Synthesis and Crystal Structure of a New Two-Dimensional Coordination Polymer, $\{[\mathrm{Co^{II}(imbz)_2}]\cdot\mathrm{H_2O}\}_n$ [$\mathrm{imbz^-}$ = 4'-(Imidazol-1-ylmethyl)benzoate Anion]

Wei-Yin Sun,* Yan-An Zhang, Taka-aki Okamura,† Tao Ye, and Norikazu Ueyama†
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China
†Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received August 7, 2000; CL-000758)

A new coordination polymer, $\{[\mathrm{Co^{II}(imbz)_2}]\cdot\mathrm{H_2O}\}_n$ [$\mathrm{imbz^-}$ = 4'-(imidazol-1-ylmethyl)benzoate anion] was synthesized and characterized by X-ray crystallography. Each Co(II) atom is coordinated by four imbz ligands, two of which using N atoms of imidazole and the other two using O atoms of benzoate, and each imbz ligand connects two Co(II) to generate an infinite 2D network. The crystal water molecules locate in the voids of two adjacent layers through C–H---O and O–H---O hydrogen bonds.

In the recent years, there are great interests in the study of coordination polymers with network structures due to their possible chemical and physical properties.[1] A number of unique networks have been obtained by reactions between transition metal ions and rationally designed organic ligands.[1,2] From these studies, it is known that the assembly of coordination networks was not only controlled by metal ions due to their different geometric need but also determined by the nature of ligands (building blocks). We focus our attention on construction of supramolecular frameworks with one- and two-dimensional network structures by using imidazole- or pyridine-containing organic ligands.[3] In the present study, a novel ligand with imidazole and carboxylate groups, namely 4'-(imidazol-1-ylmethyl)benzoic acid (imbzH) and its cobalt(II) complex $\{[\mathrm{Co^{II}(imbz)_2}]\cdot\mathrm{H_2O}\}_n$ (**1**), will be described. It is well known that both imidazole and carboxylate are functional groups for coordination to transition metal ions to form complexes.[4] However, ligands containing both imidazole and carboxylate groups are rare except the histidine residue and its derivatives.[5]

The imbzH ligand was prepared readily by hydrolysis of 4'-cyanobenzyl-1-imidazole in hydrochloric acid.[6] Compound **1** was obtained as purple prism in about 80% by slow diffusion between two layers of aqueous solution (10 mL) of $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ or $\mathrm{Co(ClO_4)_2{\cdot}6H_2O}$ and piperidinium salt of imbzH in methanol (10 mL) in the molar ratio 1:2 at room temperature. The structure of **1** was determined by X-ray crystallography.[7]

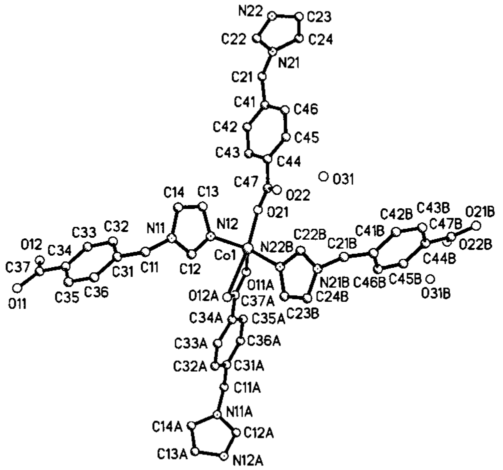

Figure 1. Crystal structure of complex **1** around the Co(II) atom with labeling scheme. Selected bond length (Å) and angles (°): Co1-O11A 2.044(3), Co1-O21 1.990(2), Co1-N12 2.037(3), Co1-N22B 2.036(3), O11A-Co1-O21 100.4(1), O11A-Co1-N12 123.3(1), O11A-Co1-N22B 107.4(1), O21-Co1-N12 98.2(1), O21-Co1-N22B 114.0(1), N12-Co1-N22B 112.6(1).

The coordination environment around the Co(II) atom of complex **1** is exhibited in Figure 1 with atom numbering scheme. The X-ray crystal structure of the complexes confirms that each Co(II) atom is coordinated by four imbz ligands, two of which using N12 and N22B atoms of imidazole and the other two using O21 and O11A atoms of benzoate anion. Therefore, the compound **1** is neutral and the coordination environment of the Co(II) atom is a distorted tetrahedral with $\mathrm{N_2O_2}$ binding set in which the coordination angles around the Co(II) varying from 98.2(1) to 123.3(1)°. The distance of 2.407 Å between the Co1 and O12A indicates the presence of weak interaction between these two atoms. The corresponding distance between Co1 and O22 is 3.149 Å. It means that two carboxylate anions coordinated to the Co1 atom are not exactly same, one is as monodentate (only using O21) and the other one is as semi-bidentate (using O11A and O12A). On the other hand, each $\mathrm{imbz^-}$ anion connects two Co(II) atoms to produce an infinite 2D network as illustrated in Figure 2. The sheet contains distorted squares formed by four $\mathrm{imbz^-}$ anions and four Co(II) atoms with a distance of 11.8 Å between two Co(II) atoms and angles of 100.4° (∠Co1F–Co1E–Co1H), 79.6° (∠Co1E–Co1F–Co1C). All the Co(II) atoms in one layer are on

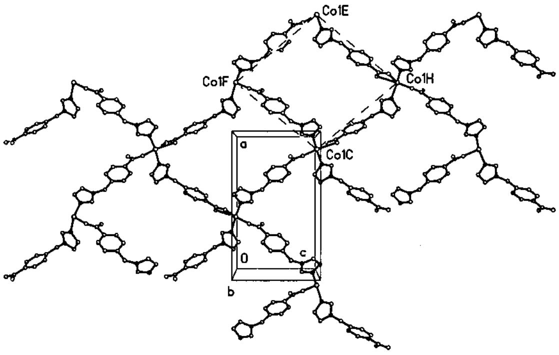

Figure 2. Infinite 2D network of complex **1** on the *ac* plane.

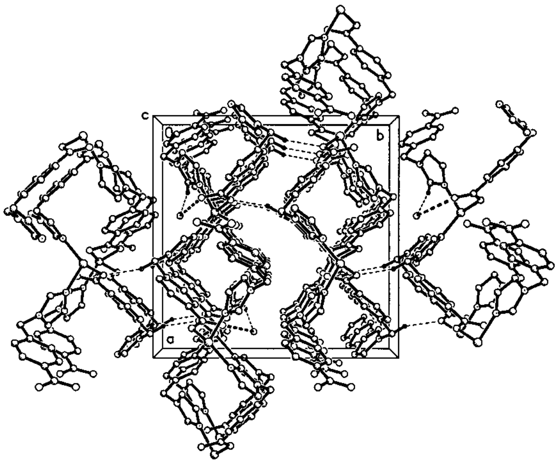

Figure 3. Crystal packing of complex **1** along the *c* axis with hydrogen bonds shown by dashed lines. Bold dashed lines refer to the shortest hydrogen bond (2.756 Å) between O31 and O22.

the same plane while the imbz ligands orientated up and down of the cobalt plane to give a corrugated and wavy network structure (Figure 3). The layers repeat in an ---ABAB--- stacking sequence along the *b* axis and two adjacent layers are staggered relative to each other so that the Co(II) atoms in one layer are located above or below the squares of adjacent layers (Figure 3). The nearest intermetallic distance between two Co(II) atoms in two adjacent layers is 9.4 Å.

There is one molecule of water per unit of $[Co^{II}(imbz)_2]$. The uncoordinated water molecules locate in the voids of two adjacent layers through C–H---O hydrogen bonds with a distance of 3.370 Å between imidazole C12A (x, y, 1+z) and O31 (Figure 3). A distance of 2.756 Å between the O22 and O31 as shown in Figure 1 indicates the existence of O31–H---O22 hydrogen bond although protons attached to the O31 atom could not be found from difference Fourier maps. Another C–H---O hydrogen bond is formed between the methylene C21B (1.5+x, 0.5–y, 1–z) and O21 with a distance of 3.235 Å.

It is worth notice that both imidazole N and carboxylic O of $imbz^-$ anion coordinated to Co(II) atoms to generate a 2D network. However, in the reported cobalt complexes with (±)-2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydro-1*H*-2-imidazole-2-yl)-nicotinic acid (Imz) and 1,4-bis(1-methylimidazole-2-ylmethyl)-7-carboxymethyl-1,4,7-triazacyclononane (LH) ligands, only mononuclear complexes $[Co(Imz)_3]\cdot 3H_2O$ and $[CoL](PF_6)_2$ were obtained.[9] In the case of Co(II) complex with hexanedioic acid and imidazole ligands, a linear polymer has been reported.[10] The results of present study demonstrate that the nature of ligand is important for rational synthesis of desired polymer framework.

The compound **1** is insoluble in all of usual organic solvents and its properties in solid state such as magnetic, desorption and resorption of uncoordinated water molecules[11] are undergoing now in our lab.

We thank the National Nature Science Foundation of China for financial support.

References and Notes

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7 Crystal data for **1**: MW = 479.36, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 15.0829(8), b = 15.399(1), c = 9.0576(4) Å, V = 2103.8(2) $Å^3$, Z = 4, D_c = 1.513 g/cm^3, $F(000)$ = 988, μ = 8.59 cm^{-1}, T = 223(1) K, λ(Mo Kα) = 0.7107 Å. A crystal of approximate dimensions 0.2 × 0.1 × 0.05 mm was selected and the data collection was carried on a Rigaku RAXIS-RAPID Imaging Plate area detector with graphite-monochromated Mo Kα radiation. The intensity data were collected with a maximum 2θ value being 55°. A total of 10937 reflections were collected, of which 4819 are used for refinements with 290 parameters. The structure was solved by direct method using SIR92[8] and expanded using Fourier techniques, and refined by full-matrix least-square calculations. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The final $R1$ = 0.034, Rw = 0.055, goodness of fit = 0.64, max. Shift/e.s.d = 0.007.

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