# Structure and Stability of a Linear Trinuclear Cobalt(II) Complex: $Co_3(PhCH{=}CHCO_2)_6(bpy)_2$

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A trinuclear cobalt(II) complex, $[Co_3(PhCH{=}CHCO_2)_6(bpy)_2]$ (**1**) (bpy = 2,2-bipyridine), was synthesized and structurally characterized by single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters: $a$ = 11.347(6), $b$ = 11.471(6), $c$ = 14.247(8) Å, $\alpha$ = 69.503(9), $\beta$ = 74.211(9), $\gamma$ = 76.812(11)°, $V$ = 1653.2(15) Å$^3$, $Z$ = 1, and $R1(F)$ = 0.026, $wR2(F^2)$ = 0.138. Complex **1** has a linear arrangement of three Co(II) centers bridged by six cinnamate carboxylate groups, four of which function in a bidentate *syn-syn* fashion linking the peripheral Co2 atoms, and two as both bidentate bridging and bidentate chelating units. The Co1 atom is located on a crystallographic inversion center and exhibits a slightly distorted octahedral coordination geometry, while the terminal Co atoms (Co2 and Co2$^{\#1}$) have a significantly distorted octahedral environment. Hydrogen bonding interactions and $\pi$-$\pi$ stacking interactions stabilize the structure.

*Key words:* Crystal Structure, Cobalt(II), Linear Trinuclear Cluster, Thermal Stability

## Introduction

Carboxylate groups display a variety of binding geometries, such as monodentate terminal, chelating, bidentate bridging and monodentate bridging, in the coordination chemistry of the active sites of metalloenzymes [1]. A significant number of metal carboxylate complexes have been prepared and well characterized due to the fascinating structures of metal carboxylate clusters and the structural details of the active site(s) that may influence the chemical mechanisms of catalysis [2 – 7]. 2,2-Bipyridine (bpy), 1,10-phenanthroline (phen) and chelating bidentate ligands have been widely used as substitutes for amino acid side groups in biomimetic chemistry and as new diagnostic and therapeutic agents that can recognize and cleave DNA [8 – 9]. Among the polynuclear metal carboxylate systems consisting of bidentate *N*-donor ligands, the trinuclear cluster complexes have attracted considerable attention due to the variety of geometries in their triangular, discrete linear and extended polymeric structures. The discrete polynuclear metal carboxylate systems are especially enchanting due to their magnetic and optical properties [10]. However, there are only few reported trinuclear metal carboxylate complexes featuring a linear arrangement: five Mn(II) carboxylate complexes [11 – 15], one Co(II)-acetate-bpy complex, $[Co_3(CH_3CO_2)_6(bpy)_2]$ [12], and one Fe(II)-acetate-bpy complex, $[Fe_3(CH_3CO_2)_6(bpy)_2]$ [16]. Recently, our group has reported the three linear trinuclear transition metals complexes $[Mn_3(PhCH{=}CHCO_2)_6(bpy)_2]\cdot H_2O$ [17], $[Zn_3(PhCH{=}CHCO_2)_6(bpy)_2]\cdot H_2O$ and $[Zn_3(PhCH{=}CHCO_2)_6(phen)_2]\cdot H_2O$ [18]. In this contribution, we present a linear trinuclear cobalt(II) cluster, $Co_3(PhCH{=}CHCO_2)_6(bpy)_2$ (**1**).

## Experimental Section

### *Measurements of physical properties*

All chemicals were reagent grade and were used without further purification. Elemental analysis was performed using a Perkin-Elmer 2400-CHNS/O analyzer. The infrared spectrum of KBr pellets in the range 4000 – 400 cm$^{-1}$ was

Table 1. Crystal structure data and numbers pertinent to the structure refinement of compound **1**.

| | |
|---|---|
| Formula | $C_{74}H_{58}Co_3N_4O_{12}$ |
| $M_r$ | 1372.03 |
| Crystal size, mm$^3$ | $0.07 \times 0.10 \times 0.34$ |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 11.347(6) |
| $b$, Å | 11.471(6) |
| $c$, Å | 14.247(8) |
| $\alpha$, deg | 69.503(9) |
| $\beta$, deg | 74.211(9) |
| $\gamma$, deg | 76.812(11) |
| $V$, Å$^3$ | 1653.2(15) |
| $Z$ | 1 |
| $D_{calcd}$, g cm$^{-3}$ | 1.378 |
| $\mu$(Mo$K_\alpha$), cm$^{-1}$ | 0.81 |
| $F$(000), e | 707 |
| *hkl* range | $-14 \le h \le 14$, $-15 \le k \le 7$,<br>$-18 \le l \le 18$ |
| $((\sin\theta)/\lambda)_{max}$, Å$^{-1}$ | 0.094 |
| Refl. measured/unique | 11434/7238 |
| $R_{int}$ | 0.047 |
| Param. refined | 421 |
| $R1(F)/wR2(F^2)$$^a$ (all refls.) | 0.026/0.138 |
| $A/B$ values for weighting scheme$^b$ | 0.0631/0.0 |
| GoF $(F^2)$$^c$ | 0.90 |
| $\Delta\rho_{fin}$ (max/min), e Å$^{-3}$ | 0.42/−0.41 |

$^a$ $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_c|$, $wR2(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; $^b$ $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, with $P = (F_o{}^2 + 2F_c{}^2)/3$; $^c$ GoF$(F^2) = S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n-p)]^{1/2}$, where $n$ is the number of reflections and $p$ is the total number of parameters refined.

recorded using a Nicolet AVATAR-370 spectrophotometer, and the UV/vis spectrum was obtained using a Perkin-Elmer Lambda35 analyzer. The combined measurement of thermogravimetric and differential thermal analysis (TG/DSC) was carried out in the range 25 – 650 °C on powdered samples in a nitrogen stream using a STA 409 PC analyzer with a heating rate of 10 °C min$^{-1}$. X-Ray powder diffraction was performed using an X'Pert PRO DY2198 diffractometer.

### *Preparation of $Co_3(PhCH{=}CHCO_2)_6(bpy)_2$ (**1**)*

Commercially available $CoCO_3$ (0.119 g, 1.0 mmol) was added to a solution of 2,2-bipyridine (0.167 g, 1.0 mmol) and cinnamic acid (0.296 g, 2.0 mmol) in 40 mL of $C_2H_5OH$/$H_2O$ (v/v 1 : 1) with vigorous stirring under reflux conditions. The resulting suspension was filtered, and the filtrate was left to stand at 45 °C. Red prismatic crystals suitable for X-ray analysis were obtained two weeks later in 85 % yield (based on the initial $CoCO_3$ input). $C_{74}H_{58}Co_3N_4O_{12}$ (1372.03): calcd. C 64.72, H 4.23, N 4.08; found C 64.68, H 4.16, N 4.12. – IR: $\nu$ = 3058m, 3020w, 1640vs, 1575vs, 1448m, 1390vs, 1242m, 977m, 877w, 769s, 736m, 592w cm$^{-1}$.

### *X-Ray structure analysis*

The reflection intensities of **1** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer using graphite-monochromatized Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and $\psi/2\vartheta$ scans. Absorption corrections were applied using the program SADABS [19]. The structure was solved by Patterson Methods and refined by full-matrix least-squares procedures on $F^2$ (SHELX-97 suite of programs [20, 21]). The hydrogen atoms associated with carbon atoms were generated geometrically. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms with isotropic displacement parameters. Detailed information about the

Table 2. Selected interatomic distances (Å) and angles (deg) for compound **1**$^a$.

| | | | | | |
|---|---|---|---|---|---|
| Co1–O3 | 2.054(2) | Co2–O1 | 2.126(2) | O6–C29 | 1.249(4) |
| Co1–O3$^{\#1}$ | 2.054(2) | Co2–N1 | 2.158(3) | O2–C11 | 1.240(4) |
| Co1–O5 | 2.111(2) | Co2–O2 | 2.313(3) | O5–C29 | 1.253(4) |
| Co1–O5$^{\#1}$ | 2.111(2) | Co2–O6 | 2.012(2) | O4–C20 | 1.240(4) |
| Co1–O1 | 2.158(3) | Co2–O4 | 2.029(3) | O1–C11 | 1.284(4) |
| Co1–O1$^{\#1}$ | 2.158(3) | Co2–N2 | 2.090(3) | O3–C20 | 1.238(4) |
| O1–Co1–O1$^{\#1}$ | 180.0 | O3$^{\#1}$–Co1–O5 | 87.40(1) | O1–Co2–O2 | 58.47(1) |
| O3–Co1–O3$^{\#1}$ | 180.0 | O3$^{\#1}$–Co1–O5$^{\#1}$ | 92.60(1) | O1–Co2–O4 | 100.1(1) |
| O5–Co1–O5$^{\#1}$ | 180.0 | O3$^{\#1}$–Co1–O1$^{\#1}$ | 93.40(1) | O1–Co2–O6 | 102.2(1) |
| O1–Co1–O3 | 93.40(1) | O5–Co1–O1$^{\#1}$ | 90.66(1) | O1–Co2–N2 | 146.6(1) |
| O1–Co1–O5 | 89.34(1) | O5$^{\#1}$–Co1–O1$^{\#1}$ | 89.34(1) | O1–Co2–N1 | 88.98(1) |
| O1–Co1–O3$^{\#1}$ | 86.60(1) | O6–Co2–N1 | 89.21(1) | O2–Co2–O4 | 92.78(1) |
| O1–Co1–O5$^{\#1}$ | 90.66(1) | O6–Co2–N2 | 107.1(1) | O2–Co2–O6 | 160.1(9) |
| O3–Co1–O5 | 92.60(1) | O6–Co2–O4 | 95.55(1) | O2–Co2–N1 | 86.04(1) |
| O3–Co1–O5$^{\#1}$ | 87.40(1) | N1–Co2–N2 | 76.02(1) | O4–Co2–N1 | 168.6(1) |
| O3–Co1–O1$^{\#1}$ | 86.60(1) | N2–Co2–O2 | 90.46(1) | O4–Co2–N2 | 92.68(1) |

Hydrogen bonding contacts (Å and deg) .

| D-H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| C1–H1···O4 | 0.93 | 2.4886 | 3.054(6) | 119.31 |
| C4–H4···O2$^{\#2}$ | 0.93 | 2.3713 | 3.197(6) | 147.74 |

$^a$ Symmetry codes:
$^{\#1}$ $1-x, 1-y, -z$;
$^{\#2}$ $2-x, -y, -z$.

crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 662995 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

## Results and Discussion

### *IR and UV/vis spectra*

The IR spectra show the unsatuated $\nu$(=C–H) stretching vibrations at 3058 and 3020 cm$^{-1}$. The absorption at 1640 cm$^{-1}$ is assigned to the $\nu_{\mathrm{as}}(\mathrm{CO_2}^-)$ stretching vibration of the cinnamate group, and the bands centered at 1390 cm$^{-1}$ to the $\nu_{\mathrm{s}}(\mathrm{CO_2}^-)$ stretching vibrations. A comparison with the characteristic carboxylate stretching vibrations of free cinnamic acid shows a significant blue-shift attributed to the coordination interactions. The bpy-based absorptions (1575, 1448, 877, 769 and 736 cm$^{-1}$) are characteristic of the chelating form of the ligand.

UV/vis spectral measurement was carried out at r. t. on a solid sample. The spectrum exhibits a broad absorption band with the maximum at *ca.* 320 nm, which can be assigned to the bpy $\pi \rightarrow \pi^*$ transitions.

### *Structure description*

Compound **1** consists of $[\mathrm{Co_3(PhCH{=}CHCOO)_6(bpy)_2}]$ complex molecules, in which the metal centers feature a linear array, with the 2,2-bipyridine ligands residing in the periphery. The cobalt atoms are bridged by six carboxylate groups, four of which act in a bidentate *syn-syn* fashion linking Co1 with the peripheral Co2 atoms, and two as both bidentate bridging and bidentate chelating (Fig. 1). The central Co1 atom, located at the crystallographic inversion center, is octahedrally coordinated by six cinnamatic carboxylate oxygen atoms, with *trans* angles of 180° and Co1–O distances ranging from 2.054(2) to 2.158(3) Å. The Co···Co separations are 3.468 Å.

The terminal metal atoms (Co2) are each surrounded by two pyridyl nitrogen atoms (N1 and N2) and four carboxylate oxygen atoms (O1, O2, O4 and O6). The apical positions are occupied by N1 and O4 with a *trans* angle of 168.61(1)°. The Co2–N1 bond (2.158(3) Å) is longer than the Co2–N2 bond (2.090(3) Å), both of which are similar to those in $[\mathrm{Co_3(CH_3CO_2)_6(bpy)_2}]$ [12], where the terminal Co–N1 and Co–N2 distances are 2.133(2) and 2.099(2) Å, respectively. The Co2–O bond lengths are also comparable to those in $[\mathrm{Co_3(CH_3CO_2)_6(bpy)_2}]$, the Co2–O2 bond length (2.313(3) Å) being longer than the other Co2–O distances (Table 2). The *cis* bond angles at the Co2 atom formed with the N and O atoms range from 76.02(1)– 100.1(1)°, suggesting a significant deviation from perfect octahedral geometry, probably due to the bpy ligand and carboxylate groups chelation.

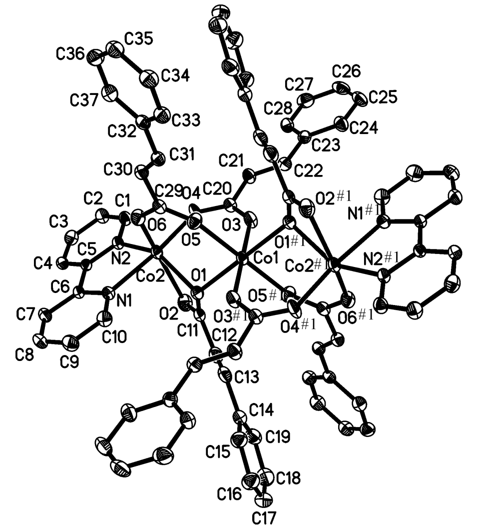

Fig. 1. ORTEP view of the complex molecule with atomic labelling for **1** (displacement ellipsoids at the 30 % probability level; symmetry codes: $^{\#1}$ $1-x$, $1-y$, $-z$).

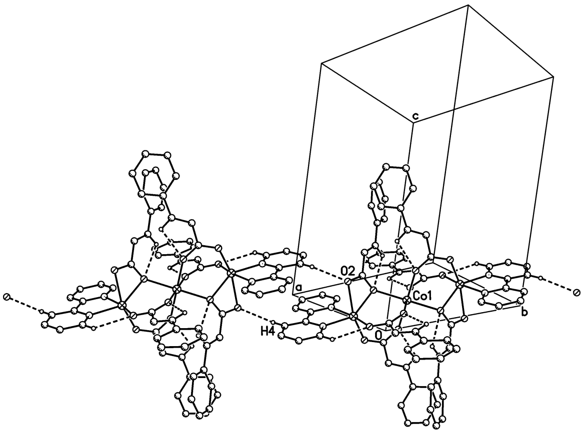

Fig. 2. The infinite chain assembled *via* hydrogen bonding interactions along the [1 $\bar{1}$ 0] direction for **1** (the dashed lines indicate the hydrogen bonds).

Hydrogen bonding interactions and $\pi$-$\pi$ stacking stabilize the structure. The carboxylate oxygen atoms

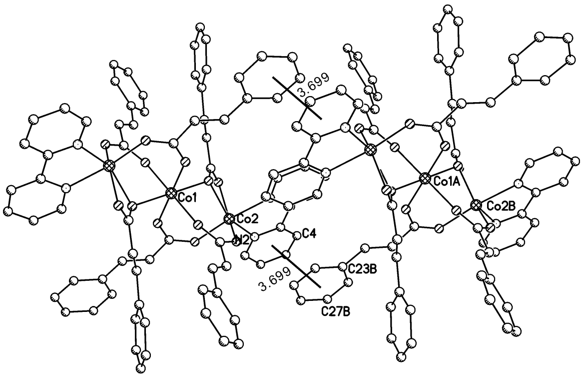

Fig. 3. Packing diagram showing the $\pi$-$\pi$ stacking interactions for **1**.

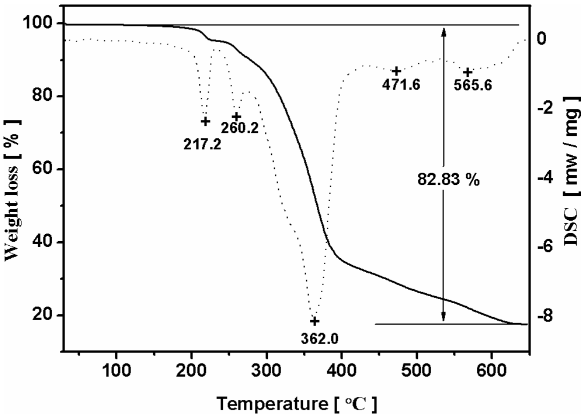

Fig. 4. Thermogravimetric analysis (TGA) diagram for **1**.

accept hydrogen atoms from bpy ligands to generate intramolecular interactions along the [1 $\bar{1}$ 0] direction (Table 2, Fig. 2). From the packing diagram of **1**, it appears that the [$Co_3(PhCH{=}CHCOO)_6(bpy)_2$] molecules are further held together by $\pi$-$\pi$ stacking interactions between pyridyl and phenyl groups with a centroid-centroid distance of 3.699 Å (Fig. 3). Based on such $\pi$-$\pi$ stacking interactions, the complex molecules are assembled into one-dimensional chains running parallel to the [010] direction.

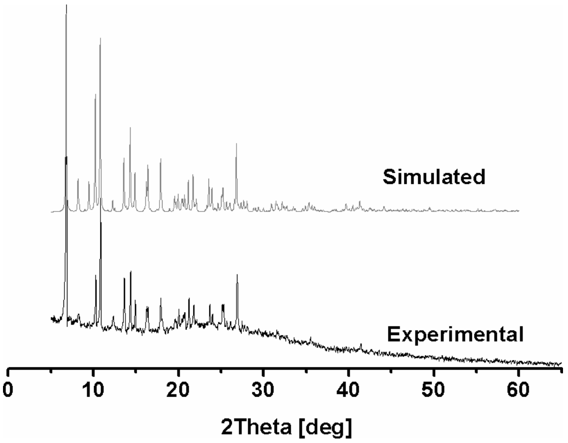

Fig. 5. Experimental and simulated XRD patterns for **1**.

### *Thermal stability and XRD patterns*

Thermogravimetric analysis (TGA) reveals that **1** possesses high thermal stability. There is no weight loss from r. t. to 200 °C. The DSC curve of **1** exhibits five endothermic peaks centered at 217, 260, 362, 472 and 566 °C (Fig. 4). The strongest endothermic reaction at 362 °C indicates that the framework collapses. Over the range 200 – 650 °C, the observed weight loss of 82.83 % is comparable to the calculated value of 83.61 % for release of the bpy ligands and all the cinnamate fragments. The powder X-ray diffraction pattern confirms the red residue of 17.17 % at 650 °C to be CoO (calcd. 16.39 %).

The experimental XRD pattern agreed well with the simulated one generated on the basis of the single crystal analysis for **1** (Fig. 5), indicating the phase purity of the product. The differences in intensity may be due to the preferred orientation of the powder samples.

### *Acknowledgement*

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