slowly. The mixture solution was stirred and refluxed for 8h at 60℃, and cooled to room temperature. The resulting red solution was filtered and left to yield red crystal. They were washed with acetone and dried in vacuum. Found(%): C 28.37, H 3.39, N 4.75, Co 9.91. $C_{14}H_{20}CoK_2N_2O_{15}$ Calc(%): C 28.33, H 3.40, N 4.72, Co 9.93. IR spectra(KBr pellet, cm^{-1}) 3500 ~ 3200(ν_{O-H}), 1622($\nu_{as}COO^-$), 1369(ν_sCOO^-).

1.2 Physical Measurements

All chemical were of analytical grade obtained commercial and used without further purification. all solvents were dried and distilled by usual methods prior to use.

Elemental analyses were performed on an ER-BA-1106 instrument (Italy). The crystal structure was determined by single-crystal X-ray diffraction. IR spectra was recorded on a Nicolet 170SX IR spectrophotometer in Nujol on CSI. Kinetics of thermal decomposition was recorded on a TG209 (German).

1.3 X-ray Data Collection, Structural Determination and Refinement

A red single crystal of the title compound with dimensions of 0.50mm × 0.40mm × 0.38mm was selected and mounted on the tip of a glass fiber with epoxy resin for X-ray diffraction studies. The determination of the unite cell and the data collection were performed with graphite monochromatized Mo $K\alpha$ rediation ($\lambda = 0.071073$nm) on a Bruker CCD area detector diffractometer. A total of 2642 independent reflections were collected in the rang of $3.51° < \theta < 27.54°$ by ω-2θ scan technique at 294(2)K, in which 2141 reflections with $I \geqslant 2\theta(I)$ were used in structural determination and refinement. The structure was solved by direct methods and Fourier syntheses, Computations were performed using the SHELXL-Pc program[6, 7]. Positional and thermal parameters were refined by the full-matrix least-squares method. Refinement of non-hydrogen atoms with anisotropic temperature. The final least- square cycle gave $R = 0.0295$ and $wR = 0.0817$ for 2141 reflections with $I > 2\sigma(I)$; all hydrogen atoms were located in calculation position and isotropically refined. Final difference Fourier calculation showed a featureless map on which the maximum peak height was 339e · nm^{-3}. The select bonds lengths and angles are listed in Table 1. The structure perspective diagram and the packing drawing of the title compounds is showed in Fig. 1 and Fig. 2, respectively.

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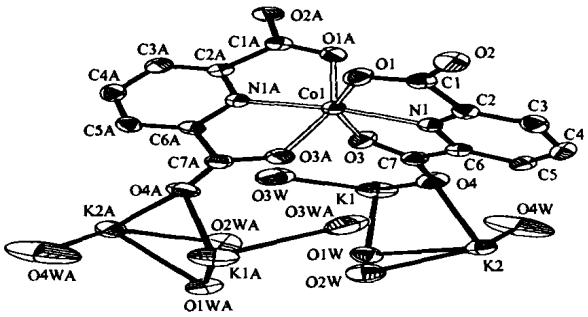

Fig. 1 Crystal structure of the title compound

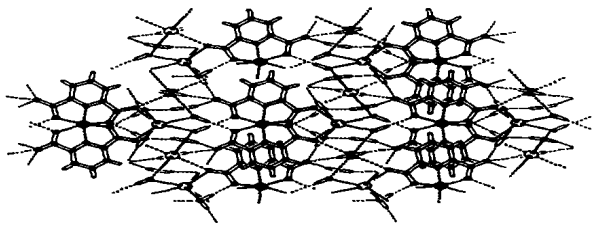

Fig. 2 Packing diagram along the z axis

Table 1　Selected Bond Distance(nm) and Bond Angle(°)

Co(1)-N(1)	0.20233(15)	O(4)-C(7)	0.1233(2)	O(3)-C(7)	0.1275(2)
Co(1)-O(3)	0.21567(12)	O(4)-K(2)	0.27301(13)	K(2)-O(4W)	0.2617(3)
Co(1)-O(1)	0.21579(12)	O(4)-K(1)	0.28773(13)	K(2)-O(2W)	0.27843(17)
O(1)-C(1)	0.1258(2)	K(1)-O(1W)	0.27866(14)	K(2)-O(1W)	0.29510(14)
O(2)-C(1)	0.1241(2)	K(1)-O(3W)	0.2971(2)	K(1)-K(2)	0.41141(6)
N(1)-Co(1)-N(1)#1	170.31(7)	O(3W)-K(1)-K(2)	92.19(4)	O(4W)-K(2)-K(1)	57.026(9)
N(1)-Co(1)-O(3)	76.10(5)	O(1W)-K(1)-K(2)#3	115.58(3)	O(4)-K(2)-K(1)	44.21(3)
N(1)-Co(1)-O(3)#1	97.03(5)	O(1W)#2-K(1)-K(2)#3	45.81(3)	O(4)#4-K(2)-K(1)	122.55(3)
O(3)-Co(1)-O(3)#1	91.51(7)	O(4)-K(1)-K(2)#3	157.89(3)	O(2W)#4-K(2)-K(1)	147.34(3)
N(1)-Co(1)-O(1)#1	111.57(5)	K(2)-K(1)-K(2)#3	159.27(2)	O(2W)-K(2)-K(1)	88.93(3)
N(1)-Co(1)-O(1)	75.85(5)	O(1W)-K(1)-H(3WA)	86.2	O(1W)#4-K(2)-K(1)	122.78(3)
O(3)-Co(1)-O(1)	151.24(5)	O(1W)#2-K(1)-H(3WA)	140.0	O(1W)-K(2)-K(1)	42.62(3)
O(3)#1-Co(1)-O(1)	98.08(5)	O(4)#2-K(1)-H(3WA)	94.9	K(1)-K(2)-K(1)#4	114.05(2)
O(1)#1-Co(1)-O(1)	86.41(7)	O(4)-K(1)-H(3WA)	56.5	O(4W)-K(2)-H(1WA)	96.2
C(1)-O(1)-Co(1)	116.56(10)	O(3W)#2-K(1)-H(3WA)	133.8	O(4)-K(2)-H(1WA)	78.6
C(7)-O(3)-Co(1)	115.44(10)	O(3W)-K(1)-H(3WA)	16.2	O(4)#4-K(2)-H(1WA)	103.5
C(7)-O(4)-K(2)	134.74(11)	K(2)-K(1)-H(3WA)	84.1	O(2W)#4-K(2)-H(1WA)	124.7
C(7)-O(4)-K(1)	124.45(11)	K(2)#3-K(1)-H(3WA)	105.9	O(2W)-K(2)-H(1WA)	43.0
K(2)-O(4)-K(1)	94.36(4)	O(4W)-K(2)-O(4)	80.55(3)	O(1W)#4-K(2)-H(1WA)	175.1
O(1W)-K(1)-O(1W)#2	84.97(6)	O(4)-K(2)-O(4)#4	161.10(6)	O(1W)-K(2)-H(1WA)	16.7
O(1W)-K(1)-O(4)	78.97(4)	O(4W)-K(2)-O(2W)	139.14(3)	K(1)-K(2)-H(1WA)	52.4
O(1W)#2-K(1)-O(4)	156.29(4)	O(4)-K(2)-O(2W)	90.11(4)	K(1)#4-K(2)-H(1WA)	136.7
O(4)#2-K(1)-O(4)	121.18(6)	O(4)#4-K(2)-O(2W)	104.26(4)	O(4W)-K(2)-H(2WB)	144.7
O(1W)-K(1)-O(3W)	81.88(4)	O(2W)#4-K(2)-O(2W)	81.72(7)	O(4)-K(2)-H(2WB)	79.0
O(1W)#2-K(1)-O(3W)	123.85(4)	O(4W)-K(2)-O(1W)	79.71(3)	O(4)#4-K(2)-H(2WB)	117.3
O(4)#2-K(1)-O(3W)	92.65(5)	O(4)-K(2)-O(1W)	78.60(4)	O(2W)#4-K(2)-H(2WB)	74.3
O(4)-K(1)-O(3W)	71.14(4)	O(4)#4-K(2)-O(1W)	97.99(4)	O(2W)-K(2)-H(2WB)	15.6
O(3W)#2-K(1)-O(3W)	147.24(6)	O(2W)#4-K(2)-O(1W)	141.15(5)	O(1W)#4-K(2)-H(2WB)	131.5
O(1W)-K(1)-K(2)	45.81(3)	O(2W)-K(2)-O(1W)	59.44(4)	O(1W)-K(2)-H(2WB)	68.2
O(1W)#2-K(1)-K(2)	115.58(3)	O(1W)#4-K(2)-O(1W)	159.41(6)	K(1)-K(2)-H(2WB)	88.6
O(4)#2-K(1)-K(2)	157.89(3)	O(4)-K(1)-K(2)	41.43(3)	O(3W)#2-K(1)-K(2)	93.62(3)

Symmetry transformations used to generate equivalent atoms: #1: x, $-y+3/2$, $-z+1/2$; #2: x, $-y+3/2$, $-z-1/2$; #3: $-x+3/2$, $y-1/2$, $-z-1/2$; #4: $-x+3/2$, $-y+1/2$, z.

2　Results and Discussion

The complex is stable in air at room temperature, it is easily soluble in DMF, DMSO, acetone and methanol.

Fig. 1 shows the molecular structure of the title compound. The cobalt (Ⅱ) cation is coordinated by two N atoms and four O atoms from two pyridine-2, 6-dicarboxylic acid forming a slightly distorted octahedron geometry with two N atoms of two pyridine-2, 6-dicarboxylic acid at the apical position. the interatomic distances of Co(1)-O(3) 0.21567(12) nm , Co(1) -O(3A) 0.21567(12) nm, Co(1) -O(1) 0.21579(12) nm, Co(1) -O(1A) 0.21579(12) nm and similar values have been observed in [(DPC)Co(μ-4, 4-bpy)Co(DPC)] · $8H_2O$[8], the bond Co-N, 0.2023(2) nm. All other bond distances and angles are with in normal rang, and in good agreement with of other pyridine-2, 6-dicarboxylic acid containing complexes[8-12] . The K(Ⅰ) and Co(Ⅱ) cations were connected by carboxyl group of pyridine-2, 6-dicarboxylic acid. The K(1) cations are coordinated by O(4) from pyridine-2, 6-dicarboxylic acid and five water molecules, the distances of K(1)-O4 0.28773(13) nm, K(1)-O(1W) 0.27866(14) nm, K(1)-O(1W)#2 0.27866(14) nm, K(1)-O(4) #2 0.28773(13) nm, K(1) -O(3W) #2 0.2971(2) nm, K(1)-O(3W) 0.2971(2) nm. The bonds are all weak coordination bond. The O(4) of pyridine-2, 6-dicarboxylic acid and O of water molecules as coor-

dination of η_2-O form connect K(1) and K(2). The heteronuclear structure containing pyridine-2, 6-dicarboxylic acid have not been reported in references. The compound is a three-dimensional network of infinite length connection with crystal waters, potassium ions and hydrogen bonds. The hydrogen bond lengths and bond angles are presented in Table 2.

Table 2 Hydrogen Bond Lengths(10^{-1}nm) and Bond Angle(°)

D-H···A	D-H	H···A	D···A	D-H···
O(1W)-H(1WA)···O(2W)	0.85	2.08	2.847(2)	150.0
O(1W)-H(1WB)···O(1)#5	0.85	1.99	2.843(2)	176.4
O(2W)-H(2WA)···O(2)#6	0.85	2.03	2.871(2)	170.9
O(2W)-H(2WB)···O(3W)#1	0.85	1.95	2.797(2)	171.0
O(3W)-H(3WA)···O(3)	0.85	1.86	2.711(2)	174.2
O(3W)-H(3WB)···O(2)#7	0.85	1.96	2.783(2)	162.8
O(4W)-H(4WA)···O(2)#8	0.85	2.20	3.049(2)	175.4

Symmetry transformations used to generate equivalent atoms: #1: $x, -y+3/2, -z+1/2$; #2: $x, -y+3/2, -z-1/2$; #3: $-x+3/2, y-1/2, -z-1/2$; #4: $-x+3/2, -y+1/2, z$; #5: $x+1/2, -y+3/2, z-1/2$; #6: $x+1/2, y, -z+1$; #7: $-x+1, y-1/2, z-1/2$; #8: $x+1/2, y, -z$.

The distance of Co(1)-O(3), Co(1)-O(3A), Co(1)-O(1), Co(1)-O(1A), Co(1)-N(1), Co(1)-N(1A), K(1)-O(1W), K(1)-O(1W)#2 are 0.21567(12), 0.21567(12), 0.21579(12), 0.21579(12), 0.2023(2), 0.2023(2), 0.27866(14), 0.27866(14) nm. The molecules possess C_2 symmetry axis which exist the go shares line of the angles O(1)-Co(1)-O(1A).

The TG-DTA thermogram of the complex reveals that the compound decomposition takes place in two steps. The TG curve shows that the first stage mass loss is 21.28% between 60℃ and 123℃, which coincides with the calculated value(21.23%) of losing 7mol H_2O from the complex. In the second stage, $K_2[Co(Dipc)_2]$ is decomposed at 278 ~ 392 ℃, with the mass loss of 48.42%, the theoretical mass is 47.55%, corresponding to the loss of 2mol pyridine-2, 6-dicarboxylic acid and the formation of CoO and KO_2. From the above analysis, the thermal decomposition process of $K_2[Co(Dipc)_2] \cdot 7H_2O$ may be expressed by the following scheme:

$$K_2[Co(Dipc)_2] \cdot 7H_2O \xrightarrow[-7H_2O]{60 \sim 123℃}$$

$$K_2[Co(Dipc)_2] \xrightarrow[-(2CO_2+2C_5H_5N)]{278 \sim 392℃} KO_2 + CoO$$

Many heteronuclear complexes containing pyridine-2, 6-dicarboxylic acid have been reported[1~4], we reported the pyridine-2, 6-dicarboxylic acid heteronuclear complex which contains potassium ion at first.

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