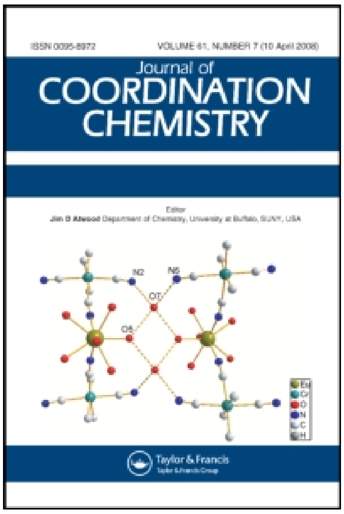

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STRUCTURES OF PYRIDINE CARBOXYLATE COMPLEXES OF COBALT(II) AND COPPER(II)

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The syntheses and crystal structures of $[Co(nic)_2(H_2O)_4]$ (**1**), $[Co(iso)_2(H_2O)_4]$ (**2**), $[Cu(nic)_2(H_2O)_4]$ (**3**), and $[Cu(iso)_2(H_2O)_4]$ (**4**) (nic = nicotinate; iso = isonicotinate) are reported. Complex **1** crystallizes in monoclinic, space group $C2/m$ with cell parameters $a = 14.150(4)$, $b = 6.883(2)$, $c = 8.497(2)$ Å, $\beta = 118.28(2)°$ and $Z = 2$. The other crystals, **2**, **3**, and **4**, are all triclinic, $P\bar{1}$; $a = 9.777(3)$, $b = 6.348(4)$, $c = 6.888(3)$ Å, $\alpha = 113.10(6)$, $\beta = 110.55(3)$, $\gamma = 97.61(5)°$, and $Z = 1$ for **2**; $a = 7.0281(4)$, $b = 7.7176(6)$, $c = 8.6978(7)$ Å, $\alpha = 68.103(7)$, $\beta = 68.526(5)$, $\gamma = 62.550(6)°$, and $Z = 1$ for **3**; $a = 9.1807(4)$, $b = 6.3334(3)$, $c = 6.8871(3)$ Å, $\alpha = 108.213(4)$, $\beta = 99.433(4)$, $\gamma = 105.190(4)°$, and $Z = 1$ for **4**. The arrangements around the metal ions are *trans*-octahedra with two pyridyl nitrogens and two aqua oxygens in the equatorial positions and two aqua oxygens in the axial positions, although the Cu(II) complexes show a larger Jahn-Teller distortion.

Keywords: X-ray structures; cobalt(II); copper(II); nicotinate; isonicotinate

INTRODUCTION

Pyridine monocarboxylic acids have three isomers according to the position of carboxylic acid on the pyridine ring, *i.e.*, picolinic acid (pyridine-2-carboxylic acid (pic)), nicotinic acid (pyridine-3-carboxylic acid (nic)), and isonicotinic acid (pyridine-4-carboxylic acid (iso)). Previously, X-ray diffraction studies of crystals of the zinc(II) complexes containing them

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have been carried out with respect to the following three isomers $[Zn(II)(pic)_2(H_2O)_2]\cdot 2H_2O$,[1,2] $[Zn(II)(nic)_2(H_2O)_4]$,[3–6] and $[Zn(II)(iso)_2(H_2O)_4]$,[7] in which the crystals of the three isometric complexes have different space groups, *i.e.* $P2_1/c$, $C2/m$ and $P\bar{1}$ for the picolinato, nicotinato and isonicotinato complexes, respectively. In the picolinato complex, the zinc(II) ion forms a distorted octahedron coordinated by the two pyridine nitrogens of two picolinate molecules, two carboxyl oxygens of two picolinate molecules, and two coordinated water oxygens. On the other hand, the zinc(II) ions in the nicotinato and isonicotinato complexes are surrounded by the four aqueous oxygen atoms and two pyridine nitrogen atoms, which are in a slightly distorted octahedral arrangement. Crystals of $[Co(II)(pic)_2(H_2O)_2]\cdot 2H_2O$[8] and $[Co(II)(nic)_2(H_2O)_4]$[9] have also been examined previously and their structures are the same as the respective zinc(II) isomers. The detailed crystal structure of $[Co(II)(iso)_2(H_2O)_4]$, however, has not been clarified, although the structure has been reported to be the same as the zinc(II) one from powder X-ray diffraction measurements.[10] In the case of the copper(II) complexes, the crystal structure of the picolinato complex has been investigated.[11] The complex crystallizes in space group $P\bar{1}$ with a composition of $[Cu(II)(pic)_2]\cdot 2H_2O$, which is different from those of the corresponding zinc(II) and cobalt(II) complexes. Coordination around the copper(II) ion gives an axially elongated octahedron with the two nitrogen and two oxygen atoms of two picolinate ligands at equatorial positions and two carboxyl oxygens belonging to adjacent layers at axial positions. Therefore, the structures and compositions of the nicotinato and isonicotinato complexes of copper(II), which have never been investigated, may also differ from those of the zinc(II) and cobalt(II) complexes.

In this paper the crystal structures of $[Co(II)(nic)_2(H_2O)_4]$ (**1**), $[Co(II)(iso)_2(H_2O)_4]$ (**2**), $[Cu(II)(nic)_2(H_2O)_4]$ (**3**), and $[Cu(II)(iso)_2(H_2O)_4]$ (**4**) are reported in order to give an answer to the above problem. Although the crystal structure of **1** has previously been reported by Anagnostopoulos *et al.*,[9] positional and thermal parameters have not been given. Here, we redetermined its structure.

EXPERIMENTAL

Preparation

The pyridine carboxylic acids were all commercially available and were used without further purification. Each ligand (0.62 g, 5.0 mmol) was dissolved in $20\,cm^3$ of distilled water by addition of NaOH at 60°C (final pH *ca* 6), and then the metal(II) chloride (0.59 g or 0.43 g for $CoCl_2\cdot 6H_2O$ or

$CuCl_2 \cdot 2H_2O$, 2.5 mmol) was added to the solution. After stirring the solutions for two hours, they were cooled to room temperature. The powdery products were filtered off, and then dissolved in distilled water again. Crystals suitable for X-ray examination were obtained from aqueous solution by slow evaporation during several days. The cobalt(II) complexes, **1** and **2**, were obtained as salmon pink, plate-like crystals, and the copper(II) species, **3** and **4**, give blue, plate-like crystals.

Elemental analyses (C, H, N) were performed using a LECO CHN-900 elemental analyzer. *Anal.*: Calcd. for $C_{14}H_{11}N_2Co$ (%): C, 38.41; H, 4.27; N, 7.47. Found for **1**: C, 38.35; H, 4.32; N, 7.41. Found for **2**: C, 38.16; H, 4.40; N, 7.40. Calcd. for $C_{14}H_{11}N_2Cu$ (%): C, 37.93; H, 4.21; N, 7.38. Found for **3**: C, 38.89; H, 4.25; N, 7.34. Found for **4**: C, 37.93; H, 4.25; N, 7.33.

X-ray Structure Determination

Crystal data and experimental details are listed in Table I. Diffraction data were collected with an Enraf-Nonius CAD4 four-circle diffractometer using graphite monochromated MoKα radiation. The intensities were monitored by three standard reflections every 2 hours. There was no significant variation in intensities during the data collections. The intensities were converted to F_o data in the usual manner. All the reflections were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS[12] was applied after isotropic refinement for non-hydrogen atoms.

The structures were solved by the heavy atom method and refined by full-matrix least-squares methods. Several cycles of refinement including anisotropic thermal parameters for non-hydrogen atoms were carried out. All H atoms were located from difference Fourier maps and were refined isotropically. Scattering factors and anomalous dispersion terms for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography*.[13] Calculations were performed on an INDY workstation computer using the SDP-Mol EN program[14] and partially on a CRAY C90 supercomputer at the Supercomputer Laboratory of the Institute for Chemical Research of Kyoto University. Final atomic parameters are summarized in Table II.

RESULTS AND DISCUSSION

The molecular structures of complexes **1**, **2**, **3**, and **4** are shown in Figure 1(a), (b), (c), and (d), respectively. Each crystal consists of a discrete *trans*-$[M(II)L_2(H_2O)_4]$ molecule (M(II) = Co(II) or Cu(II); L = nic or iso) in the

TABLE I Crystal data and experimental conditions for **1**, **2**, **3**, and **4**

	Complex **1**	*Complex* **2**	*Complex* **3**	*Complex* **4**
Formula	$C_{12}H_{16}N_2O_8Co$	$C_{12}H_{16}N_2O_8Co$	$C_{12}H_{16}N_2O_8Cu$	$C_{12}H_{16}N_2O_8Cu$
Formula weight	375.20	375.20	379.82	379.82
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	14.150(4)	9.777(3)	7.0281(4)	9.1807(4)
b/Å	6.883(2)	6.348(4)	7.1760(6)	6.3334(3)
c/Å	8.497(2)	6.888(3)	8.6978(7)	6.8871(3)
α/°		113.10(6)	68.103(7)	108.213(4)
β/°	118.28(2)	110.55(3)	68.526(5)	99.433(4)
γ/°		97.61(5)	62.550(6)	105.190(4)
V/Å^3	728(8)	349(2)	351(1)	353.7(1)
Z	2	1	1	1
D_{calc}/g cm^3	1.712	1.785	1.797	1.783
Crystal size/mm	0.3 × 0.15 × 0.05	0.2 × 0.2 × 0.05	0.5 × 0.5 × 0.25	0.3 × 0.5 × 0.1
T/K	298	298	298	298
F(000)	386	193	195	195
μ(MoKα)/cm^{-1}	12.2	12.7	16.0	15.9
Radiation (MoKα)	0.71069	0.71069	0.71069	0.71069
Unit cell determination	25 reflections $19.44 \le 2\theta \le 31.72$	25 reflections $19.72 \le 2\theta \le 28.18$	25 reflections $23.60 \le 2 \le 28.62$	25 reflections $21.64 \le 2\theta \le 32.82$
Scan mode	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Maximum 2θ/°	60	60	60	60
hkl range	+19, +9, ±11	+13, ±8, ±9	+9, ±10, ±12	+11, ±7, ±8
Scanning rate/° min^{-1}	6.0	6.0	6.0	6.0
Scan width/°	$0.70 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$	$0.85 + 0.59 \tan\theta$
No. of total reflections measured	1224	2032	2164	1528
No. of reflections used ($\lvert I_o\rvert > 3\sigma\lvert I_o\rvert$)	948	1706	1974	1358
Parameters refined	88	138	138	138
R	0.035	0.054	0.025	0.035
R_w	0.049	0.068	0.041	0.052
Weighting schemes	$1/(\sigma(F_o))^2$	$1/(\sigma(F_o))^2$	$1/(\sigma(F_o))^2$	$1/(\sigma(F_o))^2$

TABLE II Atomic parameters for **1**, **2**, **3**, and **4**[a]

Atom	*x/a*	*y/b*	*z/c*	B_{eq} *or* B_{iso} (Å^2)
Complex **1**				
Co	0	0	0	1.54(1)
O(1)	0.0590(1)	0.2176(3)	−0.1062(2)	2.33(3)
O(2)	0.3161(2)	0	0.8848(3)	2.98(6)
O(3)	0.1372(2)	0	0.7185(3)	3.31(6)
N	0.1476(2)	0	0.2468(3)	1.78(5)
C(1)	0.2439(2)	0	0.2502(4)	2.13(6)
C(2)	0.3405(2)	0	0.4079(5)	2.53(7)
C(3)	0.3391(2)	0	0.5697(4)	2.31(7)
C(4)	0.1473(2)	0	0.4040(4)	1.79(6)
C(5)	0.2400(2)	0	0.5679(4)	1.75(6)
C(6)	0.2311(3)	0	0.7373(4)	2.12(7)
H(1)	0.242(3)	0	0.134(6)	4(1)
H(2)	0.404(3)	0	0.399(6)	4(1)
H(3)	0.403(3)	0	0.678(6)	4(1)
H(4)	0.082(3)	0	0.405(6)	4(1)
H(5)	0.097(2)	0.328(5)	−0.041(4)	4.0(7)
H(6)	0.090(2)	0.172(6)	−0.163(4)	4.0(7)
Complex **2**				
Co	0	0	0	1.34(1)
O(1)	−0.0428(3)	−0.2117(4)	0.1518(4)	1.89(5)
O(2)	0.0818(3)	0.3036(4)	0.3385(4)	2.47(6)
O(3)	0.7333(3)	−0.1927(4)	0.3122(4)	2.51(6)
O(4)	0.8014(3)	0.2077(4)	0.5150(5)	2.68(6)
N	0.2316(3)	−0.0140(5)	0.0936(4)	1.71(6)
C(1)	0.2692(4)	−0.2178(6)	0.0597(6)	1.95(7)
C(2)	0.4184(3)	−0.2196(5)	0.1428(5)	1.66(6)
C(3)	0.5010(4)	0.2059(6)	0.2956(5)	1.79(6)
C(4)	0.3488(4)	0.1935(5)	0.2051(5)	1.73(5)
C(5)	0.5387(3)	−0.0043(5)	0.2662(4)	1.34(6)
C(6)	0.7033(4)	0.0043(6)	0.3714(5)	1.88(6)
H(1)	0.181(5)	−0.362(8)	−0.022(7)	3(1)
H(2)	0.437(5)	−0.360(7)	0.115(7)	3(1)
H(3)	0.580(5)	0.357(7)	0.372(7)	3(1)
H(4)	0.320(5)	0.334(8)	0.214(7)	3(1)
H(5)	−0.106(6)	−0.186(8)	0.218(8)	5(1)
H(6)	0.037(6)	−0.206(9)	0.249(9)	6(1)
H(7)	0.124(5)	0.267(8)	0.452(8)	4(1)
H(8)	0.116(6)	0.447(9)	0.377(8)	5(1)
Complex **3**				
Cu	0	0	0	1.479(4)
O(1)	0.2615(2)	−0.2522(2)	−0.0720(2)	2.68(3)
O(2)	0.2016(2)	0.2376(2)	−0.0874(2)	2.36(2)
O(3)	−0.1750(2)	−0.4004(2)	0.8296(1)	2.21(2)
O(4)	−0.4118(2)	−0.2472(2)	0.6622(1)	2.77(3)
N	0.0601(2)	−0.1206(2)	0.2331(1)	1.52(2)
C(1)	0.2608(2)	−0.1641(2)	0.2500(2)	1.83(3)
C(2)	0.3127(2)	−0.2472(2)	0.4067(2)	1.95(3)
C(3)	0.1570(2)	−0.2948(2)	0.5516(2)	1.77(2)
C(4)	−0.0922(2)	−0.1636(2)	0.3737(2)	1.49(2)
C(5)	−0.0499(2)	−0.2544(2)	0.5352(2)	1.42(2)
C(6)	−0.2268(2)	−0.3040(2)	0.6876(2)	1.63(2)
H(1)	0.369(3)	−0.134(3)	0.146(3)	2.1(4)

TABLE II (*Continued*)

Atom	x/a	y/b	z/c	B_{eq} or B_{iso} (Å^2)
H(2)	0.455(3)	−0.273(3)	0.413(3)	2.9(4)
H(3)	0.179(3)	−0.353(3)	0.662(2)	2.8(4)
H(4)	−0.233(3)	−0.123(3)	0.359(3)	2.6(4)
H(5)	0.269(4)	−0.373(4)	0.005(3)	4.8(6)
H(6)	0.378(3)	−0.254(3)	−0.147(3)	4.2(6)
H(7)	0.111(4)	0.354(4)	−0.127(3)	4.3(6)
H(8)	0.207(4)	0.266(3)	−0.001(3)	4.2(6)
Complex **4**				
Cu	0	0	0	1.804(8)
O(1)	0.0416(2)	−0.1531(3)	0.2042(3)	2.17(3)
O(2)	−0.0943(3)	0.2456(3)	0.2681(3)	3.29(5)
O(3)	0.7145(2)	0.9298(3)	0.4384(3)	2.99(4)
O(4)	0.7944(2)	0.6267(3)	0.2980(3)	3.06(4)
N	0.2190(2)	0.2322(3)	0.1246(3)	1.71(4)
C(1)	0.2486(3)	0.4667(4)	0.2014(4)	2.33(5)
C(2)	0.3980(3)	0.6256(4)	0.2762(4)	2.10(5)
C(3)	0.4943(3)	0.3038(4)	0.1968(4)	2.05(5)
C(4)	0.3422(3)	0.1543(4)	0.1282(4)	2.08(5)
C(5)	0.5248(3)	0.5463(4)	0.2719(3)	1.78(4)
C(6)	0.6917(3)	0.7133(4)	0.3424(4)	2.01(5)
H(1)	0.161(3)	0.521(4)	0.214(4)	2.7(6)
H(2)	0.419(4)	0.775(5)	0.339(4)	3.2(7)
H(3)	0.574(3)	0.244(4)	0.196(4)	2.1(6)
H(4)	0.319(4)	−0.013(5)	0.076(5)	3.4(7)
H(5)	0.117(4)	−0.049(6)	0.332(6)	5.2(9)
H(6)	−0.035(3)	−0.268(5)	0.225(5)	3.0(7)
H(7)	−0.120(4)	0.158(5)	0.353(6)	5(1)
H(8)	−0.120(5)	0.384(7)	0.296(7)	8(1)

${}^{a}B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.
H atoms were refined isotropically.

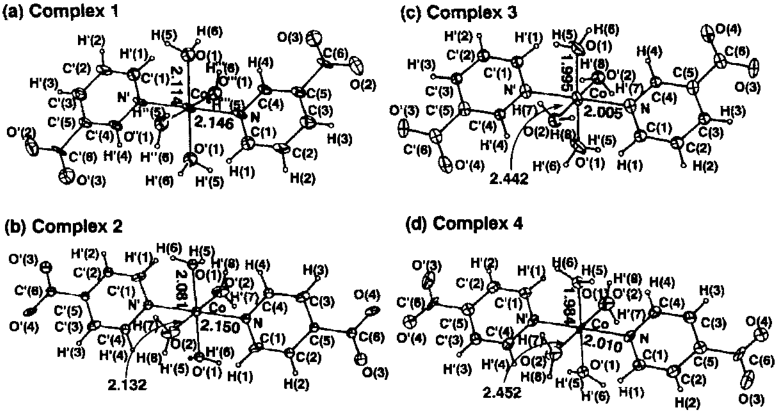

FIGURE 1 ORTEP[15] drawings of complexes **1** (a), **2** (b), **3** (c), and **4** (d). Non-H and H atoms are represented by thermal ellipsoids scaled at the 30% probability level and small circles with 0.1 Å radius, respectively.

unit cell. Selected interatomic distances and angles for **1**, **2**, **3**, and **4** are listed together in Table III. Hydrogen bond distances and angles are given in Table IV.

Crystals of **1** are monoclinic, space group *C*2/*m*, isomorphous with the corresponding Zn(II) complex reported previously. The crystal structure is essentially the same as that reported by Anagnostopoulos *et al.*[9]: the coordination sphere is an octahedron, with four aqueous oxygens related by 2/*m* symmetry and two nicotinato nitrogens lying on the mirror plane. The Co–N bond (2.146(2) Å) agrees well with values reported for six-coordinated Co(II) complexes with pyridine ligands (2.004–2.172 Å)[16] and the Co–O(1) bond (2.114(2) Å) is within the usual range observed for Co(II) complexes with water molecules (2.059–2.123 Å).[16]

The complex **2** crystallizes in the triclinic space group $P\bar{1}$, and is essentially isomorphous with that of the corresponding Zn(II) complex with nic. Coordination around the Co(II) atom forms a slightly distorted octahedral geometry with two aqueous oxygens and two isonicotinato nitrogens in the equatorial positions and two aqueous oxygens in the axial positions. The Co–O(2) bond (2.132 Å) is slightly longer than those of Co(II) complexes with water molecules reported previously (2.059–2.123 Å),[16] although another Co–O(1) bond (2.081(2) Å) lies within the range of usual values. The Co–N bond (2.150(3) Å) is also within the range of usual values (2.004–2.172 Å).[16] Although the substituent effect of the carboxyl group on the pyridine ring was expected to be reflected in the Co–N bonds between complexes **1** and **2**, no apparent difference was observed.

The complex **3** crystallizes in the triclinic space group $P\bar{1}$, different from the corresponding Zn(II) and Co(II) complexes. The coordination around the Cu(II) atom shows an axially-elongated octahedral geometry with Jahn-Teller distortion, with two aqueous oxygens and two nicotinato nitrogens in equatorial positions and two aqueous oxygens in axial positions. The axial Cu–O(2) bond (2.442(1) Å) lies in the range (2.275–2.520 Å)[16] reported previously for Cu(II) complexes with Jahn-Teller distortion and the equatorial Cu–O(1) bond (1.995(1) Å) is slightly longer than those in the six-coordinated Cu(II) complexes with water molecules (1.950–1.973 Å).[16] The Cu–N (2.005(1) Å) bond is shorter than those reported for six-coordinated Cu(II) complexes with pyridine ligands (2.039–2.055 Å).[16]

Crystals of **4** are also triclinic, space group $P\bar{1}$. The molecular structure shows an extreme Jahn-Teller distortion around the Cu(II) atom in comparison with that in complex **3**. The axial Cu–O(2) bond (2.452(2) Å) is longer than that of complex **3** (2.442(1) Å) and the equatorial Cu–O(1) bond (1.984(2) Å) is shorter than that of **3** (1.995(1) Å), although the Cu–N bond

TABLE III Interatomic distances (Å) and angles (°) for the complexes **1**, **2**, **3**, and **4**[a]

Complex **1**							
Co–O(1)	2.114(2)	Co–N	2.146(2)	N–C(1)	1.349(5)	N–C(4)	1.337(5)
C(1)–C(2)	1.389(4)	C(2)–C(3)	1.382(6)	C(4)–C(5)	1.388(3)	C(5)–C(3)	1.396(5)
C(5)–C(6)	1.501(5)	C(6)–O(2)	1.260(3)	C(6)–O(3)	1.262(5)	C(1)–H(1)	0.98(5)
C(2)–H(2)	0.94(5)	C(3)–H(3)	0.94(4)	C(4)–H(4)	0.93(5)	O(1)–H(5)	0.94(3)
O(1)–H(6)	0.85(4)						
O(1)–Co–O′(1)	180	O(1)–Co–O″(1)	89.77(8)	O(1)–Co–O‴(1)	90.23(8)	O(1)–Co–N	90.98(7)
O(1)–Co–N′	89.02(7)	O′(1)–Co–O″(1)	90.23(8)	O′(1)–Co–O‴(1)	89.77(8)	O′(1)–Co–N	89.02(7)
O′(1)–Co–N′	90.98(7)	O′(1)–Co–O‴(1)	180	O″(1)–Co–N	89.02(7)	O″(1)–Co–N′	90.98(7)
O‴(1)–Co–N	90.98(7)	O‴(1)–Co–N′	89.02(7)	N–Co–N′	180	Co–O(1)–H(5)	124(2)
Co–O(1)–H(6)	113(3)	H(5)–O(1)–H(6)	109(3)	Co–N–C(4)	120.8(2)	Co–N–C(1)	121.8(2)
C(1)–N–C(4)	117.4(2)	N–C(1)–C(2)	123.0(4)	N–C(1)–H(1)	116(2)	C(2)–C(1)–H(1)	121(2)
C(3)–C(2)–C(1)	119.1(4)	C(3)–C(2)–H(2)	123(3)	C(1)–C(2)–H(2)	118(3)	C(5)–C(3)–C(2)	118.6(3)
C(5)–C(3)–H(3)	121(4)	C(2)–C(3)–H(3)	120(4)	N–C(4)–C(5)	123.5(3)	N–C(4)–H(4)	119(3)
C(5)–C(4)–H(4)	118(3)	C(4)–C(5)–C(3)	118.6(3)	C(4)–C(5)–C(6)	119.5(3)	C(3)–C(5)–C(6)	122.0(2)
O(2)–C(6)–O(3)	125.4(4)	O(2)–C(6)–C(5)	118.5(3)	O(3)–C(6)–C(5)	116.1(2)		
Complex **2**							
Co–O(1)	2.081(3)	Co–O(2)	2.132(2)	Co–N	2.150(3)	N–C(1)	1.346(5)
N–C(4)	1.350(4)	C(1)–C(2)	1.370(5)	C(2)–C(5)	1.391(4)	C(5)–C(3)	1.387(5)
C(3)–C(4)	1.374(5)	C(5)–C(6)	1.497(4)	C(6)–O(3)	1.263(5)	C(6)–O(4)	1.252(3)
C(1)–H(1)	0.97(4)	C(2)–H(2)	0.89(5)	C(3)–H(3)	0.96(4)	C(4)–H(4)	0.95(5)
O(1)–H(5)	0.88(6)	O(1)–H(6)	0.81(6)	O(2)–H(7)	0.88(6)	O(2)–H(8)	0.82(5)
O(1)–Co–O′(1)	180	O(1)–Co–O(2)	86.7(1)	O(1)–Co–O′(2)	93.3(1)	O(1)–Co–N	91.5(1)
O(1)–Co–N′	88.5(1)	O′(1)–Co–O(2)	93.3(1)	O′(1)–Co–O′(2)	86.7(1)	O′(1)–Co–N	88.5(1)
O′(1)–Co–N′	91.5(1)	O(2)–Co–O′(2)	180	O(2)–Co–N	88.3(1)	O(2)–Co–N′	91.7(1)
O′(2)–Co–N	91.7(1)	O′(2)–Co–N′	88.3(1)	N–Co–N′	180	Co–O(1)–H(5)	118(4)
Co–O(1)–H(6)	112(5)	H(5)–O(1)–H(6)	107(6)	Co–O(2)–H(7)	111(3)	Co–O(2)–H(8)	128(4)
H(7)–O(2)–H(8)	114(4)	Co–N–C(1)	123.8(2)	Co–N–C(4)	119.1(2)	C(1)–N–C(4)	117.0(3)
N–C(1)–C(2)	122.9(3)	N–C(1)–H(1)	114(3)	C(2)–C(1)–H(1)	123(3)	C(1)–C(2)–C(5)	119.9(3)
C(1)–C(2)–H(2)	119(3)	C(5)–C(2)–H(2)	121(3)	C(4)–C(3)–C(5)	119.3(3)	C(4)–C(3)–H(3)	120(3)
C(5)–C(3)–H(3)	120(3)	N–C(4)–C(3)	123.2(3)	N–C(4)–H(4)	116(2)	C(3)–C(4)–H(4)	121(3)
C(2)–C(5)–C(3)	117.5(3)	C(2)–C(5)–C(6)	121.8(3)	C(3)–C(5)–C(6)	120.6(2)	O(3)–C(6)–O(4)	124.6(3)
O(3)–C(6)–C(5)	118.1(2)	O(4)–C(6)–C(5)	117.2(3)				

Complex **3**							
Cu–O(1)	1.995(1)	Cu–O(2)	2.442(1)	Cu–N	2.005(1)	N–C(1)	1.349(2)
N–C(4)	1.342(1)	C(1)–C(2)	1.380(2)	C(2)–C(3)	1.385(2)	C(3)–C(5)	1.397(2)
C(4)–C(5)	1.389(2)	C(5)–C(6)	1.510(2)	C(1)–H(1)	0.97(2)	C(2)–H(2)	0.95(2)
C(3)–H(3)	0.93(2)	C(4)–H(4)	0.94(2)	C(6)–O(3)	1.264(2)	C(6)–O(4)	1.249(2)
O(1)–H(5)	0.87(2)	O(1)–H(6)	0.84(2)	O(2)–H(7)	0.82(2)	O(2)–H(8)	0.86(3)
O(1)–Cu–O′(1)	180	O(1)–Cu–O(2)	95.48(5)	O(1)–Cu–O′(2)	84.52(5)	O(1)–Cu–N	88.73(5)
O(1)–Cu–N′	91.27(5)	O′(1)–Cu–O(2)	84.52(5)	O′(1)–Cu–O′(2)	95.48(5)	O′(1)–Cu–N	91.27(5)
O′(1)–Cu–N′	88.73(5)	O(2)–Cu–O′(2)	180	O(2)–Cu–N	92.14(5)	O(2)–Cu–N′	87.86(5)
O′(2)–Cu–N	87.86(5)	O′(2)–Cu–N′	92.14(5)	N–Cu–N′	180	Cu–O(1)–H(5)	112(1)
Cu–O(1)–H(6)	129(2)	H(5)–O(1)–H(6)	116(2)	Cu–O(2)–H(7)	101(2)	Cu–O(2)–H(8)	112(2)
H(7)–O(2)–H(8)	101(3)	Cu–N–C(1)	119.4(1)	Cu–N–C(4)	122.1(1)	C(1)–N–C(4)	118.6(1)
N–C(1)–C(2)	122.2(1)	N–C(1)–H(1)	117(1)	C(2)–C(1)–H(1)	121(1)	C(1)–C(2)–C(3)	119.3(1)
C(1)–C(2)–H(2)	119(1)	C(3)–C(2)–H(2)	121(1)	C(2)–C(3)–C(5)	118.9(1)	C(2)–C(3)–H(3)	125(1)
C(5)–C(3)–H(3)	116(1)	N–C(4)–C(5)	122.6(1)	N–C(4)–H(4)	117(1)	C(5)–C(4)–H(4)	121(1)
C(3)–C(5)–C(4)	118.4(1)	C(3)–C(5)–C(6)	121.7(1)	C(4)–C(5)–C(6)	119.9(1)	O(3)–C(6)–O(4)	125.5(1)
O(3)–C(6)–C(5)	117.3(1)	O(4)–C(6)–C(5)	117.1(1)				
Complex **4**							
Cu–O(1)	1.984(2)	Cu–O(2)	2.452(2)	Cu–N	2.010(2)	N–C(1)	1.345(3)
N–C(4)	1.346(4)	C(1)–C(2)	1.371(3)	C(3)–C(4)	1.371(3)	C(2)–C(5)	1.385(4)
C(3)–C(5)	1.391(3)	C(5)–C(6)	1.512(3)	C(1)–H(1)	0.96(3)	C(2)–H(2)	0.86(3)
C(3)–H(3)	0.91(3)	C(4)–H(4)	0.95(3)	C(6)–O(3)	1.265(3)	C(6)–O(4)	1.242(4)
O(1)–H(5)	0.94(3)	O(1)–H(6)	0.94(3)	O(2)–H(7)	0.94(4)	O(2)–H(8)	0.94(5)
O(1)–Cu–O′(1)	180	O(1)–Cu–O(2)	85.97(8)	O(1)–Cu–O′(2)	94.03(8)	O(1)–Cu–N	89.85(8)
O(1)–Cu–N′	90.15(8)	O′(1)–Cu–O(2)	94.03(8)	O′(1)–Cu–O′(2)	85.97(8)	O′(1)–Cu–N	90.15(8)
O′(1)–Cu–N′	89.96(9)	O(2)–Cu–O′(2)	180	O(2)–Cu–N	91.24(7)	O(2)–Cu–N′	88.76(7)
O′(2)–Cu–N	88.76(7)	O′(2)–Cu–N′	*91.24(7)*	N–Cu–N′	*180*	*Cu–O(1)–H(5)*	*113(3)*
Cu–O(1)–H(6)	124(2)	H(5)–O(1)–H(6)	112(3)	Cu–O(2)–H(7)	104(2)	Cu–O(2)–H(8)	138(3)
H(7)–O(2)–H(8)	117(4)	Cu–N–C(1)	122.3(2)	Cu–N–C(4)	119.9(1)	C(1)–N–C(4)	117.9(2)
N–C(1)–C(2)	122.4(3)	N–C(1)–H(1)	118(2)	C(2)–C(1)–H(1)	120(1)	C(1)–C(2)–C(5)	120.0(2)
C(5)–C(2)–H(2)	116(2)	C(1)–C(2)–H(2)	123(2)	C(4)–C(3)–C(5)	119.5(3)	C(4)–C(3)–H(3)	110(1)
C(5)–C(3)–H(3)	121(1)	N–C(4)–C(3)	122.6(2)	N–C(4)–H(4)	117(2)	C(3)–C(4)–H(4)	121(2)
C(2)–C(5)–C(3)	117.6(2)	C(3)–C(5)–C(6)	120.1(2)	C(2)–C(5)–C(6)	122.3(2)	O(3)–C(6)–O(4)	125.5(2)
O(3)–C(6)–C(5)	117.2(3)	O(4)–C(6)–C(5)	117.3(2)				

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[a] Estimated standard deviations are given in parentheses. Symmetry transformations used to generate equivalent atoms: (′) $-x, -y, -z$; (″) $-x, y, 1-z$; (‴) and $x, -y, -1+z$.

TABLE IV Hydrogen bond distances (Å) and angles (°)

	Hydrogen bond X·····H–O	*Distance* X·····O	*Angle* X·····H–O
Complex **1**	O(2)^{a}···H(5)–O(1)	2.699	168
	O(3)^{b}···H(6)–O(1)	2.690	162
Complex **2**	O(3)^{c}···H(5)–O(1)	2.773	169
	O(4)^{d}···H(6)–O(1)	2.641	172
	O(3)^{d}···H(7)–O(2)	2.858	164
	O(4)^{e}···H(8)–O(2)	2.781	177
Complex **3**	O(3)^{f}···H(5)–O(1)	2.750	159
	O(4)^{g}···H(6)–O(1)	2.597	167
	O(3)^{h}···H(7)–O(2)	2.817	163
	O(3)^{i}···H(8)–O(2)	2.806	166
Complex **4**	O(3)^{e}···H(5)–O(1)	2.726	160
	O(4)^{j}···H(6)–O(1)	2.627	154
	O(3)^{j}···H(7)–O(2)	2.959	151
	O(4)^{c}···H(8)–O(2)	2.822	168

Equivalent positions: $^{a}1/2-x,\ 1/2-y,\ 1-z$; $^{b}x,\ y,\ -1+z$; $^{c}-1+x,\ y,\ z$; $^{d}1-x,\ -y,\ 1-z$; $^{e}1-x,\ 1-y,\ 1-z$; $^{f}-x,\ -1-y,\ 1-z$; $^{g}1+x,\ y,\ -1+z$; $^{h}x,\ 1+y,\ -1+z$; $^{i}-x,\ -y,\ 1-z$; $^{j}-1+x,\ -1+y,\ z$.

(2.010(2) Å) is almost the same (2.005(1) Å). Interestingly, the apparent discrepancy was not detected between Cu–N bonds in **3** and **4**.

As described above, the crystal structures of the nicotinato and isonicotinato complexes of Co(II) and the isonicotinato complex of Cu(II) are isomorphous with the corresponding Zn(II) complexes, although differences in the degree of distortion around the octahedral units appear. The nicotinato and isonicotinato complexes, therefore, form similar intermolecular hydrogen bonds between the coordinating water molecules and carboxyl oxygens of adjacent molecules, as listed in Table IV. Such hydrogen bond networks may contribute to the stabilities of the crystal structures.

Supplementary Material

Tables of calculated and observed structure factors and lists of anisotropic thermal parameters are available on request.

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