# A Rare Example of a Dinuclear Cobalt(II) Complex with Dipicolinate and Bridging 2-Aminopyrazine Ligands. Preparation, Structural, Spectroscopic and Thermal Characterization

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A dinuclear cobalt(II) complex, $[Co_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$ (dipic$H_2$ = pyridine-2,6-dicarboxylic (dipicolinic) acid, apyz = 2-aminopyrazine) (**1**), has been hydrothermally synthesized and characterized by elemental analyses, spectroscopic methods (IR, UV/Vis), thermal analysis as well as by X-ray diffraction studies. The dinuclear complex is composed of two cobalt(II) ions bridged by a 2-aminopyrazine molecule. Each cobalt(II) ion is coordinated by one nitrogen and two oxygen atoms of the tridentate dipicolinate anion, one heterocyclic nitrogen atom of the 2-aminopyrazine and two oxygen atoms of coordinated water molecules. The resulting geometry for the $CoN_2O_4$ coordination environment can be described as distorted octahedral. Various hydrogen bonds of the type O–H···O and N–H···O are also present in the crystal structure. This arrangement leads to the formation of a 3D structure.

*Key words:* Cobalt, Dipicolinic Acid, 2-Aminopyrazine, Dinuclear Complex, X-Ray Diffraction

## Introduction

Binuclear complexes are of great interest due to their potential applications as magnetic materials and in catalytic and electron transfer reactions. Bi- or multidentate bridging ligands containing N- or O-donors are most important because they greatly influence the structures of coordination compounds. Polycarboxylate anions and polynitrogen-containing ligands, two excellent classes of bridging ligands, are used to bind metal centers, generating a number of one- two- and three-dimensional infinite metal frameworks. Among polycarboxylic acids, pyridine-2,6-dicarboxylic (dipicolinic) acid (dipic$H_2$) has attracted much interest in coordination chemistry. It is a desirable ligand for metal ions because of its low toxicity and amphiphilic nature [1]. Dipicolinic acid displays a large number of coordination modes due to the relative position of its carboxylate groups and its nitrogen atom, with the potential to act as a bidentate, tridentate and/or bridging ligand [2 – 5].

Dinuclear dipicolinate complexes, with pyrazine [6, 7] or 4,4-bipyridine [8, 9] as bridging molecules, are known but rather rare in the literature. Metal ions found in these complexes are nickel(II) [6] and copper(II) [7] in the case of pyrazine, and just copper(II) in the case of 4,4-bipyridine [8, 9]. A variety of cobalt complexes containing the dipicolinate ligand bound in a tridentate-*N*,*O*,*O*′ fashion are also known [10]. Similar dinuclear complexes of cobalt(II) and nickel(II) with *N*-(phosphonomethyl)iminodiacetate [11] (instead of dipicolinate) and bridging pyrazine exist, as well as of copper(II) with pyrazine and nitrilotriacetate [12] or iminodiacetate [13, 14]. Only two cobalt(II) complexes containing 2-aminopyrazine are known [15, 16], with 2-aminopyrazine bound as a terminal ligand in both cases.

In continuation of our earlier work on the synthesis of metal complexes with polycarboxylate ligands in the presence of some amino compounds [17 – 21], we here present the preparation, spectroscopic characterization, thermal properties and crystal structure of a dinuclear cobalt(II) complex formulated as $[Co_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$ (**1**). Complex **1** is the first example of a cobalt(II) complex with a bridging 2-aminopyrazine ligand.

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## Experimental Section

### *Materials and instrumentation*

All purchased chemicals were of reagent grade and used without further purification. IR spectra were recorded using an FTIR Spectra Bruker Tensor 27 spectrometer (KBr pellets, 4000 – 400 $\mathrm{cm^{-1}}$). Absorption spectra were recorded on a Shimadzu Model 160-A UV/Vis spectrophotometer with a 1-cm quartz cell. TGA/DTA measurements were performed at a heating rate of 10 °C $\mathrm{min^{-1}}$ in the temperature range of 25 – 800 °C, under a nitrogen flow of 20 mL $\mathrm{min^{-1}}$ on a Shimadzu DTG-50H instrument.

### *Preparation of [$Co_2(H_2O)_4(dipic)_2(\mu$-apyz)] (1)*

Pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) and NaOH (0.08 g, 2 mmol) were dissolved in deionized water (10 mL), and the mixture was stirred for 30 min at r. t. Then an aqueous solution of $\mathrm{Co(NO_3)_2 \cdot 4H_2O}$ (0.290 g, 1 mmol) and 2-aminopyrazine (0.095 g, 1 mmol) was added. The reaction mixture was placed in a Parr Teflon-lined stainless-steel vessel, sealed and heated at 130 °C for 8 h. It was then gradually cooled to r. t. and kept at 4 °C until red crystals of **1** suitable for X-ray diffraction were obtained. – IR (KBr pellet): $\nu$ = 3317 – 3080 (b), 1638, 1608 (s), 1575 (s), 1541 (s), 1464 (m), 1430 (s), 1360 (m), 1286 (s), 1182 (s), 1080 (s), 1022 (m), 911 (m), 767 (s), 729 (s), 689 (m), 581 (m), 444 (m) $\mathrm{cm^{-1}}$. – UV/Vis (aqueous solution): $\lambda$ = 217, 260, 310, 491 nm. – $\mathrm{C_{18}H_{19}Co_2N_5O_{12}}$ (615.24): calcd. C 35.11, H 3.09, N 11.38; found C 35.01, H 3.00, N 11.29.

### *Single-crystal structure determination*

A suitable single crystal of **1** was selected and mounted in air onto a thin glass fiber. The data collection for **1** was carried out on an Oxford Diffraction Xcalibur four-circle kappa geometry diffractometer equipped with a Xcalibur Sapphire 3 CCD detector, using graphite-monochromatized Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and the CRYSALIS Software system [22] at r. t. (296 K). Data reduction was achieved using the same program.

The X-ray diffraction data were corrected for Lorentz and polarization effects and for absorption, the latter by multi-scan techniques. The structure was solved by Direct Methods (SHELXS-97 [23]). Refinement by full-matrix least-squares methods based on $F^2$ values against all reflections was performed with SHELXL-97 [23] including anisotropic displacement parameters for all non-H atoms.

The position of hydrogen atoms belonging to the C$sp^2$ atoms was geometrically optimized applying the riding model [0.93 Å; $U_\mathrm{iso}$(H) = 1.2 $U_\mathrm{eq}$(C)]. Hydrogen atoms belonging to the water molecules and to the amino group were found in difference Fourier maps. The distance between the water oxygen atoms and the corresponding hydrogen atoms was restrained to the average value of 0.82 Å using the SHELXL-97 DFIX instruction, while the distance between the amino group N5 atom and the corresponding hydrogen atoms was restrained to the average value of 0.86 Å using the same instruction. The isotropic $U_\mathrm{iso}$(H) values for all hydrogen atoms were fixed at $U_\mathrm{iso}$(H) = 1.2 $U_\mathrm{eq}$(O) for hydrogen atoms belonging to O atoms and at $U_\mathrm{iso}$(H) = 1.2 $U_\mathrm{eq}$(N) for those belonging to N atoms.

Table 1. Crystal data and details of the structure determination for **1**.

| | |
|---|---|
| Formula | $\mathrm{C_{18}H_{19}Co_2N_5O_{12}}$ |
| $M_\mathrm{r}$ | 615.24 |
| Color and habit | red, plate |
| Crystal system, space group | monoclinic, $P2_1/c$ |
| Crystal dimensions, $\mathrm{mm^3}$ | $0.15 \times 0.14 \times 0.08$ |
| $a$, Å | 7.5507(2) |
| $b$, Å | 39.4948(8) |
| $c$, Å | 7.3623(2) |
| $\beta$, deg | 96.408(2) |
| $V$, Å$^3$ | 2181.82(9) |
| $Z$ | 4 |
| $D_\mathrm{calcd}$, g $\mathrm{cm^{-3}}$ | 1.87 |
| $\mu$, $\mathrm{mm^{-1}}$ | 1.6 |
| $\theta$ range, deg | 3.75 – 25.00 |
| $h,k,l$ range | ±8, ±46, ±8 |
| Scan type | $\omega$, $\varphi$ |
| Measured reflections | 31870 |
| Independent reflections / $R_\mathrm{int}$ | 3799 / 0.0588 |
| Observed reflections [$I \geq 2\sigma(I)$] | 2582 |
| No. refined parameters | 364 |
| $R1^\mathrm{a}$ / $wR2^\mathrm{b}$ [$I \geq 2\sigma(I)$] | 0.0477 / 0.0946 |
| $R1^\mathrm{a}$ / $wR2^\mathrm{b}$ (all data) | 0.0836 / 0.1026 |
| Goodness of fit on $F^2$, $S^\mathrm{c}$ | 1.040 |
| Max. / min. residual electron density, e Å$^{-3}$ | 0.88 / −0.34 |

[a] $R1 = \Sigma\|F_\mathrm{o}| - |F_\mathrm{c}\|/\Sigma|F_\mathrm{o}|$; [b] $wR2 = [\Sigma w(F_\mathrm{o}{}^2 - F_\mathrm{c}{}^2)^2/\Sigma w(F_\mathrm{o}{}^2)^2]^{1/2}$, $w = [\sigma^2(F_\mathrm{o}{}^2) + (\mathrm{A}P)^2 + \mathrm{B}P]^{-1}$, where $P = (\mathrm{Max}(F_\mathrm{o}{}^2, 0) + 2F_\mathrm{c}{}^2)/3$; [c] $\mathrm{GoF} = S = [\Sigma w(F_\mathrm{o}{}^2 - F_\mathrm{c}{}^2)^2/(n_\mathrm{obs} - n_\mathrm{param})]^{1/2}$.

Calculations concerning the molecular geometry, the choice and verification of the space group, the analysis of hydrogen bonds and $\pi$-$\pi$ interactions were performed with PLATON [24]. The molecular graphics were produced with ORTEP-3 [25] and MERCURY (version 2.4) [26]. The crystal data, data collection and refinement parameters for **1** are summarized in Table 1.

CCDC 819327 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

### *Crystal and molecular structure*

An ORTEP-3 view of the molecular structure of **1** is depicted in Fig. 1. The crystal structure of **1** is shown in Fig. 2. Some selected bond lengths and angles are

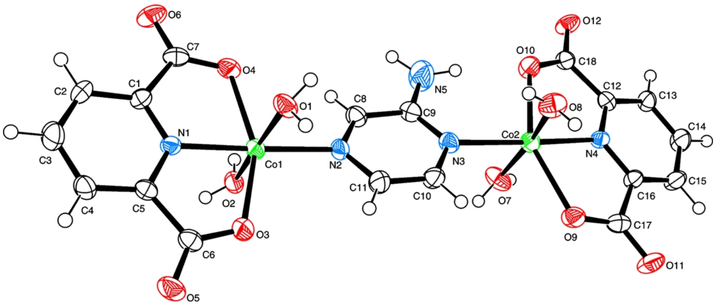

Fig. 1. ORTEP-3 drawing of $[Co_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$ (**1**), with the atom numbering scheme of the asymmetric unit. The displacement ellipsoids are drawn at the 50 % probability level at 296 K, and H atoms are shown as small spheres of arbitrary radii.

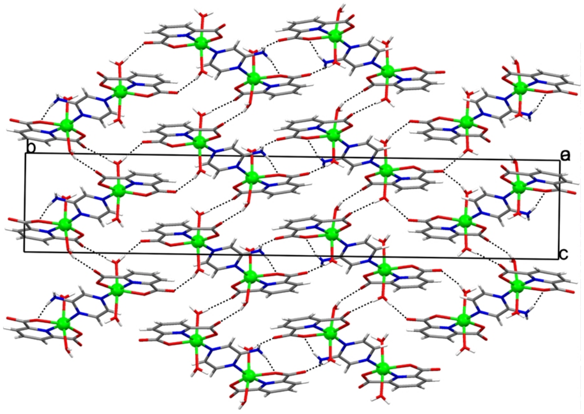

Fig. 2. A view of the crystal structure of **1** projected onto the crystallographic *bc* plane. The molecules of $[Co_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$ are linked by hydrogen bonds of the O–H···O and N–H···O type (represented by dotted lines) into a 3D structure.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.

| | | | |
|---|---|---|---|
| Co1–N1 | 2.024(3) | Co1–N2 | 2.092(3) |
| Co1–O1 | 2.154(3) | Co1–O2 | 2.123(3) |
| Co1–O3 | 2.136(3) | Co1–O4 | 2.148(3) |
| Co2–N3 | 2.136(3) | Co2–N4 | 2.037(3) |
| Co2–O7 | 2.072(3) | Co2–O8 | 2.114(3) |
| Co2–O9 | 2.202(3) | Co2–O10 | 2.146(3) |
| N1–Co1–N2 | 177.8(1) | O3–Co1–O4 | 153.2(1) |
| O2–Co1–O1 | 174.6(1) | N1–Co1–O2 | 91.6(1) |
| N2–Co1–O2 | 90.3(1) | N1–Co1–O3 | 76.3(1) |
| N2–Co1–O3 | 104.7(1) | O2–Co1–O3 | 94.3(1) |
| N1–Co1–O4 | 77.0(1) | N2–Co1–O4 | 101.9(1) |
| O2–Co1–O4 | 89.0(1) | N1–Co1–O1 | 92.4(1) |
| N2–Co1–O1 | 85.6(1) | O3–Co1–O1 | 90.3(1) |
| O4–Co1–O1 | 88.3(1) | O7–Co2–O8 | 169.5(1) |
| N4–Co2–N3 | 171.8(1) | O10–Co2–O9 | 150.9(1) |
| N4–Co2–O7 | 88.9(1) | N4–Co2–O8 | 101.4(1) |
| O7–Co2–N3 | 84.9(1) | O8–Co2–N3 | 85.0(1) |
| N4–Co2–O10 | 76.0(1) | O7–Co2–O10 | 93.2(1) |
| O8–Co2–O10 | 91.5(1) | N3–Co2–O10 | 99.0(1) |
| N4–Co2–O9 | 75.4(1) | O7–Co2–O9 | 91.4(1) |
| O8–Co2–O9 | 89.1(1) | N3–Co2–O9 | 110.1(1) |

listed in Table 2, and the hydrogen bond geometries in Table 3.

Each cobalt(II) ion in **1** is octahedrally coordinated by an *O*,*N*,*O′*-tridentate dipicolinate ligand (bound *via* the pyridine N and two carboxylate O atoms forming two five-membered chelate rings) and by a heterocyclic pyrazine N atom (from 2-aminopyrazine) in an equatorial position. The water molecules are placed in axial positions (∠O2–Co1–O1 174.6(1)°, ∠O7–Co2–O8 169.5(1)°). The 2-aminopyrazine molecule acts as a bridging ligand between the cobalt(II) centers, leading to the formation of a dinuclear complex (Fig. 1). Coordinated pyridine N atoms from dipicolinate and 2-aminopyrazine are situated in *trans* positions (∠N1–Co1–N2 177.8(1)°, ∠N4–Co2–N3 171.8(1)°). The Co–N and Co–O bond lengths (N,O atoms from dipicolinate) in **1** (Table 2) are in accordance with the values reported in the literature for the analogous bond lengths in complexes containing dipicolinate bound to cobalt(II) ions in a tridentate *N*,*O*,*O′* fashion [10], while the Co–N (N atom from 2-aminopyrazine) bond lengths in **1** are comparable with the corresponding ones in cobalt(II) complexes containing 2-aminopyrazine [15, 16] or bridging pyrazine [11].

The values of the bond angles around the two crystallographically independent cobalt(II) ions in **1** indicate a large distortion from an ideal octahedral geometry due to the coordination of the dipicolinate ligand in a tridentate *O*,*N*,*O′* fashion. The distortion is also reflected in the bite angles N1–Co1–O3, N1–Co1–O4, N4–Co2–O9 and N4–Co2–O10 with values in the range of 75.4(1) – 77.0(1)° (Table 2).

The pyrazine ring is not coplanar with the pyridine rings of both dipicolinate ligands in **1**, since the corresponding dihedral angles between the pyrazine ring and the first pyridine ring defined by atoms N1/C1/C2/C3/C4/C5 or between the second one defined by atoms N4/C12/C13/C14/C15/C16 and the same pyrazine ring are 22.6(2)° and 21.7(2)°, respectively. However, each of the two chelate rings is ap-

Table 3. Hydrogen bond parameters for **1**.

| D–H···A | $d$(D–H) (Å) | $d$(H···A) (Å) | $d$(D···A) (Å) | ∠(D–H···A) (deg) | Symmetry code of atoms A |
|---|---|---|---|---|---|
| O1–H11O···O9 | 0.82(3) | 1.99(3) | 2.802(4) | 173(5) | $-1+x, y, z$ |
| N5–H15N···O10 | 0.91(5) | 1.88(5) | 2.782(6) | 168(4) | $x, y, z$ |
| O1–H21O···O5 | 0.81(4) | 1.93(4) | 2.710(4) | 161(4) | $x, 1/2-y, -1/2+z$ |
| N5–H25N···O12 | 0.93(4) | 2.07(4) | 2.923(6) | 152(5) | $1-x, -y, 1-z$ |
| O2–H32O···O5 | 0.81(4) | 1.91(4) | 2.712(4) | 170(5) | $x, 1/2-y, 1/2+z$ |
| O2–H42O···O11 | 0.78(4) | 2.05(3) | 2.815(4) | 167(5) | $-1+x, y, 1+z$ |
| O7–H57O···O4 | 0.79(4) | 1.88(3) | 2.664(4) | 173(5) | $1+x, y, z$ |
| O7–H67O···O12 | 0.79(4) | 1.91(4) | 2.693(4) | 172(5) | $2-x, -y, 1-z$ |
| O8–H78O···O6 | 0.81(4) | 1.89(4) | 2.609(4) | 149(4) | $1+x, y, -1+z$ |
| O8–H88O···O11 | 0.81(3) | 2.27(3) | 3.064(4) | 169(5) | $-1+x, y, z$ |
| C2–H2···O2 | 0.93 | 2.42 | 3.334(5) | 169 | $-1+x, y, z$ |
| C4–H4···O1 | 0.93 | 2.55 | 3.297(5) | 138 | $x, 1/2-y, 1/2+z$ |
| C13–H13···O7 | 0.93 | 2.53 | 3.317(5) | 143 | $2-x, -y, 1-z$ |
| C15–H15···O8 | 0.93 | 2.49 | 3.399(5) | 164 | $1+x, y, z$ |

proximately coplanar with the corresponding pyridine ring. This is evident from the small values of the dihedral angles between the pyridine ring and the corresponding chelate rings of 3.9(2)° and 3.8(2)° for the N1/C1/C2/C3/C4/C5 and 5.1(2)° and 6.0(2)° for the N4/C12/C13/C14/C15/C16 pyridine ring.

There are hydrogen bonds of the type O–H···O, N–H···O and C–H···O in the crystal structure of **1** (Table 3). Generally, coordinated water molecule O atoms and amino group N atoms act as double proton donors, while coordinated and uncoordinated carboxylate O atoms participate in hydrogen bonding as proton acceptors, some of them as double proton acceptors (O5, O11 and O12). A rather complicated hydrogen bond network assembles molecules of [$Co_2$-$(H_2O)_4$(dipic)$_2$($\mu$-apyz)] into a 3D structure (Fig. 2). A $\pi$-$\pi$ stacking interaction between pyridine rings defined by the atoms N4/C12/C13/C14/C15/C16 and N4$^i$/C12$^i$/C13$^i$/C14$^i$/C15$^i$/C16$^i$ (symmetry code (i): $2-x, -y, -z$; centroid-centroid distance 3.825(2) Å, angle between the planes 0°; perpendicular distance between the planes 3.317(2) Å; slippage 1.905 Å) is also present in the packing of the molecules in **1**.

### *Infrared spectra*

The IR spectrum of **1** shows two sets of vibrations due to the coordinated water molecules and dipicolinate ligands. The carboxylate ion may coordinate to a metal atom in unidentate, bidentate or bridging modes [27]. In the spectrum of **1**, the band associated with the antisymmetric stretching mode, $\nu_{as}$(-COO$^-$), appears at 1638 cm$^{-1}$ together with $\nu_s$(-COO$^-$) at 1360 cm$^{-1}$. The value of $\Delta[\nu_{as}(\text{-COO}^-) - \nu_s(\text{-COO}^-)]$ amounts to 278 cm$^{-1}$, indicating the presence of carboxylate groups coordinated to metal ions in an unidentate mode [28, 29], which is in agreement with the crystal structure. The IR spectrum of **1** shows strong broad bands in the region 3317 – 3080 cm$^{-1}$, which could be related to the existence of O–H···O hydrogen bonding between water molecules [30]. These bands are probably coupled to other stretching frequencies of the aromatic rings which originally fall within this region [17, 18, 29]. The weak bands below 500 cm$^{-1}$ are due to the M–O stretching vibrations.

### *Electronic spectra*

The electronic spectrum of an aqueous solution of **1** displays strong absorption bands below 320 nm (217 nm, $\varepsilon$ = 1.55 × 10$^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$; 260 nm, $\varepsilon$ = 1.24 × 10$^4$ mol$^{-1}$ dm$^3$ cm$^{-1}$ and 310 nm, $\varepsilon$ = 7.833 × 10$^3$ mol$^{-1}$ dm$^3$ cm$^{-1}$), which are assigned to the $\pi \rightarrow \pi$ transitions of dipicolinate and 2-aminopyrazine ligands. The spectrum also shows a broad absorption band at 491 nm ($\varepsilon$ = 21 mol$^{-1}$ dm$^3$ cm$^{-1}$) which is assigned to the $d \rightarrow d$ transition. The shoulder appearing in the visible region of the spectrum is ascribed to the Jahn-Teller distortion in cobalt(II) complexes.

### *Thermal analysis (TGA/DTA)*

The TGA curve shows two stages of decomposition. The first stage is at 209 °C and corresponds to the loss of coordinated water molecules (experimental value 11.4 % and calculated value 11.7 %). The exothermic decomposition started at 300 °C and was finished at 520 °C indicating the complete removal of all organic parts of the complex. The main product was CoO with a residual value of 26.1 % (calcd. 24.4 %).

## Conclusion

In this paper, the preparation and spectroscopic (IR and UV/Vis) characterization, the thermal properties and the crystal structure analysis of $[Co_2(H_2O)_4(dipic)_2(\mu\text{-apyz})]$ (**1**) are presented. Complex **1** is the first example of a dinuclear cobalt(II) complex with a bridging 2-aminopyrazine ligand. Similar complexes were previously prepared using pyrazine or 4,4-bipyridine. The additional substituent (amino group) in the pyrazine ring does not show any steric effect and does not affect the coordination ability of 2-aminopyrazine to act as a bridging ligand between two cobalt(II) centers. However, the amino group influences significantly the formation of a complicated hydrogen bond network, if compared with the analogous pyrazine complexes, since the amino group N atom acts as an additional double proton donor.

In continuation of our research, we will prepare and structurally characterize similar dinuclear transition metal complexes with dipicolinate and differently substituted pyrazines. We will explore the effect of an additional substituent in a pyrazine ring on the ability of the substituted pyrazine to act as a bridging ligand, forming dinuclear complexes.

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