Hydrothermal synthesis and crystal structure of aqua(pyridine-2,6-dicarboxylato)(1,10-phenanthroline)cobalt(II) dihydrate

Sudalaandi Kumaresan*, Palani Ramadevi & Shaikh M Mobin

*Department of Chemistry, Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli 627 012, Tamil Nadu, India
National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Powai, Mumbai 400 076, India

Email: skumarmmsu@yahoo.com

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Hydrothermal reaction of cobalt(II) acetate with pyridine-2,6-dicarboxylic acid and 1,10-phenanthroline has afforded aqua(pyridine-2,6-dicarboxylato)(1,10-phenanthroline)cobalt(II) dihydrate (1). X-ray structure determination shows that complex 1 crystallized in the triclinic space group $P\overline{1}$. A one-dimensional assembly has been formed by the intermolecular $\pi-\pi$ interactions between the 1,10-phenanthroline units.

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Polycarboxylic acids are important ligands, which possess several noteworthy features. They are found to be effective in the formation of three-dimensional open-frameworks, in catalytic activity, in the synthesis of coordination polymers, and extended hydrogen-bonded networks.

The coordination chemistry of pyridinedicarboxylic acids has been reported by several groups of researchers. These acids are also found to display diverse biological activity. Pyridine-2,6-dicarboxylic acid has been shown to be versatile owing to its ability to function as a terdentate ligand and to exhibit coordination geometries because of its completely or partially deprotonated carboxylic acid groups or neutral forms.

Du Prez et al. have reported the synthesis and crystal structure of (pyridine-2,6-dicarboxylato)($N,N',N''$-tetramethyl-1,2-diaminoethane)nickel(II) dihydrate. But a thorough survey of literature revealed that there has been no report on the synthesis of divalent cobalt with pyridine-2,6-dicarboxylic acid and 1,10-phenanthroline. In continuation of our studies on the coordination chemistry of divalent zinc, cobalt, and nickel, we report herein the hydrothermal synthesis and crystal structure for the complex aqua(pyridine-2,6-dicarboxylato)(1,10-phenanthroline)cobalt(II) dihydrate (1).

Materials and Methods

All commercially available products were used without further purification. IR spectra were recorded on a Brucker IFS 66v/S spectrophotometer using KBr disks in the 4000-400 cm$^{-1}$ region. Thermogravimetric analysis was performed on a Mettler Toledo TGA 850 instrument with a heating rate of 10°C min$^{-1}$ under nitrogen.

Synthesis of (1)

A mixture of Co(OAc)$_2$·4H$_2$O (31 mg), pyridine-2,6-dicarboxylic acid (20 mg), 1,10-phenanthroline monohydrate (24 mg), and water (2.5 mL) with the molar ratio of 0.124:0.120:0.120:138 was stirred for 30 min, sealed in a 23 mL polyfluoroethylene-lined stainless steel bomb, and kept at 150°C under autogenous pressure for 72 h. After slowly cooling at a ramp of 10°C/h to room temperature, the pink coloured crystals were collected by filtration, washed with deionized water and air-dried ($\approx$ 67% yield). M. Pt. 332-335°C (uncorrected). Anal. Calc. for C$_{19}$H$_{17}$CoN$_3$O$_7$: C, 49.75; H, 3.71; N, 9.16. Found: C, 49.61; H, 3.63; N, 9.03%. Selected FT IR data (KBr, cm$^{-1}$): 3493 (w), 3448 (w), 3435 (w), 3365 (br), 3051 (w), 1664 (sh), 1619 (s), 1573 (m), 1515 (w), 1426 (m), 1368 (s), 1283 (m), 855 (m), 727 (m), and 530 (w).
Crystallographic data

Crystal data for 1: C_{19}H_{17}CoN_{3}O_{7}, M=458.28, triclinic, P-1, a=7.831(6) Å, b=9.303(6) Å, c=14.072(9) Å, α=81.54(5)°, β=81.53(6)°, γ=73.00(5)°, V=963.8(11) Å³, Z=2, Dc=1.576 mg/m³, F(000)=468, λ(Mo-Kα)=0.70930 Å, T=293(2) K. A pink coloured crystal of 1, with dimensions 0.40x0.35x0.25 mm, was mounted on a glass fiber with epoxy cement. Data were collected on a Nonius MACH 3 diffractometer equipped with graphite monochromated Mo-Kα radiation. Unit cell dimensions were obtained using 25 centered reflections in the range of 1.47<θ<24.93°. The intensity data were collected by CD-28 scan mode and corrected by Lorentz polarization and absorption effects using <1> scan (Tmax=1.000, Tmin=0.956). Three standard reflections monitored every 200 reflections and three intensity control reflections monitored every hour showed no significant changes (<3%). The structure was solved by direct methods SHELXS 97 and refined by full-matrix least squares against F² using SHELXL 97 software. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms, except for the coordinated- and non-coordinated water, were geometrically fixed and allowed to refine using a riding model. One of the hydrogen atoms of a non-coordinated water molecule could not be located. Details of the crystal parameters, data collection, and refinements for 1 are listed in Table 1.

Results and Discussion

The title complex 1 was prepared by heating a mixture of Co(OAc)₂·4H₂O, pyridine-2,6-dicarboxylic acid, 1,10-phenanthroline monohydrate, and water (0.124:0.120:0.120:1.38) at 150°C for 72 h. A multi-step synthesis of a related nickel complex had been reported. The pink coloured crystals of 1 are air-stable and sparingly soluble in methanol. FT-IR spectrum of 1 displays the stretching frequencies of the coordinated water (3493, 3435, 3365, 3051, 530 cm⁻¹) and asymmetric and symmetric carboxylate stretches of the dicarboxylate moiety (1664, 1619, 1573, 1426, 1368 cm⁻¹). The structure of 1 has been further determined by single crystal X-ray diffraction and elemental analysis. EDAX measurements indicate the presence of cobalt.

Thermal analysis (TGA) was performed between room temperature and 900°C under nitrogen atmosphere. The TGA results indicate that compound 1 gradually loses 12.53% of its mass in the temperature range of 85–180°C, corresponding to the loss of both the coordinated- and non-coordinated water molecules (calculated 11.8%). Above 340°C, the second process occurs with the loss of organic ligands.

An ORTEP drawing of 1 with the atomic numbering scheme is shown in Fig. 1. The asymmetric unit of 1 consists of one Co metal, one pyridine-2,6-dicarboxylate moiety, one coordinated aqua ligand, a 1,10-phenanthroline unit, and two non-coordinated water molecules. The formal oxidation
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The state of the Co metal is +2 (d^7). The Co atom is in a distorted octahedral environment, being bonded to the pyridine nitrogen atom and two carboxylate oxygen atoms of the pyridine-2,6-dicarboxylate ligand, two nitrogen atoms of 1,10-phenanthroline, and an oxygen atom of a water molecule. The disposition of the organic ligands may be described as nearly orthogonal with N(3) trans to N(2) and N(1) trans to the coordinated hydrate atom O(1).

The Co-O(carboxylate) distances are unequal [Co(1)-O(2)=2.14 Å and Co(1)-O(3)=2.16 Å]. These bond distances are in the range of 2.017-2.186 Å, which are comparable with those found for six-coordinate cobalt(II) complexes. Similarly there is a significant difference between the Co-N(1,10-phenanthroline) distances [Co(1)-N(1)=2.13 Å and Co(1)-N(2)=2.11 Å]. These values are comparable with those reported by Hao et al. Lengthening of these bond distances may be attributed to the non-bonded interactions due to steric overcrowding of the two bulkier ligands. Unlike in Co(III) complexes containing similar ligands, the Co(1)-N(3) bonding in the present Co(II) complex I is rather longer (2.045 Å). The bond distance between cobalt and the oxygen of the coordinated water, Co(1)-O(1) (2.098 Å), is in good agreement with the reported values.

Aqua-ligand oxygen atom O(1) is involved in hydrogen bonding with the non-coordinated solvent water O(111) and the carbonyl-oxygen O(5) through moderately strong O-H...O hydrogen bonding. The oxygen atoms, O(111) and O(222), of the non-coordinated water molecules interact with the carbonyl-oxygen atoms [O(4) and O(5)] and also with the carboxylate oxygen O(3). In addition to O-H...O hydrogen bonding, there exists weak C-H...O hydrogen bonding involving the aromatic C-H of 1,10-phenanthroline [H(3), H(6) and H(8)]. A perspective view of I along the a-axis is given in Fig. 2. The details of the hydrogen bonding are given in Table 2.

The trans bond angles related to the cobalt centre are very much deviated from the ideal 180° [N(3)-Co(1)-N(2)=171.50(7)°, O(1)-Co(1)-N(1)=167.43(8)°, and O(2)-Co(1)-O(3)=150.89(7)°] angle. The large deviation in the trans bond angle of

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**Fig. 2**—A perspective view along the a-axis. Dotted lines indicate hydrogen bonding.

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**Table 2**—Analysis of potential hydrogen bonds

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>D...A (Å)</th>
<th>D-H...A (°)</th>
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<tr>
<td>O(222)-H(22A)...O(4)</td>
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<td>2.9540</td>
<td>173.00</td>
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<tr>
<td>C(3)-H(3)...O(222)</td>
<td>3.3434</td>
<td>162.31</td>
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<tr>
<td>C(6)-H(6)...O(2)</td>
<td>3.4141</td>
<td>141.70</td>
</tr>
<tr>
<td>C(8)-H(8)...O(2)</td>
<td>3.2855</td>
<td>141.11</td>
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</table>

D = donor; A = acceptor
Fig. 3—π–π interactions; hydrogen bonding

O(2)–Co(1)–O(3) is attributed to the intrinsic structural topology of the pyridine-2,6-dicarboxylate unit.

The π–π interactions of complex I may be described considering the close centroid-to-centroid distance between the 1,10-phenanthroline units of the adjacent molecules. The centroid of each terminal aromatic ring of a 1,10-phenanthroline unit interacts with that of the middle ring of the adjacent 1,10-phenanthroline unit is evident from the short distance between them (≈3.63Å). Such interactions lead to the formation of the 1D array of the molecule (Fig. 3).

Supplementary material

Crystallographic data for complex I have been deposited with the Cambridge Crystallographic Data Centre (CCDC), deposition number CCDC 217849. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EJ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk

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References