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Co-ordination polymers containing square grids of dimension 15 × 15 Å†

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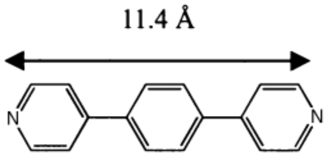
Open and interpenetrated two-dimensional networks containing square grids of dimension *ca.* 15 × 15 Å and two one-dimensional networks, linear and zigzag, were synthesized using $Ni(NO_3)_2$/$Cu(NO_3)_2$ and two linear bifunctional ligands of length 11.4 Å. The formation of these materials was characterized by single crystal X-ray diffraction studies. Interestingly, some of these structures were found to form continuous channels across the packing of grids. The channels formed were occupied by 1-D columns of guest molecules. The electron rich ligand containing an anthracene moiety was found to form open square grid networks only in the presence of electron deficient guest molecules such as nitrobenzene and cyanobenzene, whereas in the presence of benzene it formed inclined interpenetrated grids with $Ni(NO_3)_2$ and two types of 1-D complexes with $Cu(NO_3)_2$.

Introduction

A major theme in crystal engineering deals with the predictable formation of open framework materials with reasonably high empty space and stability even after removal of guest molecules. These goals are currently achieved by designing metal–organic networks *via* co-ordination. Such network materials are expected to show interesting properties similar to zeolite-like and clay-like materials.[1] In particular the synthesis of co-ordination polymers using 4,4′-bipyridine (4,4′-bpy, **1**) and transition metal ions has thus far produced several novel networks with a high degree of porosity.[2–12] The topology of the networks formed in these systems was shown to depend on several factors such as co-ordination geometry and oxidation state of the metal, metal to ligand ratio and presence of solvents and counter ions. The networks designed so far include diamondoid,[3] honeycomb,[4] square grid,[5,6] rectangular grid,[7] brick wall,[8] ladder,[8,9] bilayer,[9a,10] and helices.[11] Among all these networks the square grid polymers are of particular importance due to their predictable pore sizes and selective inclusion of guest molecules. Although several structures are reported with metal and 4,4′-bipyridine there are only a small number which exhibit square grid networks. These square grids can be classified into two categories: open[5] and interpenetrated.[6] Only a few structures dealing with longer ligands, Py–X–Py (Py = 4-pyridyl, X = CH_2CH_2, CH=CH or C≡C), than **1** are thus far reported.[9a,13] Despite the simple structural design, however, the next higher analogue, namely 1,4-bis(4-pyridyl)benzene **2**, has not been employed for the design of square grids. Here we show that one can obtain square grid networks even with bigger ligands such as **2** and **3** which are longer than **1** by 4.4 Å. The ligands **2** and **3**[14] have the same length but they differ in their electronic natures. The reaction of ligands with $Ni(NO_3)_2$/$Cu(NO_3)_2$ in 2:1 ratio in the presence of suitable guest molecules was found to form open square grid polymers for both **2** and **3** with square dimensions of 15 × 15 Å. The formation of networks in the case of **3** was found to depend on the guest as well as on the metal atom. The crystal structures of these complexes with respect to geometry and packing of the grids and host–guest and guest–guest interactions will be presented.



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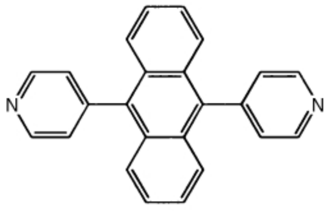

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Results and discussion

The reaction of compound **2** with $Ni(NO_3)_2$ in 2:1 ratio in the presence of benzene (G_1) resulted in the square grid open framework co-ordination polymer **4**. On the other hand, ligand **3** is expected to form open square grid polymers in the presence of electron deficient guest molecules because of the donor–acceptor interactions between guest molecules and the anthracene moiety. As anticipated it forms open square grid co-ordination polymers **5**, **6**, **7** and **8** with $Ni(NO_3)_2$ or $Cu(NO_3)_2$ only in the presence of electron deficient guest molecules such as nitrobenzene (G_2) or cyanobenzene (G_3). In the presence of a guest molecule like benzene (G_1) it formed interpenetrated square grid **9** with $Ni(NO_3)_2$ and two types of 1-D co-ordination polymers **10** and **11** with $Cu(NO_3)_2$.

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b004054l/

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Table 1 Bond lengths (Å) and angles (°) around metal atoms in the complexes **4**–**11**

Complex **4**

Ni(1)–O(11A)	2.112(6)	Ni(1)–N(31B)	2.112(3)
Ni(1)–N(31A)	2.100(7)	Ni(1)–N(11A)	2.101(6)
Ni(1)–O(12A)	2.110(6)	Ni(1)–N(11B)	2.121(3)
N(11A)–Ni(1)–N(31A)	176.47(18)	O(12A)–Ni(1)–N(31B)	89.4(3)
N(11A)–Ni(1)–O(12A)	88.0(3)	O(11A)–Ni(1)–N(31B)	90.1(3)
N(31A)–Ni(1)–O(12A)	90.8(3)	N(11A)–Ni(1)–N(11B)	88.7(3)
N(11A)–Ni(1)–O(11A)	91.4(3)	N(31A)–Ni(1)–N(11B)	87.9(3)
N(31A)–Ni(1)–O(11A)	89.8(3)	O(12A)–Ni(1)–N(11B)	90.0(3)
O(12A)–Ni(1)–O(11A)	179.2(3)	O(11A)–Ni(1)–N(11B)	90.5(3)
N(11A)–Ni(1)–N(31B)	90.9(3)	N(31B)–Ni(1)–N(11B)	179.3(4)
N(31A)–Ni(1)–N(31B)	92.5(3)		

Complex **5**

Ni(1)–N(11A)	2.066(10)	Ni(1)–N(51B)	2.139(10)
Ni(1)–N(51A)	2.103(10)	Ni(1)–O(1A)	2.152(11)
Ni(1)–N(11B)	2.054(10)	Ni(1)–O(1B)	2.077(12)
N(11B)–Ni(1)–N(11A)	92.0(5)	O(1B)–Ni(1)–N(51B)	95.8(4)
N(11B)–Ni(1)–O(1B)	85.5(4)	N(51A)–Ni(1)–N(51B)	92.9(4)
N(11A)–Ni(1)–O(1B)	90.3(4)	N(11B)–Ni(1)–O(1A)	98.5(4)
N(11B)–Ni(1)–N(51A)	176.8(5)	N(11A)–Ni(1)–O(1A)	90.1(4)
N(11A)–Ni(1)–N(51A)	88.5(2)	O(1B)–Ni(1)–O(1A)	176.0(4)
O(1B)–Ni(1)–N(51A)	91.4(4)	N(51A)–Ni(1)–O(1A)	84.6(4)
N(11B)–Ni(1)–N(51B)	86.9(2)	N(51B)–Ni(1)–O(1A)	83.9(4)
N(11A)–Ni(1)–N(51B)	173.7(4)		

Complex **6**

Cu(1)–N(11B)	1.994(10)	Cu(1)–N(51B)	2.055(10)
Cu(1)–N(11A)	2.020(10)	Cu(1)–O(1B)	2.404(12)
Cu(1)–N(51A)	2.027(10)	Cu(1)–O(1A)	2.420(13)
N(11B)–Cu(1)–N(11A)	91.4(5)	N(51A)–Cu(1)–O(1B)	90.4(4)
N(11B)–Cu(1)–N(51A)	175.7(5)	N(51B)–Cu(1)–O(1B)	97.0(4)
N(11A)–Cu(1)–N(51A)	88.8(2)	N(11B)–Cu(1)–O(1A)	97.7(5)
N(11B)–Cu(1)–N(51B)	87.0(2)	N(11A)–Cu(1)–O(1A)	88.7(4)
N(11A)–Cu(1)–N(51B)	172.5(5)	N(51A)–Cu(1)–O(1A)	86.7(4)
N(51A)–Cu(1)–N(51B)	93.3(4)	N(51B)–Cu(1)–O(1A)	84.2(5)
N(11B)–Cu(1)–O(1B)	85.3(4)	O(1B)–Cu(1)–O(1A)	176.8(3)
N(11A)–Cu(1)–O(1B)	90.2(4)		

Complex **7**

Ni(1)–N(11B)	2.098(6)	Ni(1)–O(1A)	2.108(5)
Ni(1)–N(11A)	2.100(6)		
N(11B)–Ni(1)–N(11B)	86.7(3)	N(11B)–Ni(1)–O(1A)	84.2(2)
N(11B)–Ni(1)–N(11A)	92.54(19)	N(11B)–Ni(1)–O(1A)	97.3(2)
N(11B)–Ni(1)–N(11A)	175.1(2)	N(11A)–Ni(1)–O(1A)	87.5(2)
N(11B)–Ni(1)–N(11A)	92.53(18)	N(11A)–Ni(1)–O(1A)	91.1(2)
N(11A)–Ni(1)–N(11A)	88.6(3)	O(1A)–Ni(1)–O(1A)	177.9(4)

Complex **8**

Cu(1)–N(11B)	2.021(4)	Cu(1)–O(1A)	2.400(4)
Cu(1)–N(11A)	2.026(4)		
N(11B)–Cu(1)–N(11B)	87.5(2)	N(11B)–Cu(1)–O(1A)	96.11(16)
N(11B)–Cu(1)–N(11A)	175.05(16)	N(11A)–Cu(1)–O(1A)	89.89(15)
N(11B)–Cu(1)–N(11A)	92.09(13)	N(11A)–Cu(1)–O(1A)	88.78(15)
N(11A)–Cu(1)–N(11A)	88.7(2)	O(1A)–Cu(1)–O(1A)	178.1(2)
N(11B)–Cu(1)–O(1A)	85.24(14)		

Complex **9**

Ni(1)–O(1W)	2.054(6)	Ni(1)–N(11)	2.180(7)
Ni(1)–N(51)	2.116(6)		
O(1W)–Ni(1)–O(1W)	175.6(7)	O(1W)–Ni(1)–N(11)	92.7(4)
O(1W)–Ni(1)–N(51)	87.4(3)	N(51)–Ni(1)–N(11)	92.7(2)
O(1W)–Ni(1)–N(51)	89.5(3)	N(51)–Ni(1)–N(11)	178.2(4)
N(51)–Ni(1)–N(51)	89.2(5)	N(11)–Ni(1)–N(11)	85.5(5)
O(1W)–Ni(1)–N(11)	90.5(4)		

Complex **10**

Cu(1)–O(1B)	1.9982(14)	Cu(1)–N(11)	2.0216(15)
Cu(1)–O(3A)	2.0054(14)	Cu(1)–O(1M)	2.2774(14)
Cu(1)–N(51)	2.0208(15)		
O(1B)–Cu(1)–O(3A)	173.74(6)	N(51)–Cu(1)–N(11)	170.65(6)
O(1B)–Cu(1)–N(51)	90.88(6)	O(1B)–Cu(1)–O(1M)	88.55(5)
O(3A)–Cu(1)–N(51)	91.18(6)	O(3A)–Cu(1)–O(1M)	85.41(5)
O(1B)–Cu(1)–N(11)	89.52(6)	N(51)–Cu(1)–O(1M)	93.71(5)
O(3A)–Cu(1)–N(11)	89.41(6)	N(11)–Cu(1)–O(1M)	95.64(5)

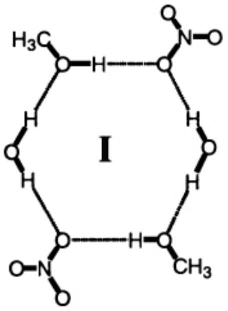
Complex **11**

Cu(1)–N(11)	1.9914(19)	Cu(1)–O(3)	2.0053(16)
Cu(1)–N(11)	1.9914(19)	Cu(1)–O(3)	2.0053(16)
N(11)–Cu(1)–N(11)	96.38(11)	N(11)–Cu(1)–O(3)	156.59(8)
N(11)–Cu(1)–O(3)	93.06(7)	O(3)–Cu(1)–O(3)	86.52(10)

$\{[\mathrm{Ni}(\mathbf{2})_2(\mathrm{H_2O})_2]\cdot\mathrm{G_1}\cdot 5\mathrm{MeOH}\cdot 2\mathrm{NO_3}\}_n$ **4**
$\{[\mathrm{Ni}(\mathbf{3})_2(\mathrm{NO_3})_2]\cdot 2\mathrm{G_2}\}_n$ **5**
$\{[\mathrm{Cu}(\mathbf{3})_2(\mathrm{NO_3})_2]\cdot 2\mathrm{G_2}\}_n$ **6**
$\{[\mathrm{Ni}(\mathbf{3})_2(\mathrm{NO_3})_2]\cdot 2\mathrm{G_3}\}_n$ **7**
$\{[\mathrm{Cu}(\mathbf{3})_2(\mathrm{NO_3})_2]\cdot 2\mathrm{G_3}\}_n$ **8**
$\{[\mathrm{Ni}(\mathbf{3})_2(\mathrm{H_2O})_2]\cdot 2\mathrm{NO_3}\}_n$ **9**
$\{[\mathrm{Cu}(\mathbf{3})(\mathrm{NO_3})_2(\mathrm{MeOH})]\cdot\mathrm{G_1}\cdot\mathrm{MeOH}\}_n$ **10**
$\{[\mathrm{Cu}(\mathbf{3})(\mathrm{NO_3})_2]\}_n$ **11**

The crystal structures of the complexes **4**–**8** reveal that interpenetration of the networks is eschewed by the inclusion of guest molecules, whereas **9**–**11** exhibit interpenetrated square grid, 1-D linear chain and zigzag chain formation respectively. The deviation from open square grids to different structures in complexes **9**–**11** indicates the preference of ligand **3** for electron deficient guest molecules. Bond lengths and angles around metal atoms in **4**–**11** are given in Table 1.

Complex **4** exhibited an open square grid co-ordination polymer with slightly distorted square dimensions of *ca.* 15.63 × 15.56 Å (Fig. 1a). The Ni atom has octahedral co-ordination, the equatorial positions being occupied by four pyridyls and the apical positions by two water molecules. Interestingly, the benzene molecules are enclathrated not in the cavity but between the layers that have an interlayer separation of 4.7 Å (Fig. 1b). The square cavities are occupied by two O–H···O dimers of MeOH and $\mathrm{NO_3}$ ion (O···O 2.766 and 2.883 Å). Interestingly these dimers link their neighboring layers with the co-ordinated water molecules *via* hydrogen bonded motif **I**. In a sense the whole structure can be described as a doubly interpenetrated 3-D hydrogen bonded network. The motif **I** consists of total 12 atoms that are assembled from two nitrates, two MeOH and two $\mathrm{H_2O}$ and resembles the chair conformation of cyclohexane (Fig. 1c). The O···O distances and O···O···O angles range from 2.673 to 2.883 Å and 99.3 to 138.4° respectively. As a result of linking the alternate layers through motif **I** the 2-D layers are superimposed on each other in an offset fashion on both the edges such that there are continuous channels of dimensions of a quarter of the square cavity.



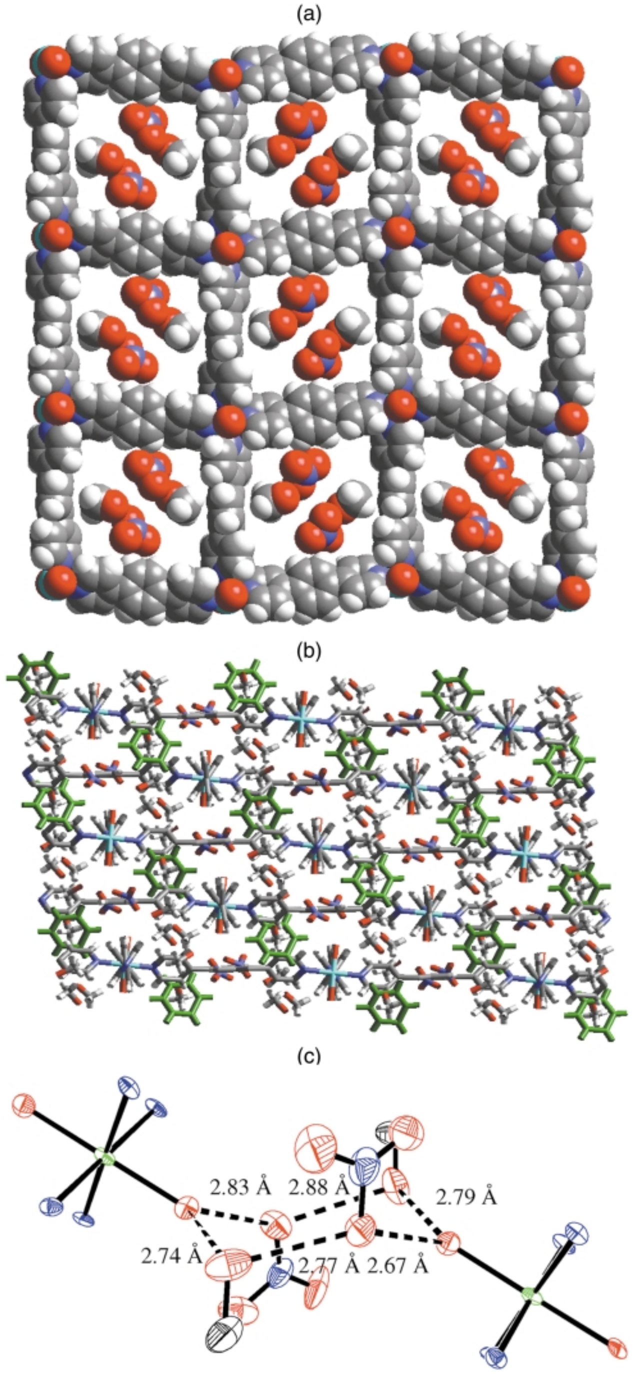


Fig. 1 The crystal structure of complex **4**. (a) Space filling representation of the open square grid network. The square cavities are occupied by two O–H···O dimers of MeOH and nitrate. (b) Offset packing of the grids with an interlayer separation of 4.7 Å. Note the benzene molecules between the grids. (c) An ORTEP[15] drawing (40% probability) showing the chair conformation of synthon **I**.

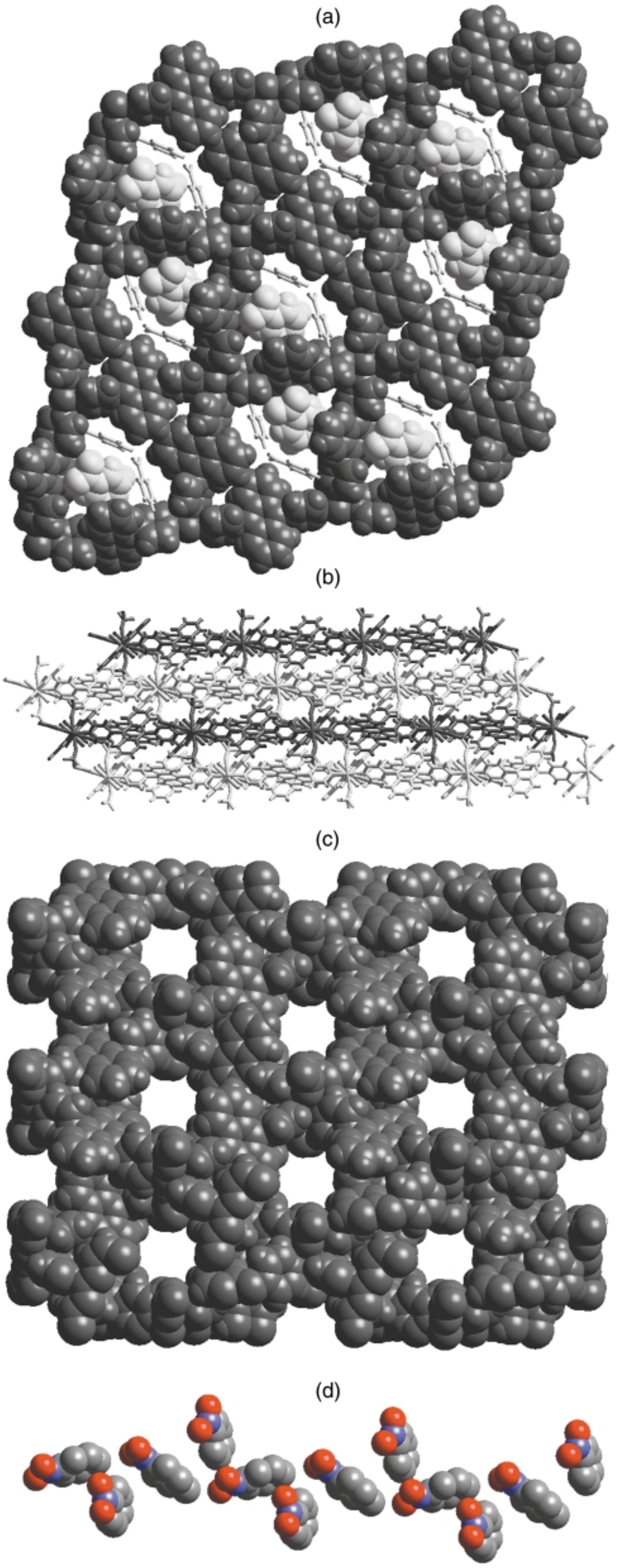


Fig. 2 The crystal structure of complex **5**. (a) Open 2-D network represented in space filling mode. The guest molecules are shown in space filling and cylinder mode in light shading. Note a 1-D aromatic stack between the guest (space filling mode) and antharacene moieties. Nitrates are not shown for the sake of clarity. (b) Slipped packing of the grids shown without guest molecules. Alternate layers are represented in dark and light shades for clarity. (c) Top view of the packing of the grids (four layers) in space filling mode showing the continuous channels. (d) A 1-D column of nitrobenzene molecules.

The ligand **3** with $Ni(NO_3)_2$ or $Cu(NO_3)_2$ was found to form open grid complexes **5** and **6**, respectively, in presence of nitrobenzene. However the grids are not square but are of rhomboid shape (Fig. 2a). The diagonal-to-diagonal distances are 24.9 × 18.7 and 24.7 × 18.4 Å and the dimensions of the grid are 15.6 × 15.5 and 15.4 × 15.4 Å in **5** and **6** respectively. The cavities of the grid are occupied by three nitrobenzene molecules: one interacts with anthracene moieties *via* π–π interactions, the distances between C atoms of C_6-rings of the outer anthracene moiety and nitrobenzene are 3.3 to 4 Å, and fully immersed in the grids, while the other two exist at the portals of the grids, only half of each molecule being within the grid. As a result of extended sandwiching in one dimension between anthracene moieties and one of the nitrobenzenes *via* strong donor–acceptor interactions the grids are distorted from square nature. Unlike in complex **4**, the nitrate ions co-ordinate to apical positions of Ni or Cu atoms in **5** or **6** respectively. The nitrobenzene accounts for 42% of the crystal volume in both **5**

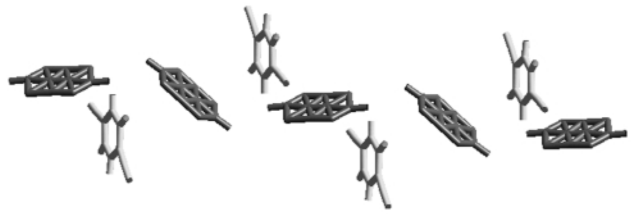
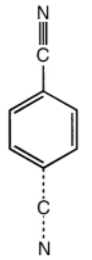


Fig. 3 A one-dimensional column of cyanobenzenes in complex **7**. Notice the disorder.

and **6**. Interestingly the grids superimpose on each other in a slightly slipped manner on both the edges (interlayer separation is 5.5 Å) such that there are continuous channels of dimension slightly less than 15 × 15 Å. These are occupied by a column of nitrobenzene (Fig. 2b and 2c) that is formed *via* C–H···O hydrogen bonds and edge to face aromatic interactions (Fig. 2d). The nitrobenzene molecules are disordered in the centrosymmetric space group but solving the structure in a non-centrosymmetric space group resulted in ordered guest molecules that are unidirectional in the channels.

Cyanobenzene also templated similar open square grid co-ordination polymers **7** and **8** with ligand **3** and Ni$(NO_3)_2$ or Cu$(NO_3)_2$ respectively. The geometry as well as the packing of the grids are completely similar to those of the above complexes. However, cyanobenzenene is found to have disorder in both centrosymmetric and non-centrosymmetric space groups. Two crystallographically independent halves of cyanobenzene exist in the asymmetric unit which differs in disorder as shown. The cyanobenzenes also form a 1-D column similar to nitrobenzenes across the grids (Fig. 3). The grid dimensions are 15.6 × 15.6 and 15.4 × 15.4 Å and diagonal-to-diagonal distances are 24.8 × 18.8 and 24.5 × 18.6 Å in **7** and **8** respectively.



The ligand **3** and Ni$(NO_3)_2$ formed a mutually interpenetrated 2-D grid structure **9** in the presence of benzene. The grids are interpenetrated with an inclination angle of 45° such that any 2-D layer has an infinite number of other layers passing thorough it (Fig. 4a). The ligand **1** is also known to form doubly interpenetrated square grids but in those the mutually interpenetrated grids are orthogonal to each other.[5a] The reduced inclination angle in **9** compared to that of **1** is to provide strong edge to face aromatic interactions between α or β carbons of the pyridine moiety and the π-electron density of the anthracene moiety. For instance the distance between α or β carbons of pyridine and the plane of the anthracene moiety is 3.6 Å. Unlike the grids in **5**–**8**, those in **9** are square with dimensions of 15.7 Å and diagonal-to-diagonal distance 23.0 × 21.4 Å (Fig. 4b). Similar to complex **4**, the Ni atoms are co-ordinated to two water molecules at apical positions and to four pyridyl groups at equatorial positions. The nitrates form hydrogen bonds with co-ordinated water molecules and occupy the channels formed between the interpenetrated grids.

Surprisingly, a reaction similar to the above but with Cu$(NO_3)_2$ resulted in the formation of completely different structures. It forms two one-dimensional co-ordination polymers **10** (minor product) and **11** (major product) in one reaction flask. The 1-D chains are linear in **10** (Fig. 5a) while they are

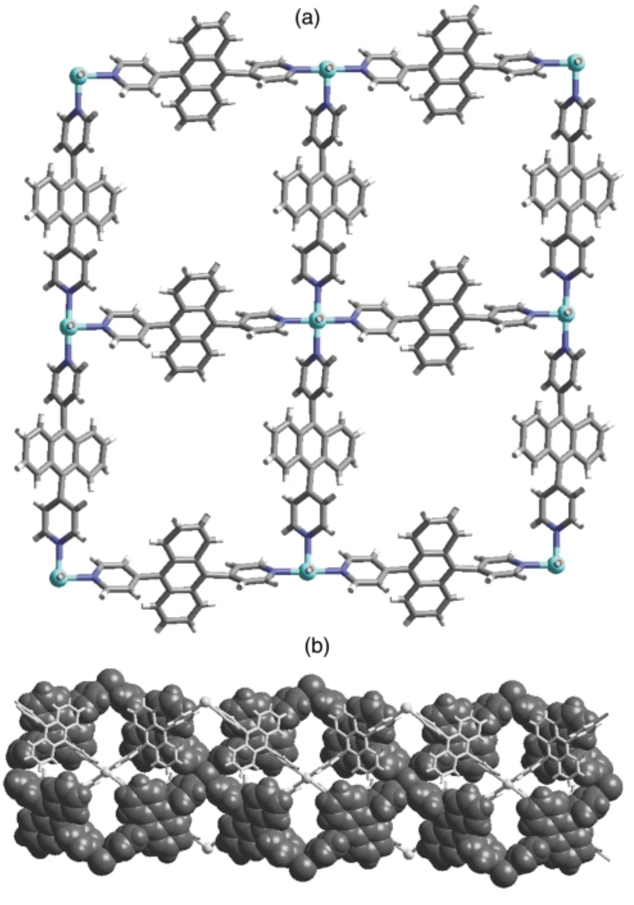


Fig. 4 The crystal structure of complex **9**. (a) Two-dimensional square grid network. O atoms are at apical positions. (b) Interpenetration of the two nets shown in space filling (dark shade) and cylinder mode (light shade). Notice that the angle of interpenetration of the nets is not orthogonal.

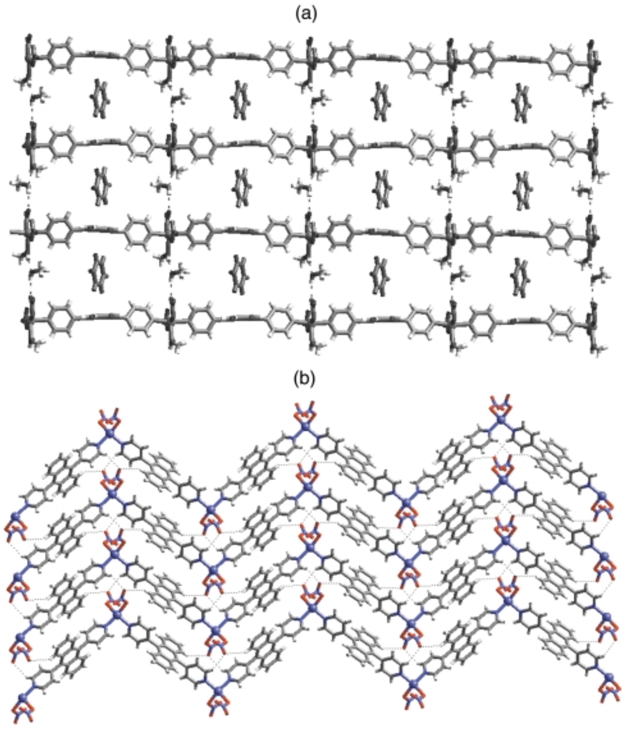


Fig. 5 (a) A rectangular grid formed by the linking of 1-D linear chains *via* hydrogen bonds in complex **10**. Note the benzene molecules that are sandwiched between anthracene moieties. (b) A 2-D layer in **11** formed by the C–H···O hydrogen bonds between the zigzag chains.

zigzag in **11** (Fig. 5b). In **10** the Cu atom has a distorted square pyramidal geometry: two pyridyl groups and two nitrates are co-ordinated in a *trans* fashion at equatorial positions and one MeOH at apical position. Interestingly, the linear chains are linked together *via* O–H···O hydrogen bonds, between co-ordinated MeOH, encapsulated MeOH and nitrate anion, to form a rectangular 2-D grid network. The grid cavities are occupied by benzene molecules. Notably, the benzene molecules are sandwiched between two anthracene moieties by edge to face aromatic interactions. In complex **11** the Cu atom has square planar geometry with the co-ordination of two pyridyls and two nitrates in *cis* fashion. As a result it forms a zigzag chain without encapsulating the guest molecules. Interestingly the zigzag chains are connected together *via* C–H···O hydrogen bonds and edge to face aromatic interactions between pyridyl C–H groups and anthracene moieties to form a 2-D sheet structure.

Conclusion

The ligands **2** and **3** were shown to form open 2-D square grid co-ordination polymers in the presence of suitable guest molecules. Ligand **3** was also shown to form interpenetrated grids with $Ni(NO_3)_2$ and two 1-D co-ordination polymers with $Cu(NO_3)_2$ in the presence of benzene. The formation of an interpenetrated network rather than an open network for **3** and $Ni(NO_3)_2$ in the presence of benzene suggests that ligand **3** prefers to interact with itself rather than with benzene. The use of electron deficient guest molecules like nitrobenzene and cyanobenzene paved the way for open network square grids of ligand **3**.

Experimental

Synthesis of compounds 2 and 3

The ligands **2** and **3** were prepared by Suzuki coupling of corresponding dibromo compounds, 1,4-dibromobenzene for **2** and 9,10-dibromoanthracene for **3**, with 4-pyridylboronic acid pinacol ester which is synthesized from 4-bromopyridine.[16] Both **2** and **3** are reasonably soluble in common organic solvents.

Preparation of crystals

The single crystals of complex **4** were prepared by layering a MeOH solution of $Ni(NO_3)_2 \cdot 6H_2O$ (6 mg in 5 mL) onto a benzene solution of **2** (9.2 mg in 15 mL). After the solution was allowed to stand for 2d the crystals formed were isolated in 60% yield by filtration. Similarly, single crystals for complexes **5**–**11** were synthesized by layering a MeOH solution of $Ni(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ over corresponding guest solutions of **3**. Yields for compounds **5**–**11**: 80, 70, 75, 65, 80 and 20 +50% (**10** + **11** obtained in one flask).

Crystal structure determinations

Single crystal X-ray diffraction data for all the complexes were collected on a Siemens SMART/CCD diffractometer equipped with a low temperature device. Data were corrected for absorption using the SADABS[17] program; SHELXTL[18] was used for the structure solution and refinement based on F^2. All non hydrogen atoms were refined anisotropically. The H atoms of the C–H groups were fixed in calculated positions and refined isotropically with thermal parameters based upon the corresponding C atoms [$U(H) = 1.2\ U_{eq}$ (C)]. The H atoms of water and MeOH molecules in **9** and **10** respectively were located and refined isotropically, whereas those in **4** could not be located. The crystal structures of **4**, **5** and **6** were refined in centrosymmetric space groups also. However, one of the MeOH in **4** and nitrobenzene molecules in **5** and **6** were disordered. Solving the

Table 2 Crystallographic parameters for complexes **4**–**11**

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Formula	$C_{43}H_{54}N_6NiO_{13}$	$C_{60}H_{42}N_8NiO_{10}$	$C_{60}H_{42}CuN_8O_{10}$	$C_{62}H_{37}N_8NiO_6$	$C_{62}H_{37}CuN_8O_6$	$C_{48}H_{36}N_6NiO_8$	$C_{32}H_{30}CuN_4O_8$	$C_{24}H_{16}CuN_4O_6$
M	921.63	1093.73	1098.56	1048.71	1053.54	883.54	662.14	519.95
T/K	193	193	193	193	193	193	193	193
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	Cc	Cc	Cc	$C2/c$	$C2/c$	$Iba2$	$P2_1/c$	$C2/c$
a/Å	16.854(2)	13.6359(18)	13.810(2)	13.645(3)	13.792(2)	9.905(2)	12.941(1)	25.142(3)
b/Å	15.626(2)	24.875(3)	24.700(3)	24.777(5)	24.529(3)	18.973(5)	19.064(2)	7.3605(10)
c/Å	19.144(2)	15.217(2)	15.286(2)	15.457(3)	15.5154(2)	23.009(6)	13.224(1)	11.872(2)
β/°	114.785(2)	99.604(2)	101.982(3)	99.560(5)	101.439(2)		107.734(2)	109.488(2)
V/Å^3	4577.5(10)	5089.0(12)	5100.3(11)	5153(2)	5144.8(10)	4324(2)	3107.4(5)	2071.1(5)
Z	4	4	4	4	4	4	4	4
μ/mm^{-1}	0.493	0.453	0.500	0.439	0.487	0.511	0.760	1.108
Measured reflections	14415	13433	16768	13696	16867	9290	19842	6582
Unique reflections	8605	6895	9892	4543	6148	3772	7419	2462
	R(int) = 0.0305	R(int) = 0.0644	R(int) = 0.0882	R(int) = 0.2088	R(int) = 0.0911	R(int) = 0.0823	R(int) = 0.0301	R(int) = 0.0416
$R1$ ($I > 2\sigma(I)$)	0.0656	0.0730	0.0764	0.0772	0.0703	0.0863	0.0351	0.0385
$wR2$ (on F^2, all data)	0.2178	0.2176	0.2386	0.1859	0.2104	0.2487	0.0933	0.0929

structures in a non-centrosymmetric space group resulted in a lower *R* factor and no disorder in **4**, whereas for **5** and **6** the *R* factor remained the same but the guest molecules are not disordered. Pertinent crystallographic data are given in Table 2.

CCDC reference number 186/2052.

See http://www.rsc.org/suppdata/dt/b0/b004054l/ for crystallographic files in .cif format.

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