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Nickel-Organic Coordination Layers with Different Directional Cavities

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The two new metal-organic coordination frameworks $[Ni_2(pydc)_2(4,4'\text{-bpy})(H_2O)_4]_n\cdot0.5n(4,4'\text{-bpy})2H_2O$ (**1**) and $[Ni_2(pydc)_2(2,2'\text{-bpy})_2(H_2O)_2]_n\cdot2nH_2O$ (**2**) (H_2pydc = pyridine-3,4-dicarboxylic acid; bpy = bipyridine) have been synthesised under hydrothermal conditions and characterised by single-crystal X-ray diffraction analysis. The structure of **1** contains parallel rectangular channels that accommodate large 4,4′-bpy guests while that of **2** contains vertical channels coordinated to 2,2′-bpy ligands. Their magnetic analyses show that they exhibit different magnetic interactions. The red shifts of the peak in their emission spectra relative to those of the the free ligands could be attributable to the metal–ligand coordination.

Introduction

Recently, there has been much effort devoted to developing coordination frameworks with special and accessible cavities for use in catalysis, separations, sensors and electronics.[1,2] The assembly of pre-selected building blocks represents a new approach to the formation of novel frameworks, and multidentate carboxylate ligands are widely adopted for the construction of coordination frameworks owing to their rich coordination modes.[3–5] Another common ligand is bipyridyl, which not only acts as a space filler but also provides potential π–π stacking interactions that increase the stability of the framework. It is interesting that mixed ligands can be combined to construct a great variety of frameworks, such as two-dimensional (2D) layers and three-dimensional (3D) networks, including channel-like, interpenetrating and host–guest structures. To the best of our knowledge, 2D layers with parallel channels filled with guests have seldom been reported. In addition, the effect of co-ligands on the final structures is less common. Pyridine-3,4-dicarboxylate (pydc) ligands containing different donor atoms in the 1-, 3- and 4-positions are expected to form more diverse coordination frameworks.[6,7] To investigate the cooperation between pydc and co-ligands, we have explored their assembly with transitional metal ions. Here we report the syntheses, crystal structures and magnetic and photophysical properties of two polymeric complexes with interesting frameworks, namely $[Ni_2(pydc)_2(4,4'\text{-bpy})(H_2O)_4]_n\cdot0.5n(4,4'\text{-bpy})2H_2O$ (**1**) and $[Ni_2(pydc)_2(2,2'\text{-bpy})_2(H_2O)_2]_n\cdot2nH_2O$ (**2**) (bpy = bipyridine).

Results and Discussion

The hydrothermal reaction of $NiCl_2\cdot6H_2O$, H_2pydc and 4,4′-bpy or 2,2′-bpy in a molar ratio of about 1:1:1 yielded green crystals of **1** or **2**, respectively. X-ray single-crystal analysis revealed that the structure of **1** consists of 2D layers with parallel channels, which are stacked by hydrogen bonding. Each Ni^{II} ion is six-coordinate with two N atoms from 4,4′-bpy and pydc ligands [Ni–N = 2.087(6)–2.105(7) Å] and four O atoms from two terminal water molecules and two pydc monodentate carboxylate groups [Ni–O = 2.046(5)–2.130(5) Å], which provide a distorted octahedral coordination geometry (Figure 1). Four pairs of Ni^{II} ions are linked by 4,4′-bpy ligands that act as four edges, which are further linked by four three-connecting pydc ligands in a *syn-syn* bis-monodentate mode to form a cubane-like building block (Figure 2). These building blocks are extended through the Ni–O bonds to form a 2D double-layered framework. Consequently, this gives rise to novel parallel rectangular channels (11.99×7.92 Å^2) along the *a* axis (Figure 3). It is interesting that 4,4′-bpy acts not only as a bridging linker but also as a guest that is accommodated within each channel in a stacked arrangement. There are π–π stacking interactions between the pyridyl rings of adjacent 4,4′-bpy guests, with a face-to-face distance of 3.263 Å; this distance consolidates the stacking. The dihedral angle between the mean plane of the pyridyl rings and the transect plane of the channel is 59.0°. The 2D layers are stacked by hydrogen bonding between the oxygen atoms of the lattice water, coordinated water and carboxylate groups. However, van der Waals interactions are not

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observed between the 4,4′-bpy guests and the channels – the closest distance is 5.66 Å.

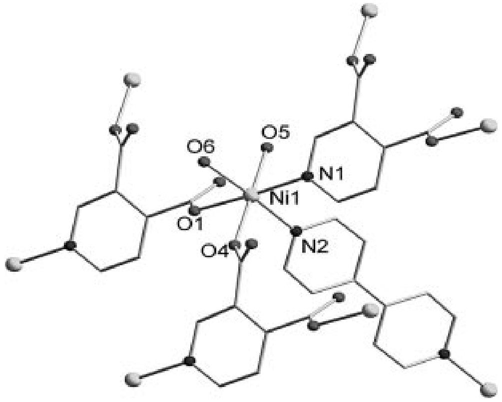

Figure 1. Coordination environments of Ni^{II} atoms in compound **1**.

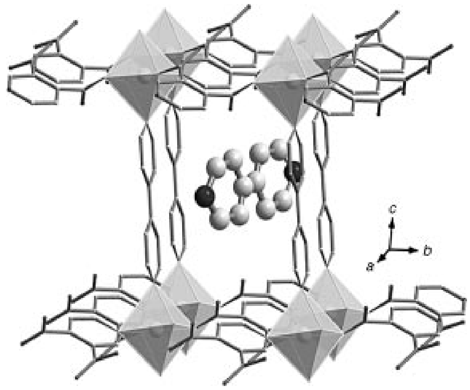

Figure 2. Cubane-like building block in **1** showing the Ni coordination octahedra and 4,4′-bpy guests.

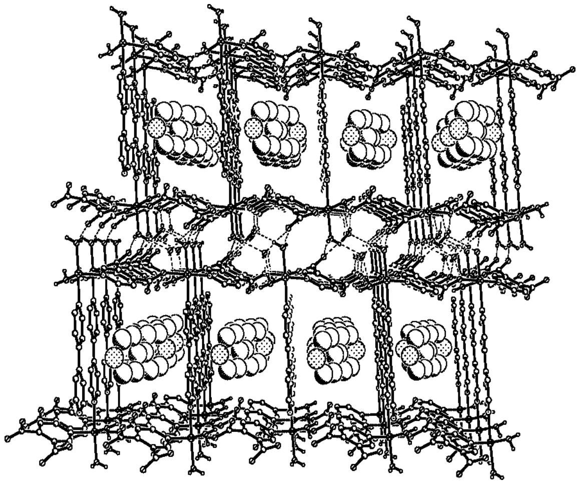

Figure 3. Packing structure of compound **1** along the *a* axis.

In compound **2**, two independent Ni^{II} ions are both in distorted octahedral coordination geometries. Each of them is coordinated by three N atoms from 2,2′-bpy and pydc ligands [Ni–N = 2.058(5)–2.128(5) Å] and by three O atoms from a coordinated water molecule and two pydc carboxylate groups [Ni–O = 2.069(5)–2.094(5) Å] (Figure 4). The two independent Ni^{II} ions are both bridged by two pydc ligands by *anti*-*syn* bis-monodentate carboxylate groups, which results in two types of binuclear units (Ni1···Ni1^{i} = 5.330 Å and Ni2···Ni2^{ii} = 5.581 Å; symmetry codes: *i*: $1 - x$, $1 - y$,$1 - z$; *ii*: $2 - x$, $-y$, $-z$). Furthermore, every four binuclear units are connected through their pydc spacers alternately to form a large rectangular grid (7.3 × 10.3 Å^2), as shown in Figure 5. Each Ni^{II} ion is attached by a chelating bpy ligand within the rectangular grid. There are π–π stacking interactions between the 2,2′-bpy pyridyl rings and the pydc aromatic rings, with face-to-face distances of 3.03–3.40 Å. The rectangular grids stretch to a 2D layer parallel to the *bc* plane in a tiled manner. The interlayer free water molecules are hydrogen bonded to the O atoms of the pydc carboxylate groups or coordinated water molecules in the adjacent layers (Figure 6). These 2D layers are stacked along the *c* axis into a 3D supramolecular architecture through hydrogen bonding.

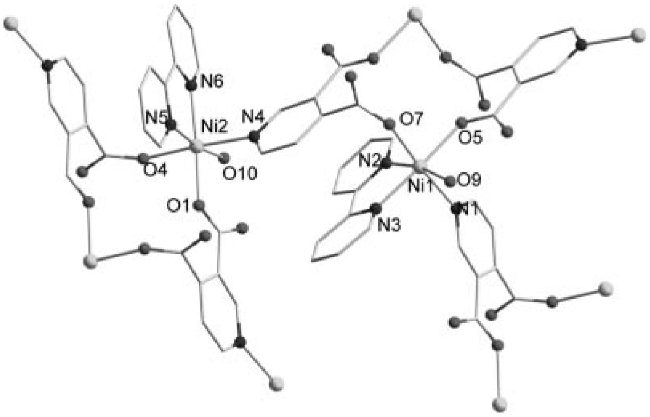

Figure 4. Coordination environments of the Ni^{II} atoms in compound **2**.

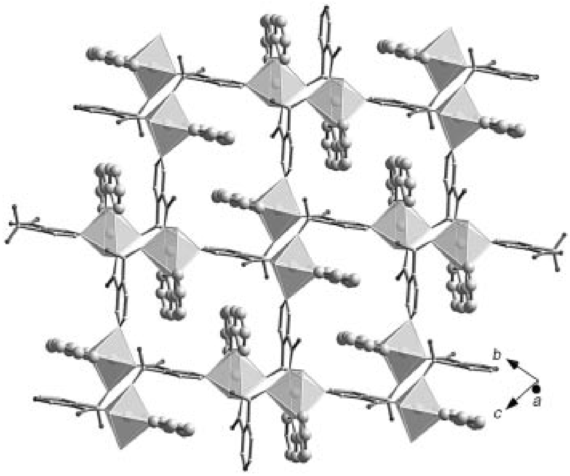

Figure 5. View of the 2D layer in compound **2**.

To investigate their thermal stabilities, thermogravimetric analyses (TGA) of **1** and **2** were carried out at a heating rate of 10 °C min^{-1} under N$_2$. Compound **1** shows a two-

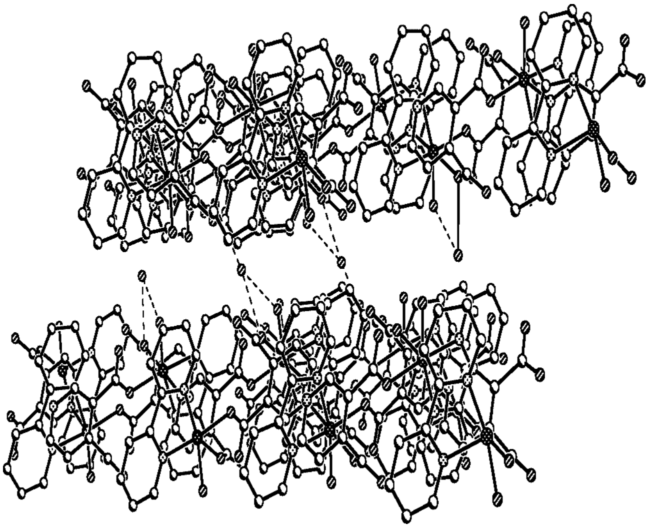

Figure 6. Packing structure of compound **2**.

step weight loss between 150 and 400 °C. The first weight loss between 150 and 230 °C cannot be distinguished clearly from the second one as the coordinated water molecules are involved in the dehydration process (observed: 14.36%; expected: 13.68%), thus implying that the big guest molecules (4,4′-bpy) cannot depart freely without the collapse of the coordination channels. The second step between 230 and 400 °C is assigned to the decomposition of organic ligands in a continuous fashion. The thermal behaviour of compound **2** shows a two-step weight loss between 145 and 430 °C. The first weight loss between 145 and 200 °C corresponds to the dehydration process (observed: 8.4%; expected: 8.6%). The second step between 290 and 430 °C is also assigned to the decomposition of organic ligands.

Temperature-dependent magnetic susceptibilities of compounds **1** and **2** were measured between 5 and 300 K (Figure 7). At room temperature, $\chi_m T$ is 2.03 cm^3 mol^{-1} K for **1** and 2.14 for **2**, which is slightly higher than the expected value of 2.00 cm^3 mol^{-1} K for two uncoupled spin-only Ni^{II} ions (S = 1/2, g = 2). For **1**, $\chi_m T$ is almost constant from 300 K to 36 K, then increases as the temperature is lowered and reaches a maximum value of 2.14 cm^3 mol^{-1} K at 12 K. Finally, it decreases to 1.75 cm^3 mol^{-1} K at 5 K, which shows that there may be both weak ferromagnetic interactions and single-ion zero-field-splitting (D) of isolated Ni^{II} ions. For **2**, the observed $\chi_m T$ value decreases slightly to 1.95 cm^3 mol^{-1} K from 300 K to 40 K, and then quickly decreases to 1.11 cm^3 mol^{-1} K at 5 K, which suggests that the global features of **2** are characteristic either of weak antiferromagnetic intramolecular interactions and/or of the presence of single-ion zero-field-splitting of isolated Ni^{II} ions. In view of the complicated 2D structures of **1** and **2**, it is very difficult, even impossible, to estimate the magnitude of the magnetic coupling in this system. Therefore, two different simple treatments were carried out by using the Fisher model [Equation (1)] or by using the D parameter [Equation (2)] considering only a simple Ni^{II} ion.[8,9]

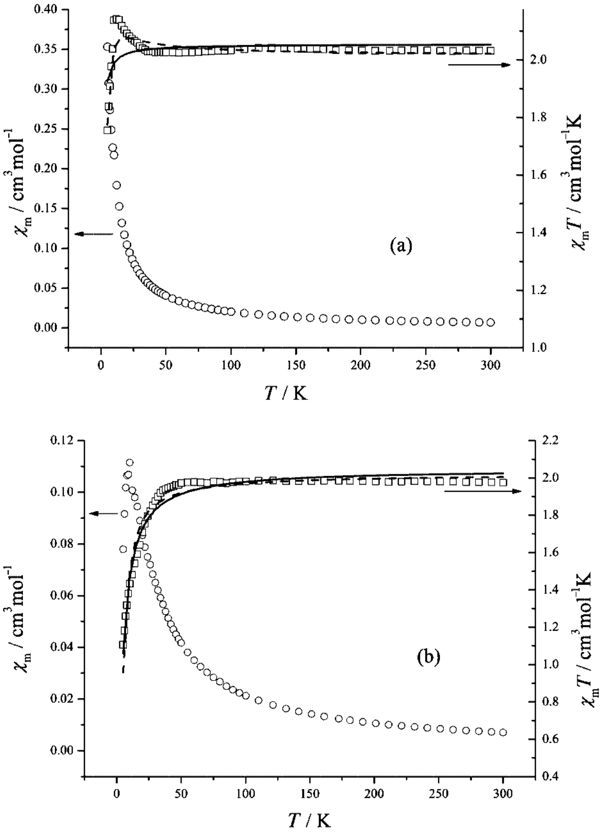

Figure 7. Plots of χ_m (○) and $\chi_m T$ (□) vs. T for **1** (a) and **2** (b) (dotted lines are the best fit with parameter D and solid lines the best fit with coupling parameter J).

$$\chi_m = \frac{\chi_{chain}}{1-(2zJ' \times \chi_{chain})/N\beta^2 g^2}$$
$$\chi_{chain} = \frac{Ng^2\beta^2 S(S+1)}{3kT}\,\frac{1+u}{1-u}$$
$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right] \qquad (1)$$

$$\chi_m = \frac{2Ng^2\beta^2}{3k(T-\theta)}\left[\frac{2kT/D - 2kT\exp(-D/kT)/D + \exp(-D/kT)}{1+2\exp(-D/kT)}\right] \qquad (2)$$

where the molecular field approximation (zJ') for interchain interactions and a Weiss-like temperature correction (θ') are applied to account for intermolecular exchange effects between Ni^{II} ions.

The best fit of the experimental data to Equations (1) and (2) yields g = 2.09, J = –0.17 cm^{-1}, zJ' = –0.07 cm^{-1} and R = 6.3×10^{-4} ($R = \Sigma[(\chi_m T)_{obsd} - (\chi_m T)_{calcd}]^2/\Sigma[(\chi_m T)_{obsd}]^2$), or g = 2.01, D = 11.58, θ = 3.22 and R = 1.6×10^{-4} for **1**; and g = 2.05, J = –1.76 cm^{-1}, zJ' = –0.03 cm^{-1} and R = 2.0×10^{-3}, or g = 2.01, D = 20.26, θ = –8.57 and R = 1.9×10^{-3} for **2**. As expected, the fit is not very good, although we can conclude that compound **1** exhibits a weak ferromagnetic interaction and **2** exhibits a weak antiferromagnetic interaction between Ni^{II} ions.

The fluorescence spectra of compounds **1** and **2** in the solid state were measured at room temperature. The emission spectra of the two compounds are almost the same, as shown in Figure 8. Upon excitation at $\lambda = 427$ nm they produce intense orange fluorescence peaks at 600 nm and 602 nm, respectively, which are assigned to the metal-to-ligand charge transfer (MLCT) states.[10] As free H_2pydc exhibits a weak luminescence at around 490 nm in the solid state at room temperature, and free 2,2′-bpy and 4,4′-bpy display a weak luminescence at around 530 and 486 nm,[11,12] respectively, the red shifts and the luminescent enhancement for both **1** and **2** may be attributed to the coordination between the ligands and Ni^{II}.[11]

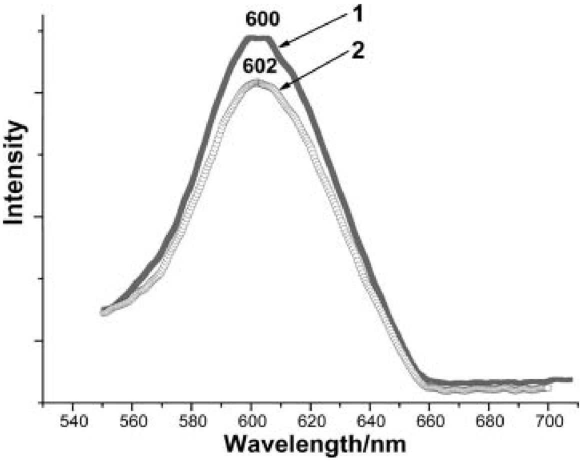

Figure 8. Fluorescent emission (λ_{ex} = 427 nm) spectra of compounds **1** and **2** at room temperature.

Conclusions

In summary, the assembly of $NiCl_2$, pydc and bipyridyl ligands results in two 2D layered coordination frameworks with different directional cavities. It is interesting that one structure contains parallel rectangular channels that accommodate large 4,4′-bpy guests whereas the other contains vertical channels with coordinated 2,2′-bpy ligands. The magnetic analyses show the presence of magnetic interactions. Excitation of compounds **1** and **2** produces an intense orange fluorescence.

Experimental Section

General: All commercially available chemicals were of reagent grade and were used as received. Elemental analyses were determined with an Elemental Vario ELIII elemental analyzer. IR spectra were measured as KBr pellets with a Perkin–Elmer Spectrum One FTIR spectrometer in the range 200–4000 cm^{-1}. Thermogravimetric analyses were carried out with a Netzsch STA 449C unit from 30 to 900 °C at a heating rate of 10 °C min^{-1} under nitrogen. Variable-temperature (5.0–300.0 K) magnetic susceptibility measurements were carried out in an external field of 10.0 kG with a Quantum Design PPMS model 6000 magnetometer. Fluorescent analyses were performed with a Perkin–Elmer LS55 luminescence spectrometer.

Synthesis of 1: A mixture of $NiCl_2\cdot 6H_2O$ (71 mg, 0.30 mmol), H_2pydc (50 mg, 0.30 mmol) and 4,4′-bpy (47 mg, 0.30 mmol) in H_2O (10 mL) was heated to 170 °C for 4 d. After cooling to room temperature, green crystals of **1** were collected by filtration, washed with distilled water and dried to afford a yield of 41% (41.56 mg) based on Ni. $C_{24}H_{22}N_4Ni_2O_{12}$ (675.84): calcd. C 42.65, H 3.28, N 8.29; found C 42.28, H 3.72, N 8.43. IR (KBr pellet): $\tilde{\nu}$ = 3286 (m), 1626 (s), 1574 (s), 1552 (s), 1489 (m), 1404 (s), 1223 (m), 1174 (m), 987 (m), 683 (m), 606 cm^{-1} (m).

Synthesis of 2: A mixture of $Ni(OAc)_2\cdot 4H_2O$ (0.25 mmol), H_2pydc (0.25 mmol) and bpy (0.25 mmol) in H_2O (10.0 mL) was heated to 170 °C for 4 d and then cooled at a rate of 5 °C h^{-1} to room temperature. Green plate-like crystals of **2** were isolated in 45% yield (46.80 mg) based on Ni. $C_{34}H_{30}N_6Ni_2O_{12}$ (832.06): calcd. C 49.08, H 3.63, N 10.10; found C 49.01, H 3.48, N 10.02. IR (KBr pellet): $\tilde{\nu}$ = 3444 (m), 3124 (m), 1614 (s), 1568 (s), 1477 (m), 1444 (m), 1390 (s), 1194 (w), 1026 (w), 827 (m), 768 (m), 683 (m), 656 cm^{-1} (w).

X-ray Crystallography: Intensity data for compounds **1** and **2** were measured on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 173 K. Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector. The structures were solved by direct methods and all calculations were performed with the SHELXL-97 program. The metal atoms were found in the electron density map, and subsequent difference Fourier syntheses gave all the coordinates of the non-hydrogen atoms, which were refined anisotropically. All hydrogen atoms were added in the riding model and refined isotropically with C–H = 0.96 Å.

Crystal Data for Compound 1: Triclinic, space group $P\bar{1}$, a = 7.0457(3) Å, b = 7.9225(4) Å, c = 16.3125(1) Å, α = 78.445(2)°, β = 77.782(3)°, γ = 75.833(3)°, V = 852.20(6) Å^3, Z = 2, T = 293(2) K, D_c = 1.539 g cm^{-3}, μ(Mo-K_α) = 1.179 mm^{-1}, F(000) = 407, 2969 independent reflections (R_{int} = 0.0476) with $2\theta \leq 50.18°$. Refinement of 247 parameters converged at final R_1 [for selected data with $I > 2\sigma(I)$] = 0.0694, wR_2 = 0.2095 and S = 1.107.

Crystal Data for Compound 2: Triclinic, space group $P\bar{1}$, a = 11.5331(8) Å, b = 12.0447(8) Å, c = 14.4712(9) Å, α = 71.811(2)°, β = 69.716(2)°, γ = 68.285(2)°, V = 1712.3(2) Å^3, Z = 2, T = 293(2) K, D_c = 1.614 g cm^{-3}, μ(Mo-K_α) = 1.175 mm^{-1}, F(000) = 856, 5946 independent reflections (R_{int} = 0.0491) with $2\theta \leq 50°$. Refinement of 511 parameters converged at final R_1 [for selected data with $I > 2\sigma(I)$] = 0.0640, wR_2 = 0.1679 and S = 0.987.

CCDC-232641 (**1**) and -290754 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): TGA curves for compounds **1** and **2**.

Acknowledgments

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