



Synthesis, structure and thermochemical study of a cobalt energetic coordination compound incorporating 3,5-diamino-1,2,4-triazole and pyridine-2,6-dicarboxylic acid



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ABSTRACT

An energetic coordination compound $[\text{Co}_2(\text{C}_2\text{H}_5\text{N}_5)_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ ($\text{Hdatrz}(\text{C}_2\text{H}_5\text{N}_5)$ = 3,5-diamino-1,2,4-triazole, $\text{H}_2\text{pda}(\text{C}_7\text{H}_3\text{NO}_4)$ = pyridine-2,6-dicarboxylic acid) has been synthesized and characterized by elemental analysis, chemical analysis, IR spectroscopy, single-crystal X-ray diffraction and thermal analysis. X-ray diffraction analysis confirmed that the compound possessed a di-nuclear unit and featured a 3D super-molecular structure. Furthermore, a reasonable thermochemical cycle was designed based on the preparation reaction of the compound and the standard molar enthalpy of dissolution of reactants and products was measured by the RD496-2000 calorimeter. Finally, the standard molar enthalpy of formation of the compound was determined to be $-(2475.0 \pm 3.1) \text{ kJ} \cdot \text{mol}^{-1}$ in accordance with Hess's law. In addition, the specific heat capacity of the compound at $T = 298.15 \text{ K}$ was determined to be $(1.13 \pm 0.02) \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$ by RD496-2000 calorimeter.

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1. Introduction

Research in the field of high energy material is now directing simple synthesis of molecules with high energy, high density, high heat resistance and low sensitivity [1]. Recently, considerable attention has been paid to the study of high-nitrogen heterocyclic materials as ligands to coordinate with metals because of varied structures and favorable energetic properties [2–6]. Our group is currently investigating the chemistry of triazole derivatives and carboxylic acid with respect to the continuous interest in high nitrogen and high oxygen compounds as ingredients for propellants and explosives [7–9].

As one of triazole derivatives, 3,5-diamino-1,2,4-triazole, is a significant energetic intermediate with nitrogen content 70.67%, and it has been studied and produced some energetic compounds [10,11]. Pyridine-2,6-dicarboxylic acid is a familiar and useful ligand for constructing crystalline architectures due to its rigid and planar nature, proton donating and accepting capabilities for hydrogen bonding via the oxygen atoms of its carboxylate groups [12]. Cobalt(II) exhibits a good ability when coordinating with different kinds of ligand, and is more environmental friendly compared to the toxic heavy metal ions as lead and mercury.

The datum of the standard molar enthalpy of formation and specific heat capacity plays important role in theoretical study, application development and industrial production of a compound as a basis of theoretical analysis [13–15]. In spite of that, to our best knowledge, there is little reliable experimental data available for such compounds.

Herein, in this paper, we report the synthesis, structure, thermal decomposition, standard molar enthalpy of formation and specific heat capacity of the title coordination compound.

2. Experimental

2.1. Materials, equipment and analytical methods

All chemicals involved were acquired from commercial sources at analytical grade and used without further purification; detailed information is provided in table 1. Elemental analysis was carried out with an Elementar Vario EL III CHNOS analyser. The chemical compositions of the sample were determined by EDTA titration for Co^{2+} . The IR spectra were recorded with a Bruker FTTR instrument as KBr pellets (4000 to 400 cm^{-1}). Thermogravimetric measurements were performed with a Netzsch STA449C apparatus under a static air atmosphere with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ from $T = (303$ to $873) \text{ K}$. UV-Visible spectra were recorded with an HITACHI U-3010 spectrophotometer.

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TABLE 1

Provenance and mass fraction purity of chemicals used in this study.

Chemical name	Source of supply	State	Mass fraction purity
CoCl ₂ ·6H ₂ O	Aladdin Reagent Co., Ltd, China	Powder	≥ 0.995
NaOH	Aladdin Reagent Co., Ltd, China	Powder	≥ 0.995
Pyridine-2,6-dicarboxylic acid	Tokyo Kashi Kogyo, Japan	Powder	≥ 0.99
3,5-Diamino-1,2,4-triazole	Tokyo Kashi Kogyo, Japan	Powder	≥ 0.99
Benzoic acid	Aladdin Reagent Co., Ltd, China	Powder	≥ 0.9995

TABLE 2

Crystal data and structure refinement parameters for title compound.

Empirical formula	C ₁₈ H ₂₄ Co ₂ N ₁₂ O ₁₂
Formula weight	718.35
Crystal system	Orthorhombic
Space group	Pna21
Temperature/K	273
a/nm	1.2434(2)
b/nm	1.3279(2)
c/nm	1.5403(3)
α/°	90
β/°	90
γ/°	90
V/nm ³	2.5432(7)
Z	4
Density, calculated/(g · cm ⁻³)	1.876
M/mm ⁻¹	1.395
F(000)	1464
Independent reflections	12065
Data/restraint/param	4522/7/387
Goodness-of-fit on F ²	1.017
Final R indices [I > 2σ(I)]	R ₁ = 0.0717, wR ₂ = 0.1649
R indices (all data)	R ₁ = 0.0823, wR ₂ = 0.2050
Largest peak and hole/(e · nm ⁻³)	3.871 and -0.522

2.2. Synthesis and characterization of title compound

The aqueous solution (10 cm³) containing NaOH (0.008 g, 0.2 mmol) and H₂pda (0.017 g, 0.1 mmol) was slowly added to the aqueous solution (10 cm³) containing both CoCl₂·6H₂O (0.024 g, 0.1 mmol) and Hdatrz (0.010 g, 0.1 mmol) with stirring for about one hour. The resulting solution was filtered and evaporated slowly at room temperature for 6 days. Red block-like

crystals suitable for X-ray analysis were obtained in 32% yield (based on Co²⁺). IR (KBr, cm⁻¹): 3423(br), 3090(m), 1706(w), 1625(s), 1542(s), 1460(s), 1371(s), 1198(s), 1088(w), 925(w), 790(w), 735(m).

2.3. Crystal structure determination

Single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.071073 nm) using ω and φ scan mode. All structures were solved by direct methods and refined with full-matrix least-squares refinements based on F² using SHELXS-97 and SHELXL-97 [16,17]. All non-H atoms were located using subsequent Fourier-difference methods. In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection parameters and refinement statistics are given in table 2.

2.4. Calorimetric experiment

The 1 mol · dm⁻³ HCl(aq) solvent can dissolve all components of the reaction (6) in the designed thermochemical cycle as shown in figure 1, and its concentration of 1.0004 mol · dm⁻³ was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g · cm⁻³ (taken from chemical handbook [18]), its concentration can also be expressed as the form of HCl·54.561H₂O. The molar enthalpies of solution of CoCl₂·6H₂O(s), C₂H₅N₅(s), C₇H₅NO₄(s), [Co₂(C₂H₃N₅)₂(C₇H₃NO₄)₂(H₂O)₂·2H₂O(s) in corresponding solvents were measured, respectively. In all these determinations, strict control of the stoichiometries in each step of

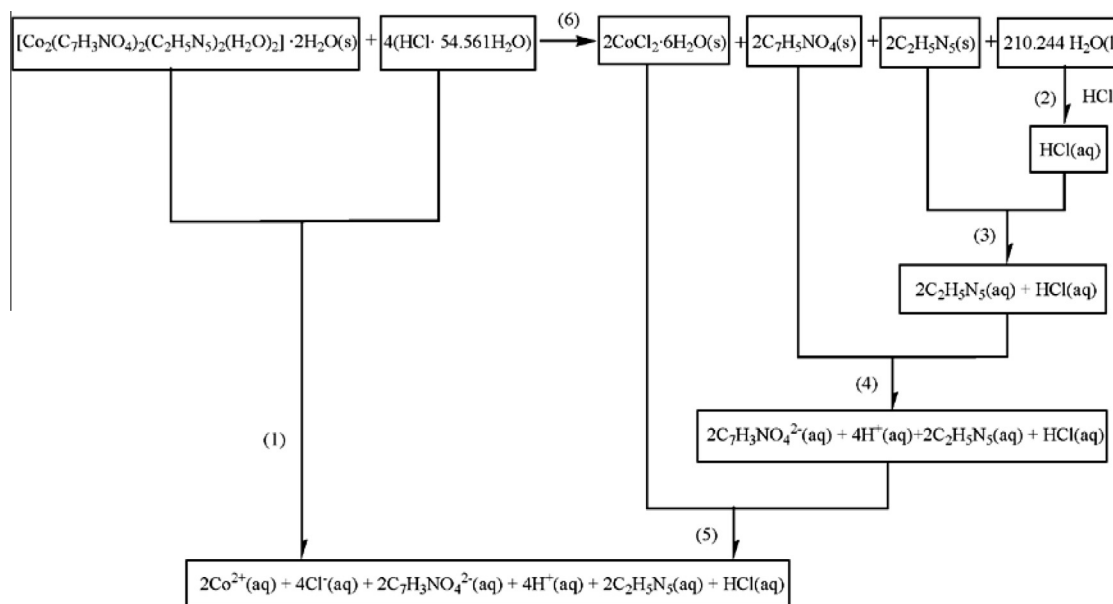


FIGURE 1. Thermochemical cycle of the coordination reaction.

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