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## Coordination complex of dipicolinato cobalt(III) complex cation and anion

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Two examples of a new class of high oxidation state complexes having complex anion and complex cation of cobalt(III) are presented. The complexes  $[\text{CoL}(\text{py})_3][\text{CoL}_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{CoL}(\text{im})_3][\text{CoL}_2] \cdot \text{H}_2\text{O}$  (**2**) (where L = dipicolinato anion, py = pyridine and im = imidazole) are characterized by determining their crystal structures and studying their properties in solution. The complex anionic and cationic parts form layered structures through hydrogen-bond interactions with water molecule of crystallization. Alternate layers of complex cations and anions hydrogen bond with water molecules of crystallization to make tight packed structures.

**Keywords:** Cobalt(III); Complex cations and anions; Pyridine; Imidazole; Layered structure; Hydrogen-bonded assembly

### 1. Introduction

Cobalt(III) complexes find important applications in catalysis [1–6], bioinorganic chemistry [7, 8], and in non-conventional energy generation [9, 10]. Dipicolinato ligands with nitrogen donors such as pyridine and imidazole were used for synthesis of metallo-organic frameworks [11]. Mononuclear dipicolinato complexes of cobalt in +2 and +3 oxidation states have special interest for their structural variations and medicinal value [12]. Picolinate is multidentate [13, 14] with additional carboxylates making it further attractive to study. Cobalt(II) dipicolinato complexes having insulin-like properties were structurally characterized, but the corresponding cobalt(III) dipicolinato complex was explored only in solution [12]. The advantage of studying cobalt(III) diamagnetic complexes is kinetic stability. Large numbers of cobalt(III) complexes have been synthesized and characterized to understand fundamental aspects of coordination chemistry [15–20]. We describe here two simple cobalt(III) complexes, which have complex cation and anion of cobalt(III).

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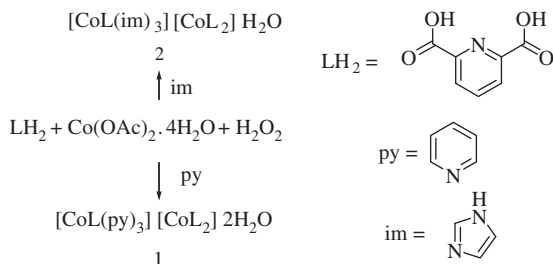
## 2. Results and discussion

Complexes **1** and **2** were synthesized under ambient condition by the reaction of dipicolinic acid with cobalt(II)acetate tetrahydrate and hydrogen peroxide followed by treatment with pyridine or imidazole (scheme 1). The crystallographic parameters of the two complexes are listed in table 1.

Complex **1** exhibits two mononuclear complex ions, each having distorted octahedral geometry around cobalt(III). The cation  $[\text{CoL}(\text{py})_3]^+$  has one dipicolinato anion (L) and three pyridines (py) coordinated to cobalt(III); the anion  $[\text{CoL}_2]^-$  consists of a distorted octahedral cobalt(III) with two meridionally coordinated dipicolinato ligands (figure 1a). Complex **1** has two water molecules of crystallization. The two cobalt(III) centers are separated by 7.89 Å.  $[\text{CoL}_2]^-$  consists of two dipicolinato anions in octahedral environment. In addition to electrostatic interactions, the complex is also stabilized by hydrogen-bond interactions of the two water molecules with the carboxylato oxygen of  $[\text{CoL}_2]^-$ . The carboxylato oxygen of the anion exhibits extensive hydrogen bonds with crystallized water molecules while the carboxylato oxygen of the cation is involved only in C–H...O interactions. The second type of non-covalent forces stabilizing the crystal lattice of **1** is from face-to-face  $\pi$ – $\pi$  stacking interactions between two pyridine rings of dipicolinato anion in  $[\text{CoL}_2]^-$ . The centroid-to-centroid distance between two such pyridine rings is 4.21 Å.

The cation and anion complex ions are closely packed (density, 1.622 g cm<sup>-3</sup>) in an alternate manner throughout the lattice extending along the crystallographic *c*-axis (figure 2). The two molecules of water occupy interstitial space of the lattice and display hydrogen bonds only with the carboxylato oxygen of  $[\text{CoL}_2]^-$ . Complex **1** is soluble and stable in water. The stability of the complex in aqueous solution is revealed by <sup>1</sup>H-NMR spectra in solution after different time intervals, which showed no change in the spectra. The complex has characteristic peaks of pyridine and dipicolinato ligands as shown in figure 3. There are triplet (7.9 ppm) and two doublets (8.7 and 8.45 ppm) from the dipicolinato ligands, whereas there are six other signals, of which three in one set are for one pyridine and three in another set from two other pyridines. The pyridine molecules are thus in two different environments. This is reflected in the X-ray crystallography (figure 1b) with two pyridines *trans* to each other and the other pyridine *cis* with respect to the two *trans* pyridines.

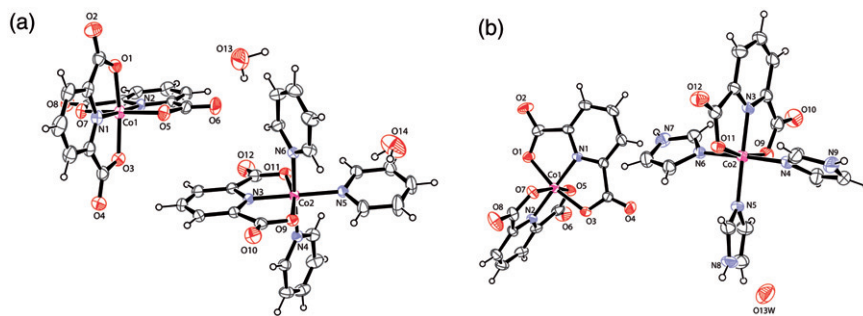
Complex **2** crystallizes as complex cations and anions similar to **1** but the cation has three imidazoles in the place of pyridine and there is only one water molecule of crystallization (figure 4). Each complex ion  $[\text{CoL}(\text{im})_3]^+$  and  $[\text{CoL}_2]^-$  can be considered



Scheme 1. Synthesis of cobalt(III) dipicolinato complexes.

Table 1. Crystallographic parameters of **1** and **2**.

Parameters	<b>1</b>	<b>2</b>
Formula	C <sub>36</sub> H <sub>28</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>14</sub>	C <sub>30</sub> H <sub>25</sub> Co <sub>2</sub> N <sub>9</sub> O <sub>13</sub>
Formula weight	886.50	837.43
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2(1)/c</i>	<i>P2(1)/c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	13.4899(7)	13.3116(4)
<i>b</i>	16.5385(9)	15.9824(5)
<i>c</i>	16.3709(8)	15.3478(4)
$\alpha$	90.00	90.00
$\beta$	96.2630(10)	91.160(2)
$\gamma$	90.00	90.00
Volume (Å <sup>3</sup> ), <i>Z</i>	3630.6(3), 4	3264.60(17), 4
Calculated density (g cm <sup>-3</sup> )	1.622	1.700
Absorption coefficient (mm <sup>-1</sup> )	0.994	1.100
<i>F</i> (0 0 0)	1808	1696
Crystal size (mm <sup>3</sup> )	0.34 × 0.22 × 0.14	0.30 × 0.16 × 0.10
Reflections collected	33,353	36,331
	[ <i>R</i> (int) = 0.0544]	[ <i>R</i> (int) = 0.0546]
Independent reflection	8642	5190
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.935	0.891
Final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0345, <i>wR</i> <sub>2</sub> = 0.0851	<i>R</i> <sub>1</sub> = 0.0333, <i>wR</i> <sub>2</sub> = 0.0666
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0509, <i>wR</i> <sub>2</sub> = 0.0900	<i>R</i> <sub>1</sub> = 0.0542, <i>wR</i> <sub>2</sub> = 0.0711
CCDC Number	789552	789551

Figure 1. Structures of (a) **1** and (b) **2** drawn with 30% thermal ellipsoids.

as a distinct octahedral unit. The cation [CoL(im)<sub>3</sub>]<sup>+</sup> is built up of one dipicolinato anion (L) and three imidazoles coordinated to the cobalt(III). Cobalt(III) centers are separated by a distance of 7.78 Å.

The coordination polyhedron around the cobalt(III) center of the cation has three nitrogen donors from imidazole and two oxygen donors along with nitrogen from dipicolinate occupying the six coordination sites. Extensive hydrogen bonding between the carboxylato oxygen of the anion and the unbound imidazole nitrogen of the cation stabilizes **2**. [CoL<sub>2</sub>]<sup>-</sup> is similar to **1** with minor differences in bond parameters around cobalt (figure 1b). The packing patterns of **1** and **2** are similar (figures 2 and 4), displaying a supramolecular architecture built up of anionic and cationic discrete units

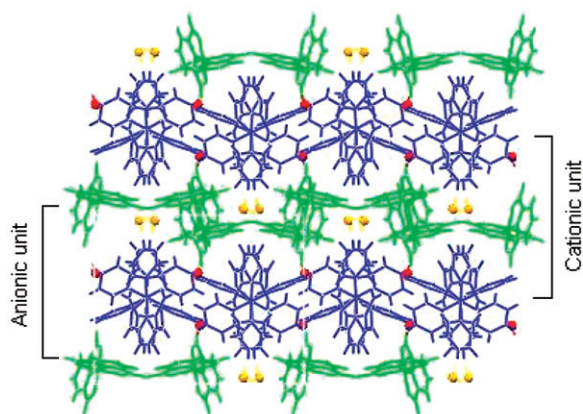


Figure 2. Parallel cationic and anionic chains in the lattice of **1**.

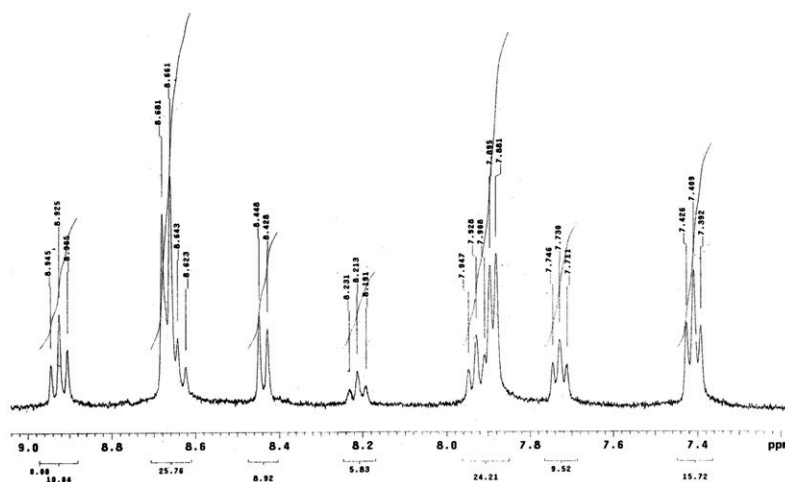


Figure 3. The aromatic region of the 400 MHz  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ ) spectrum of **1**.

to afford lamellar close packed structure. Close packing in the crystal of **2** is reflected by the relatively high density of **2** ( $1.70 \text{ g cm}^{-3}$ ) versus that of **1** ( $1.62 \text{ g cm}^{-3}$ ). The only crystallized water molecule present in the asymmetric unit of **2** shows hydrogen contact with  $[\text{CoL}_2]^-$ . In addition to electrostatic and hydrogen-bonding interactions, face-to-face  $\pi$ - $\pi$  stacking interactions also contribute to the stability of the lattice. The centroid-to-centroid distances between two neighboring dipicolinato pyridine rings of anions are 3.65 and 3.73 Å, respectively. The Co-N distances between the central cobalt(III) with pyridine nitrogen is longer than the imidazole nitrogen, which may be attributed to the smaller size of imidazole. Although the magnetic moment of **2** is negligible at room temperature (almost diamagnetic), the  $^1\text{H-NMR}$  spectrum is broad [21]. We have taken up the structural chemistry of dipicolinato complexes in order to generate layered structures, in which we observed coordination of cations [22] and cation encapsulations [23]; however, in the present case this does not occur as

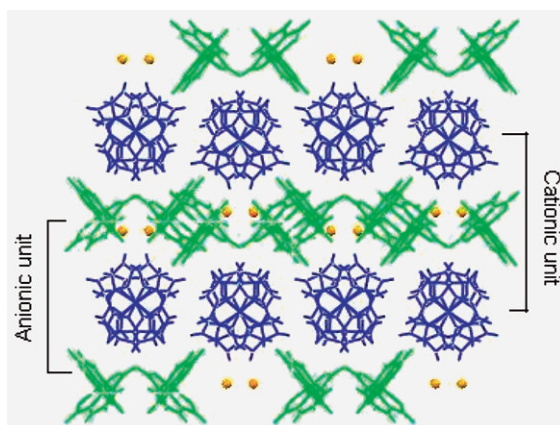


Figure 4. Packing diagram of **2** along the crystallographic *c*-axis.

cations formed are comparable in size with anions and they themselves are associated in layer-like structure formations. The molar conductances of complexes **1** and **2** in water are 53.0 and 68.0 S cm<sup>2</sup> mol<sup>-1</sup>, respectively, slightly low for a 1 : 1 electrolyte. The lower value is attributed to low ionic mobility of the moderately sized charged species in aqueous solution. Thermogravimetric analysis reveals loss of water at 60–130°C for both the complexes, which agrees with the compositions.

In conclusion, a new class of high oxidation state complexes having both anion and cation cobalt(III) centers with possibility to ion-exchange for various applications [22] and having relevance as structural replica of medicinal compounds is described. The synthesis of these complexes has opened a door to synthesize cationic and anionic cobalt(III) complexes with varied environments.

### 3. Experimental

#### 3.1. Physical measurements

IR spectra (KBr pellets) were recorded with a Perkin Elmer Spectrum One FTIR spectrophotometer in the 4000–400 cm<sup>-1</sup> spectral region. Thermal analyses (thermogravimetric/differential thermal analyzer) were performed on a Mettler Toledo TGA/SDTA851e thermal analyzer in air (79% N<sub>2</sub>/21% O<sub>2</sub>) with a heating rate of 10°C. Visible spectra were recorded using a Perkin Elmer Lambda 750 UV-Visible spectrophotometer. NMR spectra were recorded on a 400 MHz Varian Mercury Plus FT-NMR spectrometer system. Elemental analyses were performed with a Perkin Elmer 2400 series micro analytical analyzer. Molar conductance measurements of the complexes were calculated using Elico conductivity meter, model CM 180.

#### 3.2. X-ray structural studies

X-ray crystallographic data were collected at 296 K with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a Bruker Nonius SMART CCD diffractometer equipped with

a graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All non-hydrogen atoms were refined in the anisotropic approximation against  $F^2$  of all reflections. The hydrogens attached to water were located in the difference Fourier synthesis maps and refined with isotropic displacement coefficients. Labile hydrogens on water oxygen could not be located in **2** and are refined without the hydrogens.

Synthesis of  $[\text{CoL}(\text{py})_3][\text{CoL}_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{CoL}(\text{im})_3][\text{CoL}_2] \cdot \text{H}_2\text{O}$  (**2**): a solution of cobalt(II) acetate tetrahydrate (374 mg, 1.5 mmol) in 10 mL methanol was stirred at ambient conditions with  $\text{H}_2\text{O}_2$  (1 mL, 30%) to obtain a dark green solution of cobalt(III) salt. To this solution, 2,6-pyridine dicarboxylic acid (351 mg, 2.25 mmol) was added. A dark red solution obtained was stirred and left overnight at ambient temperature. Slow evaporation from a 1:1 mixture of water/pyridine or water/imidazole afforded dark red rhombic crystals of **1** or **2**, respectively, in 2–3 days. For **1**: Isolated yield, 62%. Elemental Anal. Calcd for  $\text{C}_{36}\text{H}_{28}\text{Co}_2\text{N}_6\text{O}_{14}$ : C, 48.73; H, 3.16. Found: C, 48.58; H, 3.06. IR (KBr,  $\text{cm}^{-1}$ ): 3415 (bs), 1689 (s), 1673 (s), 1448 (m), 1325 (s), 1312 (w), 1163 (m).  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ , 400 MHz, ppm): 8.9 (2H, t,  $J=8.0$  Hz), 8.7 (6H, d,  $J=8.0$  Hz), 8.45 (2H, d,  $J=8.0$  Hz), 8.2 (1H, t,  $J=7.2$  Hz), 7.9 (6H, dt,  $J=6.4$  Hz,  $J=8.0$  Hz), 9.5 (2H, t,  $J=7.6$  Hz), 7.4 (3H, t,  $J=6.8$  Hz).

Molar conductance:  $53.0 \text{ S cm}^2 \text{ mol}^{-1}$  in water. Vis ( $\text{H}_2\text{O}$ )  $\lambda_{\text{max}}$ : 513.0 nm;  $\epsilon = 923 \text{ mol}^{-1} \text{ cm}^{-1}$ . Thermal analysis:  $\sim 60\text{--}130^\circ\text{C}$  loss of two water molecules of crystallization; further decomposition occurs at  $\sim 285^\circ\text{C}$ . For **2**: Isolated yield, 66%. Elemental Anal. Calcd for  $\text{C}_{30}\text{H}_{25}\text{Co}_2\text{N}_9\text{O}_{13}$ : C, 42.99; H, 2.99. Found: C, 42.76; H, 2.88. IR (KBr,  $\text{cm}^{-1}$ ): 3479 (m), 3149 (bm), 1662 (s), 1651 (s), 1330 (s), 1069 (w). Vis ( $\text{H}_2\text{O}$ )  $\lambda_{\text{max}}$ : 515.0 nm;  $\epsilon = 681 \text{ mol}^{-1} \text{ cm}^{-1}$ . Thermal analysis:  $\sim 75^\circ\text{C}$  to  $125^\circ\text{C}$ , loss of one water molecule of crystallization; further decomposition occurs at  $\sim 235^\circ\text{C}$ .

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