



The syntheses, crystal structures, spectroscopic and thermal characterization of new pyridine-2,5-dicarboxylate compounds

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ABSTRACT

In this study, four new M(II)-isonicotinomeric acid (pyridine-2,5-dicarboxylic acid) complexes with ethylenediamine (en) and 2,2'-bipyridine (bipy), namely $[Co(en)_3][Co(pydc)_2(H_2O)_2] \cdot 2H_2O$ (**1**), $[Ni(Hpydc)_2(H_2O)_2]$ (**2**), $[Cu(en)_2(H_2O)][Cu_3(pydc)_4(en)_2(H_2O)_2] \cdot 3H_2O$ (**3**) and $[Cu(bipy)_3][Cu(pydc)(bipy)] \cdot 2Cl \cdot 12H_2O$ (**4**) (H_2Pydc = pyridine-2,5-dicarboxylic acid), have been synthesised. Elemental, thermal analyses and IR spectroscopic studies have been carried out in order to characterise the complexes. The molecular structures of the complexes have been determined using single crystal X-ray diffraction. The geometry displayed by the Co^{II} (**1**) and Ni^{II} (**2**) ions is distorted octahedral. The Cu^{II} ions display a square pyramidal geometry and distorted octahedral geometry in **3**, while each Cu^{II} ion exhibits a distorted octahedral geometry in **4**. Molecules of each complex are linked into a 3D framework structure by N–H···O, O–H···O and C–H···O hydrogen bonds.

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1. Introduction

The self-assembly of organic molecular building blocks with transition metal ions into single crystal coordination compounds is providing access to new materials of scientific interest and potential applications [1]. The effective assembling of primary and secondary interactions has been applied in the engineering study of inorganic–organic hybrid materials and the building of metal–organic coordination supramolecular compounds [2]. Carboxylic acids are valuable ligands, which can form various coordination compounds with amazing structures due to their diverse coordination modes. Moreover, they are an important source for hydrogen bonds and Van Der Waals interactions [3–8]. Pyridinedicarboxylic acids have been widely used as organic ligands for the construction of organic–inorganic hybrid materials which have been of great interest in recent years [9–12]. These types of ligands combine the advantages of both organic multdicarboxylic acids and aromatic compounds [13–15]. 2,5-Pyridinedicarboxylic acid, with different functional groups which could show further possibilities for the formation of bridging coordination and hydrogen bonds, is very interesting and has

potential for self-assembly [16]. Both the ethylenediamine and 2,2'-bipyridine ligands have two units with N donor atoms. The first of these compounds has an aliphatic structure, while the other has an aromatic structure. Ethylenediamine is actually a stronger base than 2,2'-bipyridine, however, the crystal structures formed by 2,2'-bipyridine ligand π – π interactions cannot be found with ethylenediamine. These two ligands have acquired a special place in coordination chemistry. Our purpose in this study was to synthesise mixed ligand complexes using strong ligands such as H_2Pydc , ethylenediamine and bipy. Thus, we have investigated supramolecular interactions in monomeric mixed-ligand complexes using both aliphatic and aromatic ligands.

Our group has synthesised compounds of this acid with Co^{II} , Ni^{II} and Cu^{II} in the previous year: mer- $[Co(pydc)(H_2O)_3(ina) \cdot H_2O]$, $(2a3mpyH)_2[Co(pydc)_2(H_2O)_2] \cdot 2H_2O$, $(2a6mpyH)_2[Co(pydc)_2(H_2O)_2] \cdot 2H_2O$ (ina = isonicotinamide, $2a3mpy$ = 2-amino-3-methylpyridine, $2a6mpy$ = 2-amino-6-methylpyridine) [17], trans- $(H_2ben)[Co(pydc)_2(H_2O)_2] \cdot 4H_2O$, trans- $(H_2dmpen)[Co(pydc)_2(H_2O)_2] \cdot 2H_2O$ (ben = 1,4-butanediamine, $dmpen$ = 2,2-dimethylpropane-1,3-diamine) [18], $[Co(pydc)(bipy)] \cdot 5H_2O$, [19], $[Co(Hpydc)_2(phen)] \cdot H_2O$, ($phen$ = 1,10-phenanthroline) [20], $(Hampy)_2[Ni(pydc)_2(H_2O)_2] \cdot 2H_2O$ ($ampy$ = 2-amino-3-methylpyridine) [16], $[Ni(pydc)(bipy)] \cdot 7H_2O$, $[Ni(pydc)(phen)] \cdot 6.5H_2O$, [21] $[Ni(pydc)(phen)] \cdot 6.5H_2O$ [20], $[Cu(pydc)(H_2O)(4-Meim)] \cdot H_2O$

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Table 1Crystal data and structure refinement parameters for complexes **1–4**.

Crystal data	1	2	3	4
Empirical formula	C ₂₀ H ₃₈ Co ₂ N ₈ O ₁₂	C ₁₄ H ₁₂ N ₂ NiO ₁₀	C ₃₆ H ₅₆ Cu ₄ N ₁₂ O ₂₂	C ₅₇ H ₄₃ Cl ₂ Cu ₂ N ₁₁ O ₁₆
Formula weight	700.44	426.97	1263.09	1336.00
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	C ₂ /c	P ₁	P ₂ 1/c	P ₁
<i>a</i> (Å)	14.063(5)	5.0868(2)	16.5091(2)	13.1686(3)
<i>b</i> (Å)	17.629(6)	6.6513(2)	13.0013(2)	15.3465(3)
<i>c</i> (Å)	13.226(5)	12.2534(4)	24.3865(3)	35.4814(8)
α (°)	90.00	94.612(2)	90.00	85.246(1)
β (°)	119.982(4)	98.850(3)	115.975(1)	91.00(1)
γ (°)	90.00	98.850(3)	90.00	64.59(2)
<i>V</i> (Å ³)	2840.2(17)	379.26(2)	4705.57(12)	6443.4(11)
<i>Z</i>	4	1	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.638	1.869	1.783	1.377
μ (mm ⁻¹)	1.24	1.35	1.88	0.82
θ range (°)	2.3–27.5	3.3–27.6	1.8–28.1	2.2–28.3
Measured reflections	24099	3760	67211	65283
Independent reflections	3266	1324	17977	23807
<i>R</i> _{int}	0.041	0.037	0.039	0.069
<i>S</i>	1.09	1.11	1.00	0.97
<i>R</i> ₁ / <i>wR</i> ₂	0.043/0.106	0.030/0.077	0.043/0.103	0.091/0.311
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.87/–0.62	0.46/–0.39	0.75/–0.48	1.69/–1.04

Table 2Selected bond distances and angles for complexes **1–4** (Å, °).

1					
N1–Co1	1.950(3)	N2–Co1	1.964(3)	N3–Co1	1.959(2)
N4–Co2	2.105(2)	O4–Co2	2.085(2)	Co2–O5	2.090(2)
N1–Co1–N3 ⁱ	90.36(11)	N1–Co1–N3	91.65(11)	N3–Co1–N3 ⁱ	86.34(14)
N1–Co1–N2 ⁱ	92.38(12)	N1–Co1–N2	85.72(12)	N3–Co1–N2	90.44(11)
N3–Co1–N2 ⁱ	174.85(11)	N2–Co1–N2 ⁱ	93.05(16)	O4–Co2–O5	90.36(9)
O4–Co2–O5 ⁱⁱ	89.64(9)	O4–Co2–N4	78.41(8)	O4–Co2–N4 ⁱⁱ	101.59(8)
O5–Co2–N4	91.47(9)	O5–Co2–N4 ⁱⁱ	88.53(9)		
2					
N1–Ni1	2.0765(18)	Ni1–O4	2.0546(15)	Ni1–O5	2.0644(16)
O4–Ni1–O5	89.72(6)	O4–Ni1–O5 ⁱ	90.28(6)	O4 ⁱ –Ni1–N1 ⁱ	80.25(6)
O4–Ni1–N1 ⁱ	99.75(6)	O5–Ni1–N1 ⁱ	88.20(7)	O5 ⁱ –Ni1–N1 ⁱ	91.80(7)
3					
N1–Cu1	1.9797(14)	N2–Cu1	1.9888(13)	O1–Cu1	1.9405(14)
O6–Cu1	1.9477(14)	Cu1–O5	2.2378(18)	N3–Cu2	2.0195(16)
N4–Cu2	2.0113(15)	O7–Cu2	2.4889(14)	N5–Cu3	2.0277(16)
N6–Cu3	1.9938(14)	O16–Cu3	2.5451(15)	N7–Cu4	1.9930(16)
N8–Cu4	2.0072(16)	N9–Cu4	2.0080(18)	N10–Cu4	2.0073(15)
Cu4–O10	2.4736(17)	N11–Cu5	1.9845(13)	N12–Cu5	1.9851(14)
O11–Cu5	1.9515(14)	O15–Cu5	1.9426(14)	Cu5–O19	2.2014(17)
O1–Cu1–O6	172.08(7)	O1–Cu1–N1	83.07(6)	O6–Cu1–N1	96.13(6)
O1–Cu1–N2	95.53(6)	O6–Cu1–N2	83.31(6)	N1–Cu1–N2	165.93(7)
O1–Cu1–O5	95.24(7)	O6–Cu1–O5	92.66(7)	N1–Cu1–O5	98.53(7)
N2–Cu1–O5	95.54(7)	N4–Cu2–N3	84.78(7)	N4–Cu2–N3 ⁱ	95.22(7)
N6 ⁱⁱ –Cu3–N5	94.72(7)	N6–Cu3–N5	85.28(7)	N7–Cu4–N8	85.58(7)
N7–Cu4–N10	95.10(7)	N8–Cu4–N10	179.10(8)	N7–Cu4–N9	178.05(8)
N8–Cu4–N9	95.05(8)	N10–Cu4–N9	84.26(7)	N7–Cu4–O10	87.24(6)
N8–Cu4–O10	85.84(7)	N10–Cu4–O10	94.79(7)	N9–Cu4–O10	94.65(8)
O15–Cu5–O11	171.13(6)	O15–Cu5–N11	94.62(6)	O11–Cu5–N11	83.29(6)
O15–Cu5–N12	83.18(6)	O11–Cu5–N12	96.55(6)	N11–Cu5–N12	164.68(6)
O15–Cu5–O19	95.03(7)	O11–Cu5–O19	93.81(7)	N11–Cu5–O19	99.18(7)
4					
N1–Cu1	2.122(6)	N2–Cu1	2.112(7)	N3–Cu1	2.119(7)
N4–Cu1	2.129(7)	N5–Cu1	2.105(7)	N6–Cu1	2.130(7)
N7–Cu2	2.114(7)	N8–Cu2	2.159(7)	N9–Cu2	2.110(6)
N10–Cu2	2.154(6)	N11–Cu2	2.081(7)	N12–Cu2	2.120(7)
N13–Cu3	1.994(6)	N14–Cu3	2.074(5)	N15–Cu3	2.011(6)
N16–Cu3	2.277(6)	N17–Cu3	2.352(6)	N18–Cu4	2.329(6)
N19–Cu4	2.254(6)	N20–Cu4	2.046(6)	N21–Cu4	2.067(6)
N22–Cu4	2.009(5)	O1–Cu3	2.044(5)	O5–Cu4	2.019(5)
O5–Cu4–N20	92.5(2)	O5–Cu4–N21	168.9(2)	O5–Cu4–N19	86.5(2)
O1–Cu3–N16	86.8(2)	O1–Cu3–N17	75.58(19)	N22–Cu4–O5	93.0(2)
N13–Cu3–O1	93.2(2)	N15–Cu3–O1	92.4(2)	O1–Cu3–N14	169.0(2)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$ for **1**; (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y, -z + 1$ for **2**; (i) $-x + 2, y, -z + 3/2$; (ii) $-x + 3/2, -y + 3/2, -z + 1$ for **3**.

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