SHORT PAPER

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Synthesis and structural analysis of novel supramolecular structures based upon *N*-(2-pyridyl)-3-pyridinecarboxamide[†]

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The transition metal Cu(II) and Co(II) complexes based on *N*-(2-pyridyl)-3-pyridinecarboxamide have been synthesised and characterised and single crystal analysis indicated that the two mononuclear complexes self-assembled into supramolecular architectures through intermolecular hydrogen bonding and π–π stacking interactions in the solid state.

Keywords: hydrogen bonding, copper(II), cobalt(II) complexes, crystal structures, 2-pyridylcarboxamide

The design and synthesis of supramolecular structures self-assembled from transition metal ions and organic ligands has been extensively studied in recent years.[1] The metal-ion-directed self-assembly has received increasing interest, not only because the generated polynuclear clusters show interesting metallic properties, but also due to their bioinorganic significance as metalloenzyme mimics.[2] To date, many types of ligands have been employed to generate supramolecular architectures.[1,3] However, few examples of extended polynuclear self-assemblies created by metal ions in order to mimic biological systems have been reported, especially peptide metal complexes,[2] which play important roles in living systems. So, it is of essential interest to investigate how peptide metal complexes exist and how they interact with each other in the solid or liquid state, so as to obtain valuable information which may be used in mimicking biological subjects. Among the factors that induce the self-assembly process, the design of the ligand and metal ion plays a crucial role in deciding between discrete or extended structures of the metal complexes. In addition, some weak interactions, such as hydrogen bonding, salt bridges, and π–π stacking also play important parts in the generation of supramolecular structures, especially in living systems.[4]

In this paper, we report on the use of *N*-(2-pyridyl)-3-pyridinecarboxamide (**L**) as an efficient ligand for the formation of hydrogen-bonded and π–π stacking linked polynuclear sheets of Cu(II) and Co(II) ions. The choice of the ligand was based on the consideration that the two pyridines, separated by an amide bond, could not bind the same metal centre in one molecule. Apart from that, the unit has an amide bond which has the affinity for forming hydrogen bonds with water molecules or nitrate ions. Therefore, in principle, the combination of coordinative, hydrogen bonding and π–π stacking interactions is fulfilled in a single ligand.

Results and discussion

The ligand **L** was prepared by the reaction of α-aminopyridine with nicotinoyl chloride in dry chloroform in the presence of triethylamine. **L** was treated with 0.5 equivalent amounts of $Cu(NO_3)_2$ and $Co(NO_3)_2$ in ethanol to give the coordinate complexes **1** and **2** (see Figs 1 and 2).

*Crystallographic study of **1***: The molecular structure of **1** with atomic labelling is given in Fig. 1. Selected distances and angles are given in Table 1. $[Cu(\mathbf{L})_2(NO_3)_2]$ crystallises in the monoclinic space group C2/c with four molecules per unit cell.

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu(\mathbf{L})_2(NO_3)_2]$ (**1**)

Bonds lengths		Angles	
Cu(1)-O(1)#1	1.929(2)	O(1)#1–Cu(1)–O(1)	180.00(14)
Cu(1)-O(1)	1.929(2)	O(1)#1–Cu(1)–N(1)#1	91.04(11)
Cu(1)-N(1)#1	2.037(3)	O(1)–Cu(1)–N(1)#1	88.96(11)
Cu(1)-N(1)	2.037(3)	O(1)#1–Cu(1)–N(1)	88.96(11)
		O(1)–Cu(1)–N(1)	91.04(11)
		N(1)#1–Cu(1)–N(1)	180.00(18)

#1 -x+1/2,-y+3/2,-z

In **1** the metal atom exist in an octahedral coordination environment. The coordination to the Cu(II) centre is provided by two pyridyl N-donors and two amide O-donors, resulting in an almost square-planar arrangement, where each **L** is *trans*-coordinated to the copper ion. The remaining sites are occupied by nitrate ions in the complex. The ligand–metal distances are 1.931(3) Å and 2.034(3) Å (for nitrate) for the Cu–O bonds and 2.034(3) Å for the Cu–N bonds. The Cu–O and Cu–N bond lengths are similar to those found in the copper complexes with similar amides.[6]

The crystal structure further shows that the mononuclear blocks are linked by nitrate anions, which act as both hydrogen-bonding bridges and donor atoms, in an infinite polynuclear string. In the nitrate one oxygen atom is coordinated to the copper ion and another interacts with the HN- group of another mononuclear complex through $NH\text{---}ONO_2$ hydrogen bonds (N---O = 2.762 Å). In the linear array the Cu–Cu distance is 8.719 Å between each neighbouring metal centre. Figure 1(b) shows the complexes in a string assembly linked by hydrogen bonds. As a result, one-dimensional linear polymer is formed along the hydrogen bond direction.

An interesting feature of this structure is the fact that there remains an uncoordinated pyridine group in each mononuclear complex and this group is parallel with another one in the neighbouring string. Calculations indicate that the distance between each parallel pyridine is 3.329 Å and the aromatic centroid-centroid distance between two strings is 3.797 Å, a value which is somewhat shorter than in analogous cases (about 4.37 Å).[6] The type of π–π stacking interactions within each of the two arrays undoubtedly contributes to the stabilisation of this supramolecular assembly of metal polymers. Therefore, intra-string hydrogen bonds and weak inter-string π–π interactions give rise to the two-dimensional aggregation.

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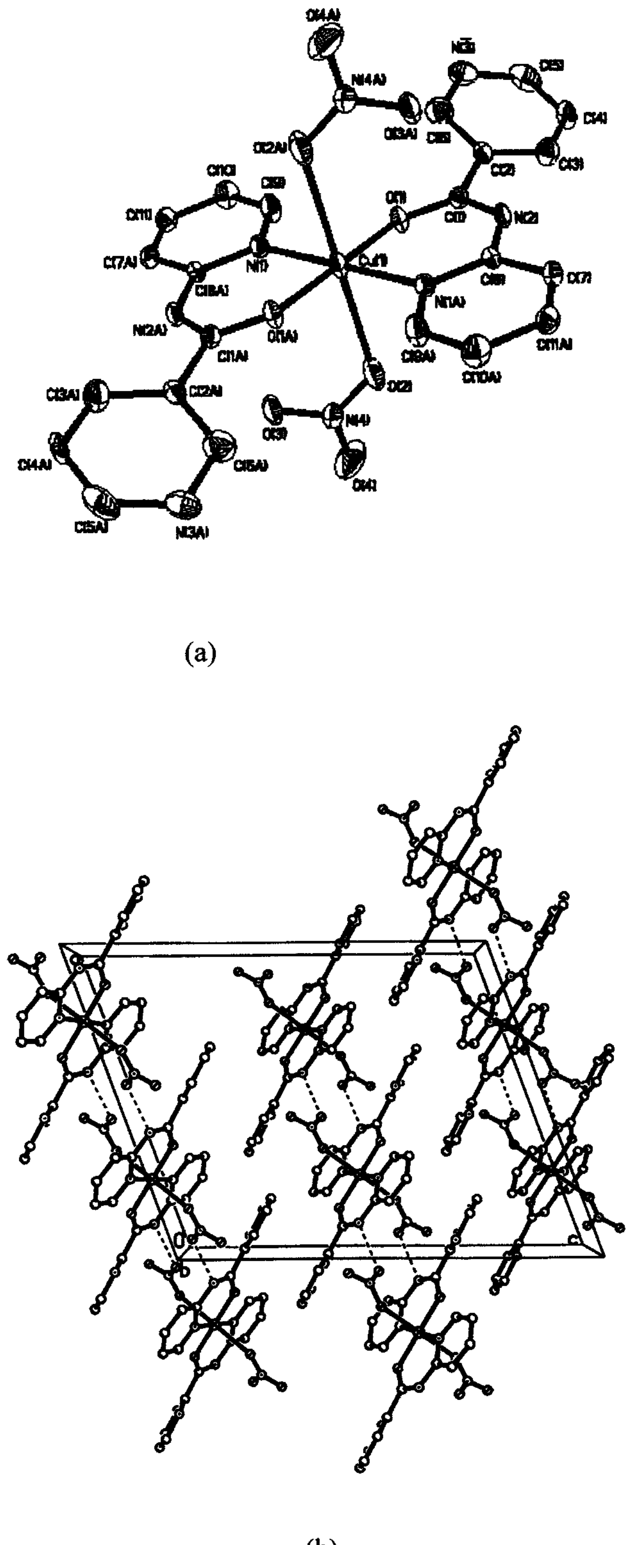
[†] This is a Short Paper. There is therefore no corresponding material in *J Chem. Research (M).*

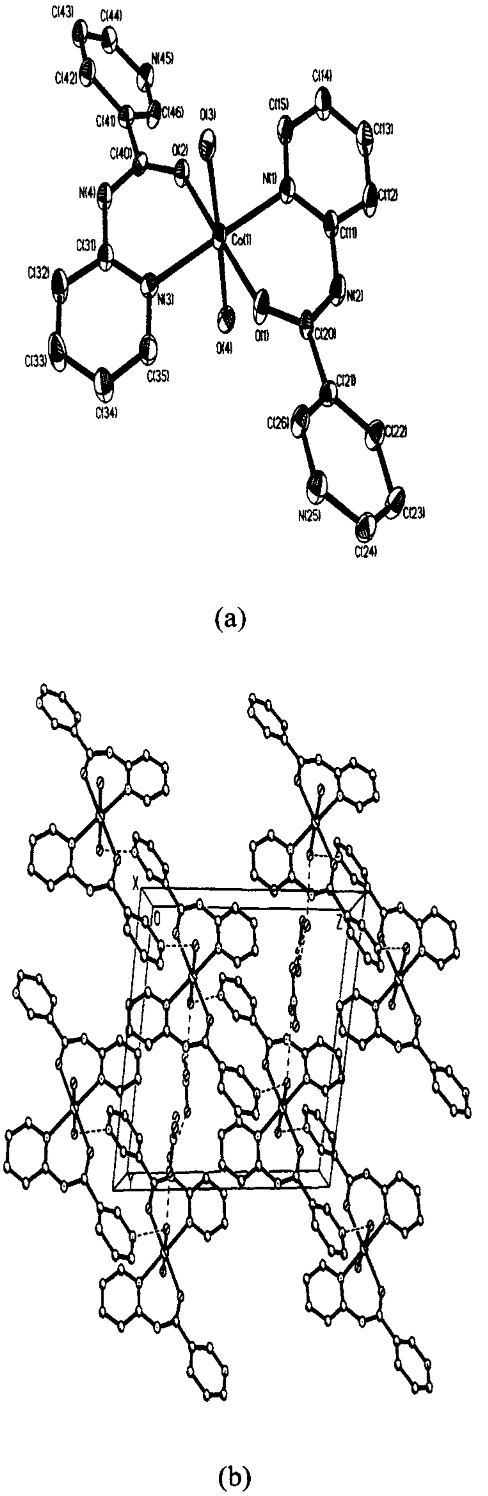


(a)

(b)

Fig. 1 (a) ORTEP diagram of **1**. (b) View of the 2 D network depicting the coordination around the metal in **1**. Noncovalent interactions in the form of NH---ONO_2 hydrogen bonding and edge-to face π–π stacking are demonstrated. The dashed lines represent all NH---ONO_2 hydrogen bonds. Hydrogens are removed for clarity.

Crystallographic study of 2: The molecular structure of **2** with atomic labelling is given in Fig 2 and selected distances and angles are given in Table 2.



(a)

(b)

Fig. 2 (a) ORTEP diagram of **2**. (b) View of the 3-D assembly of the polynuclear sheets depicting the coordination around the metal in **2**. Noncovalent interactions in the form of NH---OHO hydrogen bonding and edge-to face π–π stacking are demonstrated. The dashed lines represent all NH---OHO hydrogen bonds. Hydrogens are removed for clarity.

An X-ray diffraction study on **2** confirms that in the structure of **2** cobalt is six-coordinated, with the coordination to the Co(II) center provided by two pyridyl nitrogen atoms, two amide oxygens and the remaining two by water molecules rather than of nitrate ions. As in **1**, the **L** also adopts *trans*-coordination to cobalt. The ligand–metal distances are

Table 2 Selected bond lengths (Å) and angles (°) for $[Co(\mathbf{L})_2(NO_3)_2(H_2O)_2](H_2O)$ (**2**)

Bonds lengths	Angles		
Co(1)–O(2) 2.065(2)	O(2)–Co(1)–O(1) 178.82(8)	O(1)–Co(1)–O(4) 90.71(10)	O(3)–Co(1)–N(3) 88.13(9)
Co(1)–O(1) 2.068(2)	O(2)–Co(1)–O(3) 89.47(9)	O(3)–Co(1)–O(4) 176.75(8)	O(4)–Co(1)–N(3) 89.38(9)
Co(1)–O(3) 2.071(2)	O(1)–Co(1)–N(1) 84.46(9)	O(3)–Co(1)–N(1) 92.71(9)	O(4)–Co(1)–N(1) 89.77(9)
Co(1)–O(4) 2.076(2)	O(2)–Co(1)–N(1) 95.02(9)	N(3)–Co(1)–N(1) 179.15(9)	
Co(1)–N(3) 2.138(3)	O(1)–Co(1)–O(3) 91.62(10)	O(2)–Co(1)–N(3) 84.85(9)	
Co(1)–N(1) 2.142(3)	O(2)–Co(1)–O(4) 88.22(9)	O(1)–Co(1)–N(3) 95.65(9)	

2.065(2) 2.068(2), 2.071(2) and 2.076(2) for Co–O bonds and 2.138(3) and 2.142(3) for the Co–N bonds.

The crystal structure (Fig. 2) also shows that the mononuclear blocks are linked differently to Cu(II) by coordinated water molecules, which act as both hydrogen-bonding bridges and donor atoms, into a one-dimensional infinite polynuclear array. The hydrogen bond between the pyridyl nitrogen and the coordinated water molecule (N---HOH, N---O = 2.799 and 2.793 Å) connects the mononuclear complex into a hydrogen bonded polynuclear sheet. Within the same string, a noteworthy feature of the assembly is the presence of unutilised pyridine in the modules, which further connect the strings into a weak π–π stacking polynuclear sheet with the aromatic centroid–centroid distance of 4.175 Å.

It is to be noted that the water molecule found in the lattice forms hydrogen bonds to adjacent polymeric chains via nitrate ions and coordinated water. This interaction, as shown in Fig. 2b, gives rise to a three-dimensional hydrogen-bonded network, in which the water molecule participates in a hydrogen-bonded ring involving two nitrate anions and a water molecule. The metal–metal distances across each polymer backbone is 7.844 Å, whereas the closest metal–metal distance between neighboring strands is 9.674 Å.

The UV absorption spectrum of the complex **1** in ethanol solution exhibits a broad absorption maximum at around 740 nm (ε = 126) and a peak around 330 nm (ε = 16800), consistent with pseudo octahedral geometry for Cu(II).[7] For complex **2**, the absorptions are around 520 nm (ε = 138) and 325 nm (ε = 10800), typical for the absorption of six-coordinated Co(II).[8]

Comparison of the IR spectrum of the free ligand with the copper(II) and cobalt(II) metal complex spectra indicates that the C=O of the amide is bound to the metal center. The free ligand C=O shows absorption at 1672 cm^{-1}, where as the complexes show two C=O absorptions 1643 and1618 cm^{-1} for **1** and 1651 and 1623 cm^{-1} for **2**. The results are consistent with the fact that when amide oxygen coordinates to metal ion the C=O stretching moves to lower frequency.[9]

In summary, the results reported herein present a new type of coordination aggregation based upon the ligand *N*-(2-pyridyl)-3-pyridinecarboxamide, and demonstrate how weak intra- and inter-molecular interactions can be used to assemble metal-based supramolecular species with ordered architecture. The simply designed ligand can lead to hydrogen-bonded and π–π linked 2-D or 1-D supramolecular compounds that may have interesting solid-state properties. It is also shown that to the same organic ligand the self-assembly metal polymers may vary with different metal ions, owing to their intrinsic properties. Novel features of the metal assemblies described here are the participation of hydrogen bonds and π–π interaction connecting the mononuclear modules into the supramolecular architectures. It is expected that an extensive study of the metal ion / organic ligand self-assembly by means of manipulation of the strong coordination and weak interactions such as hydrogen bonding and π–π stacking will pave the way towards an understanding of the interesting properties exhibited by polynuclear assemblies.

Experimental

The Fourier-transform IR spectra were taken on a Bio-Rad FTS 135 spectrometer and elemental analyses on Perkin-Elmer 240C analyzer. UV absorption was carried out by UV spectral method using a Shimadzu UV-160A spectrophotometer equipped with a thermostatic cell (298 ± 0.1 K)

Crystals of **1** and **2** suitable for single-crystal X-ray diffraction with sizes 0.30 × 0.25 × 0.20 mm and 0.30 × 0.30 × 0.20 mm were selected, respectively. Structural analyses for **1** and **2** were performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation and an Enraf-Nonius CAD4 diffractometer (Mo Kα), respectively. The structures were solved by direct methods followed by Fourier difference syntheses using the SHELXTL package.[5]

*Preparation of N-(2-pyridyl)-3-pyridinecarboxamide (**L**):*

A solution of the corresponding acid chloride (25 mmol) was slowly added to an ice-cooled mixture of 2-aminopyridine (20 mmol) in dry chloroform (20 ml) with an excess of triethylamine (60 mmol). The resulting solution was stirred for 24 hours and then quenched with 20 mL of water. The organic layer was separated, washed with water and dried with magnesium sulfate and concentrated under reduced pressure. The crude products were recrystallised with methanol-water and the yield was about 75%. Calcd for $C_{11}H_9N_3O$ (199.2), C 66.32, H 4.55, N 21.09%; found C 66.57, H 4.21, N 21.24%. IR (KBr diffuse reflectance): ν = 3425, 3220, 1673, 1590, 1537, 1436, 1313, 1176, 707 cm^{-1}

*Preparation of $[Cu(\mathbf{L})_2(NO_3)_2]$ (**1**):* Solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (2mmol) in methanol and *N*-(2-pyridyl)-3-pyridinecarboxamide (**L**) (4.2mmol) in methanol were mixed. Slow evaporation of the resulting solution gave light blue plates of **1** (1.2mmol, *ca* 60%). Anal: calc. for $C_{22}H_{18}N_8CuO_8$ (585.98), C 45.09, H 3.96, N 19.12; found C 45.28, H 3.74, N 18.98. IR (KBr diffuse reflectance): ν = 3192, 1643,1618, 1478, 1384, 1374, 1323, 781, 732 cm^{-1}.

*Preparation of $[Co(\mathbf{L})_2(NO_3)_2(H_2O)_2](H_2O)$ (**2**):* Solutions of $Co(NO_3)_2{\cdot}6H_2O$ (2mmol) in methanol and *N*-(2-pyridyl)-3-pyridine carboxamide (**L**) (4.2mmol) in methanol were mixed together. The slow evaporation of the mixture afforded bright red plates of **2** (1.4mmol) with a yield about 70%. Anal: calc. for $C_{22}H_{24}N_8CoO_{11}$ (635.41), C 41.59, H 3.81, N 17.63; found C 41.70, H 3.54, N 17.84. IR (KBr diffuse reflectance): ν =3072, 1651, 1623, 1542, 1479, 1384, 788, 731, 699 cm^{-1}.

Crystal data for **1**: $(C_{22}H_{18}CuN_6O_2)(NO_3)_2$, Monoclinic, space group C2/c, *a* = 15.218(3), *b* = 8.5155(18), *c* = 19.449(4) Å, α = 90, β = 110.256(4), γ = 90°C, U = 2364.5(9) Å^3, Z = 4, Dc = 1.646 Mg/m^3, T = 298 (2) K, wavelength = 0.71073, Goodness-of-fit on F^2 was 1.012. Final R indices [I>2sigma(I)] R1 = 0.0473, wR2 = 0.1284, R indices (all data) R1 = 0.0680, wR2 = 0.1410.

Crystal data for **2**: $[(C_{22}H_{18}CoN_6O_2)\ (N\ O_3)_2\ (H_2O)_2]\ H_2O$, Triclinic, space group P-1, *a* = 9.534(2), *b* = 10.914(2), *c* = 13.713(3) Å, α = 98.71(3), β = 97.79(3), γ = 105.09(3)°C, U = 1338.7(5) Å^3, Z = 2, Dc = 1.576 Mg/m^3, T = 293(2) K, Goodness-of-fit on F^2 was 0.925. Final R indices [I>2sigma(I)] R = 0.0522, wR2 = 0.1340, R indices (all data) R = 0.0773, wR = 0.1434. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-150087 and –150088, respectively.

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