# One new carboxylato-bridged dimeric network of Co(II): Synthesis and structural aspects

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A new carboxylato-bridged Co(II) dimeric complex, formulated as {Co(H$_2$O)$_5$[Co(2,6-pdc)$_2$].2H$_2$O} (H$_2$PDC = Pyridine-2,6-dicarboxylic acid), was synthesized in solid state under mild conditions, solved by single crystal X-ray diffraction techniques and characterized by elemental analysis, IR and electronic spectra, thermogravimetric analysis and variable temperature magnetic moments. The structural investigation shows that the crystal system of the new complex is monoclinic, having space group *P2(1)/c*, *a* = 8.3545(5), *b* = 27.1474(16), *c* = 9.5882(6) Å, *β* = 99.089(1)°, and *Z* = 4. The neighbouring Co atoms are bridged by carboxylate group of one pdc ligand and the dihedral angle defined by the mean planes of two pdc ligands is 88.6°, showing that they fall almost perpendicular. The effective magnetic moment μ$_{eff}$ value of the new complex is close to 5.31 μ$_B$ at 302 K, and much larger than the spin-only value of 3.87 μ$_B$ for high-spin Co(II). The complex is extended into a three-dimensional hydrogen bonding network.

**Key words:** Crystal structure, cobalt(II), carboxylato-bridge, H$_2$-PDC, spectral studies, TGA analysis.

## INTRODUCTION

The compounds containing carboxylate group are an important class of ligands in inorganic and bioinorganic chemistry. Metal complexes containing monocarboxylic acids are well known regarding the versatility of the carboxylate group as an inner-sphere ligand [1]. Rigid dicarboxylates are parti-cularly attractive because the metal carboxylate bonding is also rigid and the use of appropriate spacers can lead to predetermined network struc-tures [2–5].

Previously it was found out that the reaction of simple transition metal salts with functionalized carboxylic and dicarboxylic acids leads to the iso-lation of soluble materials, which were structurally elucidated [6–8]. H$_2$PDC (pyridine-2,6-dicarboxylic acid) is an efficient ligand, which is usually used as a tridentate ligand, as well as a bridging linker in the chemical design of metal-organic molecular assemblies [9–13]. H$_2$PDC forms chelates with simple metal ions and oxo-metal cations and it can display widely varying coordination behaviour, functioning as a multidentate ligand. Other isomeric pyridine-dicarboxylic acids, e.g. pyridine-2,3-, 2,4- and 2,5-dicarboxylic acids, behave like picolinic acid and act as bidentate (chelating) N,O donors. A very important characteristic of these ligands is their diverse biological activity. Pyridine-2,3-dicarboxy-lic acid is an intermediate in the tryptophan de-gradation pathway and it is precursor for NAD [14]. However, reports for H$_2$PDC's coordination com-plexes having 3D open framework structures are rarely seen [15, 16].

In this regard, Ghosh *et al*. [17] reported the complex, [Co(pdc)(4,4'-bpy)].1/2MeOH, where pyridine-2,6-dicarboxylic acid has been used as a ligand for binding more than one metal ion through carboxylate bridging to form 1-D coordination polymeric chains.

On the basis of the aforementioned considera-tions, herein, we describe the crystal structure, spec-troscopic study, thermogravimetric analysis and low-temperature magnetic properties of a new carboxylato-bridged cobalt(II) complex (**1**), using pyridine-2,6-dicarboxylic acid, in which the Co(2) atom possesses a distorted octahedral geometry.

## EXPERIMENTAL

All the chemicals used for the synthesis were of reagent purity grade. Cobalt(II) nitrate and pyridine-2,6-dicarboxylic acid (Aldrich) were used as received.

C, H, and N analyses were carried out using a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 883 infra-red spectrophotometer in the range 4000–200 cm$^{-1}$

as KBr pellets. Electronic spectra were measured on a Hitachi U-3400 (UV-Vis-NIR) spectrophotometer in methanol. The thermal investigation was carried out on a Shimadzu TGA-50 thermal analyser in a dynamic nitrogen environment. Magnetic susceptibility measurements were carried out on a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the range 2–302 K.

### Synthesis of {Co(H₂O)5[Co(2,6-pdc)2].2H₂O} (1)

To a 10 ml methanolic solution of cobalt(II) nitrate (2 mmol, 0.582 g), 10 ml of aqueous solution of pyridine-2,6-dicarboxylic acid (2 mmol, 0.334 g) were added upon stirring and reaction mixture was kept at room temperature. Several days later good quality green square-shaped crystals of **1** were separated. They were filtered, washed with methanol-water mixture (1:1) and dried. Yield: 73%. Anal. Calcd. for $C_{14}H_{20}Co_2N_2O_{15}$: C 29.25, H 3.51, N 4.87%; Found: C 29.19, H 3.46, N 4.82%.

### Crystallography

The details concerning crystal data, data collection characteristics and structure refinement are summarized in Table 1. Diffraction data were measured at 100(2) K on a Bruker AXS P4 four-circle diffractometer fitted with graphite-monochromated CuKα radiation, λ = 0.71073 Å and the ω : 2θ scan technique for data collection within a θ range of 1.50–28.33°.

**Table 1.** Crystal data and refinement parameters for complex **1**.

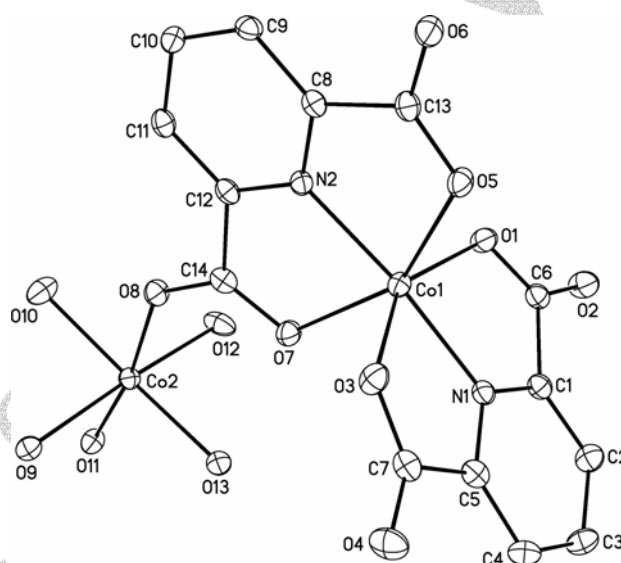| | |
|---|---|
| Chemical formula | $C_{14}H_{20}Co_2N_2O_{15}$ |
| Molecular weight | 574.18 |
| Space group | P2(1)/c |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| $a$ (Å) | 8.3545(5) |
| $b$ (Å) | 27.1474(16) |
| $c$ (Å) | 9.5882(6) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 99.089(1) |
| $\gamma$ (°) | 90 |
| $T$ (K) | 100(2) |
| $V$ (Å³) | 2153.0(2) |
| $Z$ | 4 |
| $D$ (mg/m³) | 1.771 |
| Absorptin coefficient (mm⁻¹) | 1.620 |
| $\theta$ for data collection (°) | 1.50–28.33 |
| Reflections collected | 16028 |
| Independent reflections | 5354 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0310$, $wR2 = 0.0740$ |
| $R$ indices (all data) | $R1 = 0.0378$, $wR2 = 0.0764$ |
| Largest diff. Peak and hole | 0.469 and –0.339 $e \cdot Å^{-3}$ |

The structure was solved by direct methods using the SHELXTL PLUS [18] system and refined by

full-matrix least-squares methods based on $F^2$ using SHELXL93 [19]. In this case, non-hydrogen atoms were calculated employing anisotropic displacement parameters and the hydrogen atom positions were calculated with fixed isotropic displacement parameters.

## RESULTS AND DISCUSSION

### Crystal structure section

The ORTEP representation of **1** is shown in Fig. 1 with selected bond lengths and angles summarized in Table 2.



Fig. 1. An ORTEP plot of complex **1** drawn with 40% probability level. Hydrogen atoms have been omitted for simplicity.

Complex **1** crystallizes in monoclinic system with space group *P2(1)/c*. It consists of elongated octahedral molecules, where the Co(1) centre exhibits a coordination surrounding $O_4+N_2$, of the type 4+2. The six donor atoms are the one N-pyridine and two O-carboxylate donors of each tridentate pdc ligand. They define well a mean plane (deviations < 0.032 Å), which virtually contains the metal atom (deviation of 0.019 Å). The *trans*-angles, O(1)–Co(1)–O(3) and O(5)–Co(1)–O(7), have a significantly low value. Both O–Co–O *trans*-angles of **1** reveal the rather rigid structures of such tridentate ligands, which are approximately planar (within 0.019 Å). In contrast, the *trans*-angle N–Co–N [N(1)–Co(1)–N(2)] is quite close to ∼ 180° and the dihedral angle defined by the mean planes of two pdc ligands is 88.6°, showing that they fall almost perpendicular.

The Co(1) and Co(2) atoms are held together by single *μ*-carboxylate oxygen of the pdc ligand. The Co(2) atom is chelated by one oxygen atom of

bridging-carboxylate from the pdc ligand and it coordinates five oxygen atoms from five water molecules. Thus, the Co(2) atom exhibits a distorted octahedral coordination geometry. Among the six coordination sites, the four sites are almost in an equatorial plane (the deviation from a regular square-planar structure is 9.47°) and these are occupied by four oxygen atoms from four water molecules, the two sites in the axial position are occupied by one oxygen atom from bridging-carboxylate and one oxygen atom from one water molecule. The deviation from the octahedral geometry is also indicated by the bond angles between the atoms in the *cis* positions, which vary from 79.83(5) to 99.25(5)° as well as the angles involving the *trans* positions that vary to a large extent from 168.78(5) to 176.58(5)°. The Co(2) sites are located on a crystal inversion centre.

**Table 2.** Selected bond lengths (in Å) and interbond angles 9in °) for complex **1**.

| | |
|---|---|
| Co(1)–N(1) | 2.0157(16) |
| Co(1)–N(2) | 2.0241(15) |
| Co(1)–O(1) | 2.1708(13) |
| Co(1)–O(5) | 2.1802(12) |
| Co(1)–O(3) | 2.113(13) |
| Co(1)–O(7) | 2.2148(12) |
| Co(2)–O(8) | 2.0868(12) |
| Co(2)–O(9) | 2.1681(13) |
| Co(2)–O(10) | 2.0525(14) |
| Co(2)–O(11) | 2.0877(13) |
| Co(2)–O(12) | 2.0516(14) |
| Co(2)–O(13) | 2.0832(13) |
| | |
| N(1)–Co(1)–N(2) | 171.83(6) |
| O(1)–Co(1)–O(3) | 149.90(5) |
| O(5)–Co(1)–O(7) | 151.48(5) |
| O(1)–Co(1)–O(7) | 96.82(5) |
| O(3)–Co(1)–O(5) | 85.36(5) |
| O(8)–Co(2)–O(10) | 79.83(5) |
| O(10)–Co(2)–O(9) | 86.09(5) |
| O(9)–Co(2)–O(11) | 85.65(5) |
| O(11)–Co(2)–O(13) | 99.25(5) |
| O(13)–Co(2)–O(12) | 88.31(6) |
| O(12)–Co(2)–O(8) | 87.29(5) |
| O(8)–Co(2)–O(11) | 170.37(5) |
| O(10)–Co(2)–O(13) | 168.78(5) |
| O(9)–Co(2)–O(12) | 176.58(5) |

Extensive intermolecular hydrogen bonds are formed in the crystal by means of the five coordinated water molecules O9, O10, O11, O12 and O13 and the two lattice water molecules O14 and O15, the two coordinated carboxylic oxygen atoms O1 and O5, and three uncoordinated carboxylic oxygen atoms O2, O4 and O6, respectively. Thus, the complex is extended into a three-dimensional network by means of hydrogen bonds (Fig. 2). The data on hydrogen bonds for **1** is summarized in Table 3.
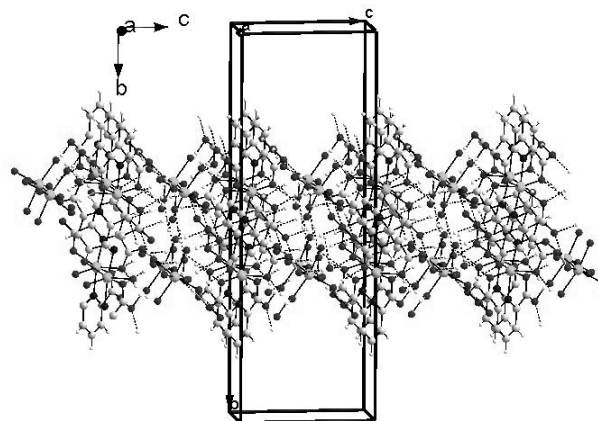


Fig. 2. The crystallographic packing diagram of complex **1** along the *a* axis.

### Spectral data section

The infrared spectrum of **1** is very consistent with the structural data presented in this paper. It shows characteristic absorption of the coordinated carboxyl groups. The strong bands at 1646 and 1400 cm$^{-1}$ for Co(1) centre and 1680 cm$^{-1}$ and 1395 cm$^{-1}$ for Co(2) centre were assigned as $\nu_{as}$ (COO$^{-}$) and $\nu_{sym}$ (COO$^{-}$) stretching vibrations, respectively. In the low energy region, a series of absorption peaks is also observed, such as $\nu_{O–C–O}$ at 1670 cm$^{-1}$, $\nu_{OH}$ at 925 cm$^{-1}$, $\nu_{C–H}$ at 1370 cm$^{-1}$ [20]. There are also three absorption peaks at 3385, 3345 and 3047 cm$^{-1}$, due to $\nu_{O–H}$ vibration modes for water molecules. The absorption bands in the 1400–1600 cm$^{-1}$ region arise from the skeletal vibrations of the aromatic rings of the ligand.

The UV-visible absorption peaks correspond to the absorptions for octahedral Co(II), which has features between 19600 and 21600 cm$^{-1}$ assigned to the $^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and $^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions, respectively [21].

**Table 3.** Data on hydrogen bonds for **1**.

| Bond | Distances, Å | Bond | Distances, Å |
|---|---|---|---|
| O11$_{cw}$…O14$_{lw}$ | 2.655 | O11$_{cw}$…O5 | 2.767 |
| O10$_{cw}$…O15$_{lw}$ | 2.986 | O10$_{cw}$…O6 | 2.636 |
| O12$_{cw}$…O15$_{lw}$ | 2.821 | O12$_{cw}$…O4 | 2.723 |
| O9$_{cw}$…O1 | 2.799 | O9$_{cw}$…O6 | 2.684 |
| O13$_{cw}$…O2 | 2.710 | O15$_{lw}$…O9$_{cw}$ | 2.938 |
| O14$_{lw}$…O4 | 2.769 | O14$_{lw}$…O2 | 2.781 |

cw = coordinated water; lw = lattice water.

### Thermogravimetric study

Thermogravimetric analysis was carried out in N$_2$ atmosphere with a heating range of 10°C·min$^{-1}$. The TGA curve indicates that complex **1** experienced three steps of weight loss. It began to lose lattice water slowly at 115°C and this ended at about 140°C. The loss of an aqua ligand began at 160°C

rapidly and ended at 190°C. This could occur because the latter has much higher bond energy than the former and higher lattice energy. Pyridine-2,6-dicarboxylate rapidly decomposes at 270°C and the process ends at 295°C.

## Magnetic moment measurements

The effective magnetic moment, $\mu_{eff}$ value of **1** is close to 5.31 $\mu_B$ at 302 K, and much larger than the spin-only value of 3.87 $\mu_B$ for high-spin Co(II). Upon cooling down, the $\mu_{eff}$ value decreases gradually to 3.96 $\mu_B$ at 18 K. The magnetic behaviour should be due to a larger orbital contribution arising from the $^4T_{1g}$ ground state of Co(II). It is very close and comparable with the $\mu_{eff}$ value on cooling 3.94 $\mu_B$, derived by Liao *et al.* [22]. The magnetic calculation has been done with the susceptibility equation based on $H = -2J(S_1S_2 + S_2S_1)$.

$$\chi_M = (Ng2\beta^2/4kT)[1 + \exp(-2J/kT) + 10\exp(J/kT)]/[1 + \exp(-2J/kT) + 2\exp(J/kT)] + N\alpha \qquad (1)$$

Where $\chi = \lambda/kT$, $\chi_M$ denotes the susceptibility per dinuclear complex, $\lambda$ is the spin-orbital coupling constant and $N\alpha$ is the temperature independent paramagnetism. Magnetic data were well fitted to Eqn. (1) in the temperature range of 18–302 K with $\lambda = -130.6$ cm$^{-1}$ and $g = 2.31$.

Very recently, Ribas and coworkers [17] derived the magneto-structural relationship for carboxylate-bridged 1-D coordination polymeric chain of Co(II) complexes, $J = -5.35$ cm$^{-1}$. Obviously, here the calculated $J$ value may be affected by the spin-orbital coupling and should be regarded only as the highest possible value for the antiferromagnetic coupling. In our present complex (1), an agreement factor has been defined as $\Sigma = (\chi^{calcd} - \chi^{obsd})^2/\Sigma(\chi^{obsd})$ and its value was $2.73 \times 10^{-5}$.

## CONCLUSION

One new carboxylato-bridged Co(II) complex, has been reported in which two different Co centres possess distorted octahedral geometry. Electronic spectra of the complex support its geometry as established based on X-ray analysis. Magnetic studies indicate that upon cooling down, the $\mu_{eff}$ value decreases gradually to 3.96 $\mu_B$ at 18 K. We are presently probing the capability of different modes of pyridine-dicarboxylic acids, like pyridine-2,3-, 2,4- or 2,5-dicarboxylic acids, to form metal-organic frameworks structures acting as bidentate (chelating) N,O donors on the Co(II) and other transition metal systems.

## Supplementary material

Crystallographic data have been submitted to the Cambridge Crystallographic Data Center with deposition number 273379. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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# НОВА ДВУМЕРНА МРЕЖА ОТ КОМПЛЕКС НА Co(II) С КАРБОКСИЛАТНИ МОСТОВЕ: СИНТЕЗ И СТРУКТУРНИ АСПЕКТИ

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(Резюме)

Синтезиран е в меки условия нов димерен комплекс на Co(II) в твърдо състояние, определен като {Co(H$_2$O)$_5$[Co(2,6-pdc)$_2$].2H$_2$O} (H$_2$PDC = пиридин-2,6-дикарбонова киселина) чрез рентгенова дифракция от монокристал и е охарактеризиран с елементен анализ, ИЧС, електронни спектри, термогравиметричен анализ и магнитен момент при различни температури. Структурните изследвания показват че кристалната система на новия комплекс е моноклинна, пространствена група *P2(1)/c*, *a* = 8.3545(5), *b* = 27.1474(16), *c* = 9.5882(6) Å, *β* = 99.089(1)°, и *Z* = 4. Съседните Co атоми са свързани с мостове от карбоксилатни групи от един PDC лиганд и пространственият ъгъл, определен от равнините на два PDC лиганда е 88.6°, показвайки, че те са почти перпендикулярни. Стойността на ефективния магнитен момент μ$_{eff}$ на новия комплекс е близо до 5.31 μ$_B$ при 302 K, много по-голям от спиновата стойност от 3.87 μ$_B$ за високоспинов Co(II). Комплексът се разраства в триизмерна мрежа чрез водородни връзки.