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Coexisting covalent and non-covalent planar networks in the crystal structures of $\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$ (M = Ni, 1; Co, 2; arene = chlorobenzene, *o*-dichlorobenzene, benzene, nitrobenzene, toluene or anisole)†

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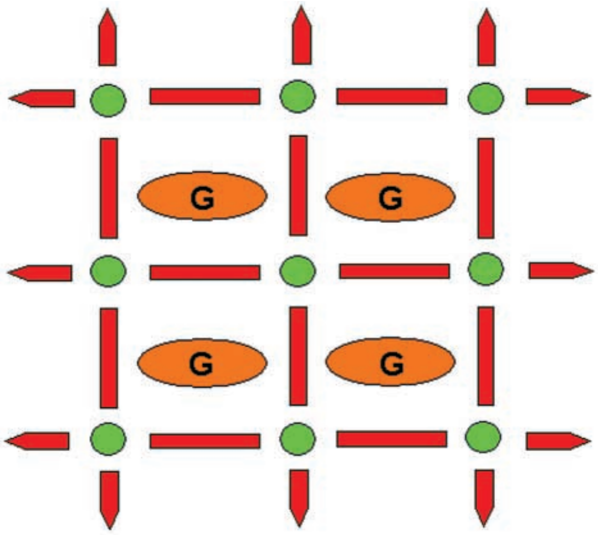
The compounds $\{[M(4,4'\text{-bipy})_2(NO_3)_2]\cdot x\ \text{arene}\}_n$ (M = Ni, **1**; Co, **2**; $x = 2$ for arene = chlorobenzene, *o*-dichlorobenzene, benzene, nitrobenzene or toluene; $x = 3$ for arene = anisole) have been prepared and their crystal structures determined. All compounds represent rare examples of interpenetrating planar networks that are chemically different. It appears that the networks coexist because the (4,4) topology of the cobalt and nickel square grids is complementary to the (4,4) and (6,3) topology of the arene networks, resulting in inclined interpenetration and a 3-D architecture. This observation is discussed in the broader context of rational design strategies for hybrid solids.

Introduction

It is becoming apparent that crystal engineering[1] offers potential for the development of rational strategies for design of new crystalline materials, in particular those with functional properties. For example, the specific network topology of a coordination polymer can be controlled by careful selection of metal coordination geometry and organic "spacer" ligands. Indeed, there already exists a wide range of 1-D,[2] 2-D[3,4] and 3-D[5–7] networks that have no precedent in naturally occurring compounds. A particularly simple example of such a designed and predictable coordination polymer network is exemplified by 2-D square grids that are generated from square planar or octahedral metal ions, M. If such moieties are coordinated to linear bifunctional "spacer" or "rod" ligands such as 4,4′-bipyridine, bipy, then square grids of general formula $[M(bipy)_2(X)_2]_n$ can result.[3] It should be noted that these compounds have cavities that are suitable for interpenetration or enclathration of a wide range of organic guest molecules (Scheme 1) and there exists potential for catalysis.[3b] Furthermore these networks are tunable as the length and width of the spacer ligand controls the size of the cavities that occur within the polymeric structure, although interpenetration can mitigate against the existence of frameworks with very large cavities.[8]



Scheme 1 A representation of square grid coordination polymers and how they inherently possess cavities that are suitable for incorporation of guest molecules.

Scheme 2 reveals how it is possible for interpenetration to occur between either identical or different networks. For example (4,4) (*e.g.* a square grid coordination polymer) and (6,3) (*e.g.* a honeycomb network) planar networks are in principle complementary from a topological sense with another (4,4) network (*e.g.* the same or a different square grid network). However, an even more intriguing situation that could have broad implications for design of new hybrid materials is exemplified by the crystal structure of the square grid coordination polymer $[Ni(bipy)_2(NO_3)_2]$ and its binary compound with pyrene (**1**·2pyrene).[9] In a preliminary communication we reported how careful examination of the crystal packing in **1**·2pyrene reveals that the pyrene molecules form a non-covalent (4,4) network that is complementary from a topological perspective with the square grid coordination polymer network. Indeed, **1**·2pyrene represents what is to our knowledge the first compound in which it has been observed that two very different types of planar network interpenetrate. Specifically, the structure can be described as interpenetration of a non-covalent net (*i.e.* a 2-D array of pyrene molecules) and a square grid metal coordination polymer. The structures of $\{[M(bipy)_2(NO_3)_2]\cdot 2\text{naphthalene}\}_n$ (M = Ni, **1**; Co, **2**)[10] can be described in a similar manner. **1**·2pyrene also illustrates how polarity in crystals can be generated from subtle packing of achiral components, as illustrated by the presence of chiral networks of pyrene molecules.

It might be argued that the existence of non-covalent networks of aromatic molecules must be dependent upon the

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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/b003733h/

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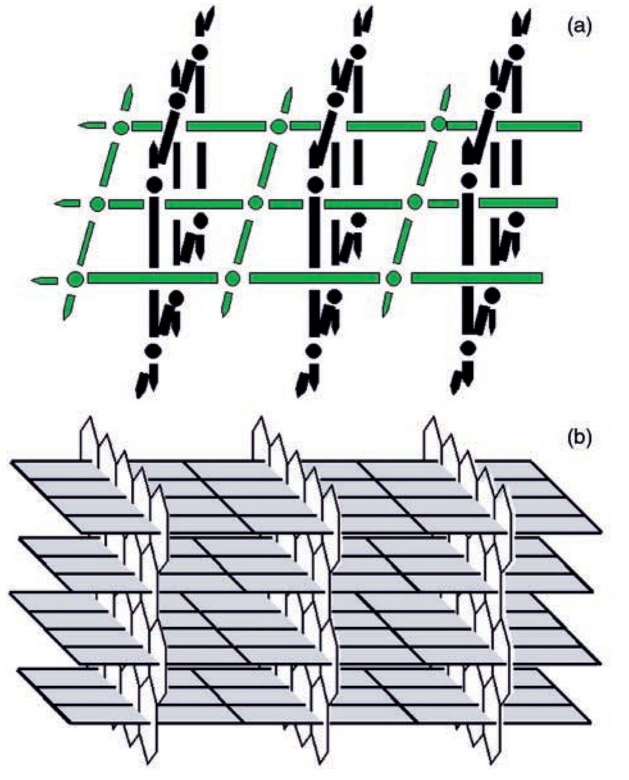


Scheme 2 A representation of how planar networks can interpenetrate to form 3-D structures: (a) complementary (4,4) networks; (b) complementary (6,3) and (4,4) networks.

presence of a rigid coordination polymer network. However, the structure of the cocrystal formed between ferrocene and pyrene[11] reveals planar networks of pyrene molecules that are almost identical to those observed in $\{[Ni(bipy)_2(NO_3)_2]\cdot 2pyrene\}_n$. In this contribution we report the results of an analysis of the crystal packing in a broader range of binary compounds that are composed of square grid coordination polymer complexes and arenes, $\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$ (M = Ni, **1**; Co, **2**; arene = chlorobenzene, *o*-dichlorobenzene, benzene, nitrobenzene, naphthalene, toluene or anisole). Particular emphasis is placed upon the presence and topology of the non-covalent planar networks.

Experimental

General

All materials were used as received from commercial sources (Sigma-Aldrich or Fisher Scientific); solvents were purified and dried according to standard methods.[12]

Synthesis

$\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$ crystals were grown *via* slow diffusion of reagents through solvent layers. In a typical reaction, a mixture of 5 ml nitrobenzene and 5 ml methanol was carefully layered over 4,4′-bipyridine (156 mg, 1 mmol) dissolved in 10 ml nitrobenzene. A solution of $Ni(NO_3)_2\cdot 6H_2O$ (145 mg; 0.5 mmol) in 10 ml methanol was then carefully layered over the methanol/nitrobenzene layer. The solution was left undisturbed for 48 h and the blue prismatic crystals of **1**$\cdot 2PhNO_2$ (337 mg, 0.45 mmol, 91%) that formed were collected by filtration. Crystals were observed to lose solvent slowly and decompose in days to weeks when removed from the mother liquor. High-resolution thermogravimetric analysis (TA Instruments TGA 2950) revealed a 34.4% weight loss at 118 °C followed by a multi-step thermal decomposition at temperatures greater than 150 °C. These data are consistent with the expected loss of two nitrobenzene molecules per unit cell (33.2%). The other compounds studied herein were prepared by manners similar to that described above and exhibit similar thermal stability.

X-Ray crystallography

Intensity data for compounds **1**$\cdot$2PhCl, **1**$\cdot 2C_6H_4Cl_2$-*o*, **2**$\cdot$2PhCl, **2**$\cdot 2C_6H_4Cl_2$-*o*, and **2**$\cdot$2PhH were recorded on an Enraf Nonius CAD-4 diffractometer using Mo(Kα) radiation in the ω scan mode. Direct methods were used to solve the crystal structures. Crystallographic calculations were effected using the PC version of the NRCVAX system[13] (no correction was made for absorption). Non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were placed in calculated positions and given isotropic U values based on the atom to which they are bonded.

Intensity data for compounds **1**$\cdot$2PhH, **1**$\cdot 2PhNO_2$, **2**$\cdot 2PhNO_2$, and **2**$\cdot 2C_6H_5Me$ were collected on a Siemens SMART/CCD diffractometer using Mo(Kα) radiation. Lorentz and polarization corrections were applied and data were also corrected for absorption with the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structure. Crystallographic calculations for **1**$\cdot$2PhH, **1**$\cdot 2PhNO_2$, **2**$\cdot 2PhNO_2$, and **2**$\cdot 2C_6H_5Me$ were effected by full-matrix least-squares methods using SHELXTL PC V 5.03.[14] Refinement of the structure of **2**$\cdot$3PhOMe was conducted by full-matrix least-squares calculations using SHELXTL NT V 5.1.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated (d_{C-H} = 0.93 Å) positions and refined using a riding model with an isotropic displacement parameter of 1.2 times the U_{eq} of the corresponding carbon atoms.

Calculations in the context of cavity dimensions and relative network volumes were effected with the Cerius^2 molecular simulation software environment.[16] Table 1 reveals salient crystallographic features of the 10 new compounds reported herein whereas Tables 2–4 present selected interatomic distances and angles.

CCDC reference number 186/2060.

See http://www.rsc.org/suppdata/dt/b0/b003733h/ for crystallographic files in .cif format.

Results and discussion

As revealed in Scheme 1, it is reasonable to assert that compounds of formula $[M(bipy)_2X_2]_n$ represent a generic class of planar network, square grid coordination polymers that are based upon square planar or octahedral metal geometries propagated by linear "spacer" ligands. It is of note that such a structure is inherently open framework since cavities are necessarily present within the plane of the 2-D network. These cavities might be filled by guest molecules, thereby forming structures that are both clay-like (*i.e.* lamellar) and zeolite-like (*i.e.* porous). Alternatively, as was the case for the prototypal example of such compounds, $[Zn(bipy)_2(H_2O)_2]SiF_6$,[3a] the cavities might be filled by interpenetration, a common phenomenon in 2-D and 3-D coordination polymers with relatively large channels and cavities.[8] The first examples of open framework square grid coordination polymers, based upon $[Cd(bipy)_2(NO_3)_2]$, were reported by Fujita *et al.* shortly thereafter.[3b] Fujita's compound was observed to exhibit the ability to clathrate aromatic guest molecules and to act as a catalyst. In this contribution we focus upon a different aspect of square grid coordination polymers. Specifically, we analyse aromatic solvates of the square grids $[M(bipy)_2(NO_3)_2]$ (M = Ni, **1**; Co, **2**) in terms of their composition and crystal structure. As might be expected from earlier reports,[9,10] **1** and **2** readily form host–guest compounds with aromatic hydrocarbon molecules as diverse in size as benzene and pyrene and with both electron rich (*e.g.* naphthalene, anisole) and electron poor (*e.g.* nitro-

Table 1 Crystallographic data

	1·2PhCl	**1**·2$C_6H_4Cl_2$-*o*	**1**·2PhH	**1**·2$PhNO_2$	**2**·2PhCl
Formula	$C_{32}H_{26}ClN_6NiO_6$	$C_{32}H_{24}Cl_2N_6NiO_6$	$C_{32}H_{28}N_6NiO_6$	$C_{32}H_{26}N_8NiO_{10}$	$C_{32}H_{26}ClCoN_6O_6$
M	720.20	789.09	651.31	741.32	720.43
T/K	293	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (no.)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)
a/Å^3	21.678(3)	21.5155(17)	21.164(2)	21.5968(13)	21.8140(12)
b/Å^3	11.4111(10)	11.4059(9)	11.4128(9)	11.4000(7)	11.52810(20)
c/Å^3	12.9139(16)	13.3137(10)	12.6597(10)	12.9303(8)	12.8767(7)
β/°	103.401(11)	103.2940(10)	101.2060(10)	103.1040(10)	102.6740(10)
V/Å^3	3107.5(7)	3179.7(4)	2999.5(4)	3100.6(3)	3159.3(3)
Z	4	4	4	4	4
μ/mm^{-1}	0.85	1.01	0.703	0.701	0.76
Reflections collected	2863	4298	4492	9438	7457
Unique reflections	2739	1670	3067	3627	3442
Final $R[I > 2\sigma(I)]$	0.054	0.098	0.0449	0.0301	0.057
R (all data)	0.054	0.098	0.0684	0.0439	0.057

	2·2$C_6H_4Cl_2$-*o*	**2**·2PhH	**2**·2$PhNO_2$	**2**·2C_6H_5Me	**2**·3PhOMe
Formula	$C_{32}H_{24}Cl_2CoN_6O_6$	$C_{32}H_{28}CoN_6O_6$	$C_{32}H_{26}CoN_8O_{10}$	$C_{34}H_{32}CoN_6O_6$	$C_{41}H_{40}CoN_6O_9$
M	789.32	651.54	741.54	679.60	819.72
T/K	293	293	293	293	193
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group (no.)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	$Pna2_1$ (33)
a/Å^3	21.6458(13)	21.3256(3)	21.7003(11)	21.7636(13)	22.8114(11)
b/Å^3	11.5193(7)	11.53050(10)	11.4961(6)	11.5176(7)	15.4407(7)
c/Å^3	13.3717(8)	12.60790(20)	12.8598(6)	12.8555(8)	11.4207(5)
β/°	102.6680(10)	100.7670(10)	102.5260(10)	102.7410(10)	
V/Å^3	3253.0(3)	3045.64	3131.8(3)	3143.1	4022.6(3)
Z	4	4	4	4	4
μ/mm^{-1}	0.91	0.61	0.623	0.601	0.489
Reflections collected	8972	8836	9721	9565	25154
Unique reflections	3547	3177	3662	3676	7759
R_{int}	0.062	0.039	0.0296	0.0379	0.0502
R (all data)	0.062	0.039	0.0340	0.0516	0.0689

Table 2 Selected bond distances (Å) and angles (°) for compounds of the type $\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$

	1·2PhCl	**1**·2$C_6H_4Cl_2$-*o*	**1**·2PhH	**1**·2$PhNO_2$	**2**·2PhCl
M–N(11)$^{1\,a}$	2.118(3)	2.115(10)	2.100(2)	2.1097(12)	2.171(3)
M–N(21)	2.136(5)	2.198(17)	2.135(3)	2.136(2)	2.193(4)
M–N(22)	2.156(5)	2.121(17)	2.135(3)	2.144(2)	2.213(4)
M–O(1)^1	2.101(3)	2.111(10)	2.107(2)	2.1128(11)	2.1022(25)
O(1)–N(1)	1.287(5)	1.281(18)	1.275(3)	1.293(2)	1.292(4)
O(2)–N(1)	1.210(6)	1.221(20)	1.197(3)	1.224(2)	1.213(4)
O(3)–N(1)	1.210(5)	1.215(19)	1.217(3)	1.225(2)	1.215(5)
O(1)–M–O(1)^1	177.55(13)	177.7(4)	179.19(11)	176.82(6)	178.23(11)
O(1)–M–N(11)	84.69(12)	83.4(4)	83.98(8)	84.87(4)	84.32(10)
O(1)–M–N(11)^1	95.15(12)	96.5(4)	95.97(8)	94.92(4)	95.56(10)
O(1)–M–N(21)	91.22(9)	91.1(3)	90.41(6)	88.41(3)	89.11(7)
O(1)–M–N(22)	88.78(9)	88.9(3)	89.59(6)	91.59(3)	90.89(7)
N(11)–M–N(21)	93.58(10)	93.6(3)	93.40(6)	86.12(3)	85.92(8)
N(11)–M–N(22)	86.42(10)	86.4(3)	86.60(6)	93.88(3)	94.08(8)
N(21)–M–N(22)	180.0	179.9	180.0	180.0	180.0
N(11)–M–N(11)^1	172.84(14)	172.9(4)	173.20(12)	172.24(7)	171.85(11)
M–O(1)–N(1)	131.76(25)	135.0(8)	133.5(2)	129.30(9)	130.97(21)

[a] Symmetry transformation used to generate equivalent atoms: 1 $-x + 1, y, -z + \frac{1}{2}$.

benzene) aromatic molecules. As we reveal herein, their crystal packing does not appear to be random or even unpredictable. Rather, it seems to be rational and based upon topological considerations.

Crystal packing of the square grid coordination polymers

If one were to ignore the packing of guest molecules and consider only the coordination polymer portion of the crystal structures, there appear to be three distinct packing modes. These modes, which are categorized based upon the stacking of adjacent 2-D grids, are designated A, B and C. There are no significant differences in interatomic bond distances or angles within the coordination polymer networks. However, as revealed by Fig. 1, there are subtle differences in the conformation within the bipy ligands and how they orient with respect to the plane of the square grid coordination polymer. There are two structures that the grids adopt in this respect: 50% of the bipy ligands are coplanar, 50% adapt a twisted conformation (Fig. 1a); or all bipy ligands contain pyridyl rings that are twisted (Fig. 1b). Grid types A and C exhibit the former structure with type A grids exhibiting greater torsion angles for the

Table 3 Selected bond distances (Å) and angles (°) for compounds of the type $\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$

	2·2$C_6H_4Cl_2$-*o*	**2**·2PhH	**2**·2$PhNO_2$	**2**·2C_6H_5Me
M–N(11)^{1}[a]	2.183(3)	2.1554(15)	2.1619(11)	2.1655(15)
M–N(21)	2.182(3)	2.190(3)	2.181(2)	2.193(2)
M–N(22)	2.224(3)	2.2077(25)	2.196(2)	2.206(2)
M–O(1)^{1}	2.1200(25)	2.1027(14)	2.1033(10)	2.0905(13)
O(1)–N(1)	1.276(4)	1.2908(22)	1.298(2)	1.298(2)
O(2)–N(1)	1.207(4)	1.225(3)	1.229(2)	1.224(2)
O(3)–N(1)	1.215(4)	1.212(3)	1.224(2)	1.220(2)
O(1)–M–O(1)^{1}	178.64(9)	179.59(6)	178.06(8)	178.49(8)
O(1)–M–N(11)	83.74(10)	83.92(6)	84.89(4)	83.61(6)
O(1)–M–N(11)^{1}	96.17(10)	96.05(6)	94.97(4)	96.29(6)
O(1)–M–N(21)	89.32(6)	89.79(4)	89.03(3)	89.24(4)
O(1)–M–N(22)	90.68(6)	90.21(4)	90.97(3)	90.76(4)
N(11)–M–N(21)	86.33(6)	86.04(5)	85.73(3)	86.13(4)
N(11)–M–N(22)	93.67(6)	93.96(5)	94.27(3)	93.87(4)
N(21)–M–N(22)	179.9	180.08	180.0	180.0
N(11)–M–N(11)^{1}	172.66(9)	172.08(7)	171.47(6)	172.26(8)
M–O(1)–N(1)	134.96(20)	133.04(12)	129.26(8)	129.94(11)

[a] Symmetry transformation used to generate equivalent atoms: 1 $-x+1, y, -z+\frac{1}{2}$.

Table 4 Selected bond distances (Å) and angles (°) for compound **2**·3PhOMe

Co(1)–O(1)	2.091(2)	O(5)–N(2)	1.198(5)	O(4)–Co(1)–N(21)	85.81(9)
Co(1)–O(4)	2.097(2)	O(6)–N(2)	1.226(5)	N(11)–Co(1)–N(21)	89.8(2)
Co(1)–N(11)	2.144(5)			N(22)–Co(1)–N(21)	177.5(2)
Co(1)–N(22)	2.146(3)	O(1)–Co(1)–O(4)	170.12(8)	O(1)–Co(1)–N(12)	90.36(14)
Co(1)–N(21)	2.146(2)	O(1)–Co(1)–N(11)	89.87(14)	O(4)–Co(1)–N(12)	88.84(13)
Co(1)–N(12)	2.189(5)	O(4)–Co(1)–N(11)	90.55(13)	N(11)–Co(1)–N(12)	177.76(8)
O(1)–N(1)	1.285(4)	O(1)–Co(1)–N(22)	95.37(9)	N(22)–Co(1)–N(12)	89.5(2)
O(2)–N(1)	1.227(5)	O(4)–Co(1)–N(22)	94.47(9)	N(21)–Co(1)–N(12)	88.0(2)
O(3)–N(1)	1.218(5)	N(11)–Co(1)–N(22)	92.7(2)	N(1)–O(1)–Co(1)	132.8(2)
O(4)–N(2)	1.291(4)	O(1)–Co(1)–N(21)	84.32(9)	N(2)–O(4)–Co(1)	126.8(2)

twisted bipy ligands than those observed for type C grids (32.5–48.9 *vs.* 25°). In type B grids all bipy ligands in one direction exhibit a torsion angle of 35–40°, those in the other direction a torsion angle of *ca.* 15°. Therefore, there is in effect some degree of flexibility in the coordination polymer framework and consequently the cavities within the grids do not have to be square.

The following nine compounds exhibit type A packing: **1**·2PhCl, **2**·2PhCl, **1**·2$C_6H_4Cl_2$-*o*, **2**·2$C_6H_4Cl_2$-*o*, **1**·2PhH, **2**·2PhH, **1**·2$PhNO_2$, **2**·2$PhNO_2$, **2**·2C_6H_5Me. These compounds are isostructural with one another: they crystallize in space group *C*2/*c* with similar cell parameters; they have 2:1 guest:host stoichiometry; their interplanar separations are ≈6 Å and they possess inner cavities with effective dimensions of *ca.* 8 × 8 Å. Fig. 2(a) illustrates how the square grids pack in type A compounds. The crystal packing of the square grids appears to be influenced by C–H···O hydrogen bond interactions between bipy ligands of one square grid and nitrate anion of the adjacent square grid. C···O separations are in the range of 2.877–3.149 Å, consistent with what would be expected for C–H···O hydrogen bonding.[17] The axial nitrate groups adopt an orientation consistent with 2-fold or inversion symmetry and can therefore be regarded as being *trans* to one another. The interplanar separations are similar within the type A compounds, even for those with larger guest molecules. The square grids do not align with a unit cell face and adjacent grids are slipped in one direction by *ca.* 20%, *i.e.* every sixth layer repeats.

There is only one type B compound in the group of compounds analysed herein, **2**·3PhOMe. It differs from type A compounds in the orientation of the nitrate ligands and the manner in which adjacent layers stack (Fig. 2b). Nitrate ligands form O···H–C hydrogen bonds with bipy ligands on adjacent layers in such a manner that larger interplanar separations than those observed for type A compounds, *ca.* 7.9 Å, occur. This facilitates incorporation of a third guest molecule. The axial nitrate ligands are oriented on the same side of the metal in a *cis*-type arrangement.

The following compounds crystallize as type C compounds: **1**·2pyrene, **1**·3naphthalene and **2**·3naphthalene. The guest molecules in these compounds are larger or there are more of them. Therefore, they occupy a greater proportion of the relative volume of the crystal lattice than type A compounds (*ca.* 49 *versus* 37% of the occupied volume). It should therefore be unsurprising that the interlayer separation is somewhat larger (8.0 Å) than that of type A compounds. Nevertheless, C–H···O hydrogen bonding between bipy ligands and nitrate ligands of adjacent grids still occurs and the C···O separations, ≈3 Å, are consistent with what would be expected.[17] However, the positioning of the grids is quite different compared with type A and type B compounds (Fig. 2c). This facilitates the inclusion of more (one in the centre of each grid and two other guest molecules between the grids) or larger arene molecules. The arene molecules engage in stacking interactions with the bipy ligands and themselves.

Crystal packing of aromatic molecules

The nature of the packing between aromatic molecules is, in our opinion, a particularly salient feature that helps one better to understand both the composition and the structural nature of the compounds reported herein.

In type A compounds the aromatic guest molecules form planar networks that are sustained by edge-to-face interactions, contain cavities with effective dimensions of *ca.* 3.5 × 6.0 Å and represent *ca.* 37% of the relative volume of the crystal. The shortest intermolecular C···C separations are in the range of 3.661–4.393 Å, close to the values reported for stacking in pure aromatic compounds.[18] The planes of the neighboring mole-

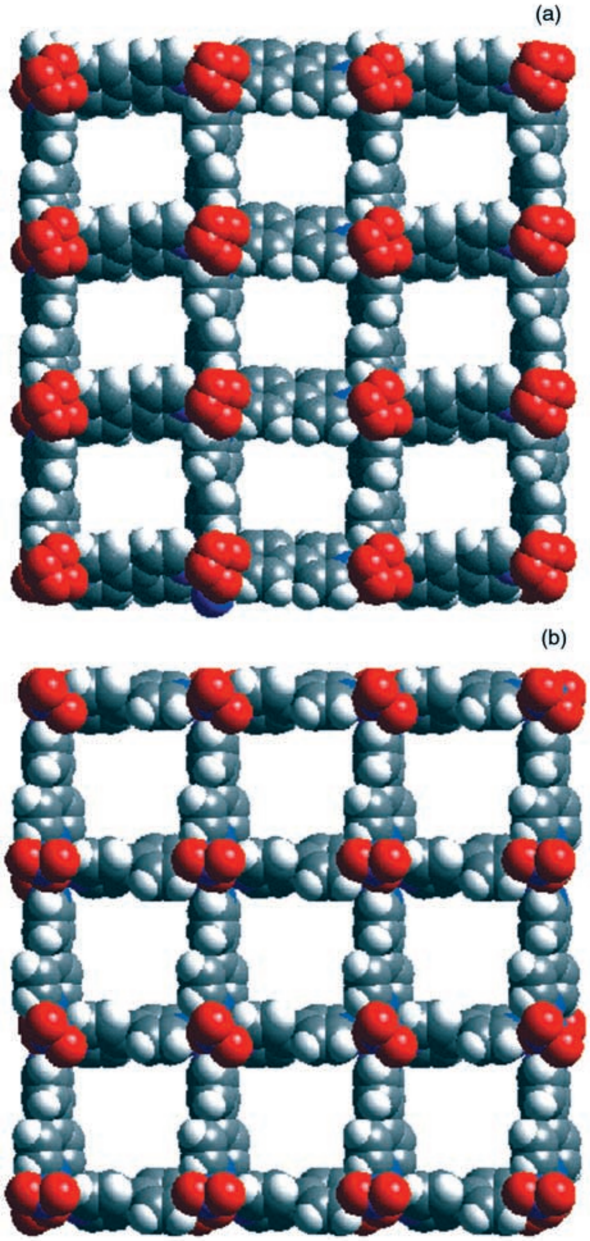


Fig. 1 Overhead views of the square grid (4,4) network, [M(bipy)$_2$(NO$_3$)$_2$]: (a) 50% coplanar/50% twisted bipy (types A and C); (b) 100% twisted bipy (type B).

cules intersect at an angle of *ca.* 77.3–82.3° and there are no face-to-face stacking interactions between the molecules.

As revealed by Fig. 3, it is possible to regard these aromatic networks as (4,4) networks if the node is the point in space at which the vectors of four aromatic planes intersect. Interestingly, in the nine new type A compounds reported herein, both the coordination polymer and aromatic networks appear to be inherently centrosymmetric and, indeed, these binary compounds crystallize in the centrosymmetric space group *C*2/*c*. However, the networks are polar in the previously communicated type A compound, {[Ni(bipy)$_2$(NO$_3$)$_2$]·2pyrene}$_n$. The origin of the polarity rests with the orientation of the pyrene molecules. They lie opposite each other in the *ac* plane, but are not related by inversion and are therefore crystallographically non-equivalent. Indeed they are not even coplanar.

In compound **2**·3PhOMe the anisole molecules form planar networks that are sustained by edge-to-face interactions, contain cavities with effective dimensions of 4.0 × 4.9 Å and occupy *ca.* 45% of the relative volume of the crystal. The shortest intermolecular C···C separations (3.63 Å) are in the range expected for aromatic stacking.[18] The planes of the neighboring molecules intersect at an angle of *ca.* 68° and there are no face-to-face stacking interactions between the molecules. If one were to consider the node as being at the point of the edge-to-face interaction then the anisole network might be regarded as a honeycomb (6,3) planar network (Fig. 4).

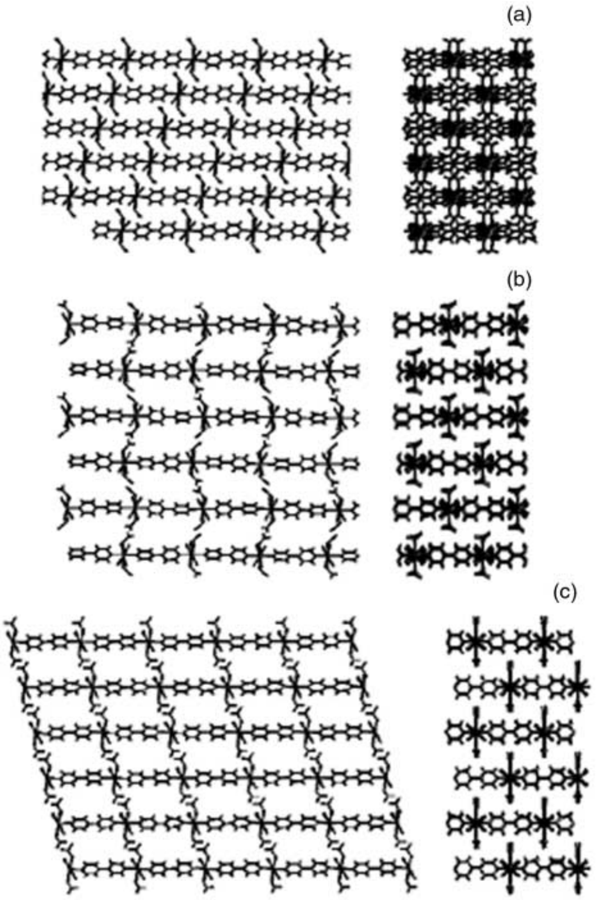


Fig. 2 Perspective views of the stacking of [M(bipy)$_2$(NO$_3$)$_2$]: (a) A type grids; (b) B type grids; (c) C type grids.

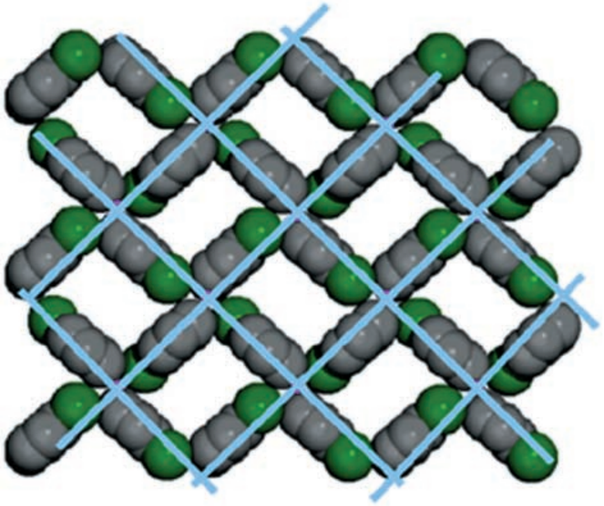


Fig. 3 An illustration of how a square grid overlays onto the square grid (4,4) network of chlorobenzene molecules in compound **2**·2PhCl.

In the type C compounds **1**·3naphthalene and **2**·3naphthalene the topology of the planar networks of naphthalene molecules may also be described as a distorted (6,3) honeycomb network in which the edges of each hexagon are defined by hydrocarbon moieties. The (6,3) network occupies *ca.* 49% of the relative volume of the crystal. Each molecule is in contact with four neighbors, and the description of the naphthalene

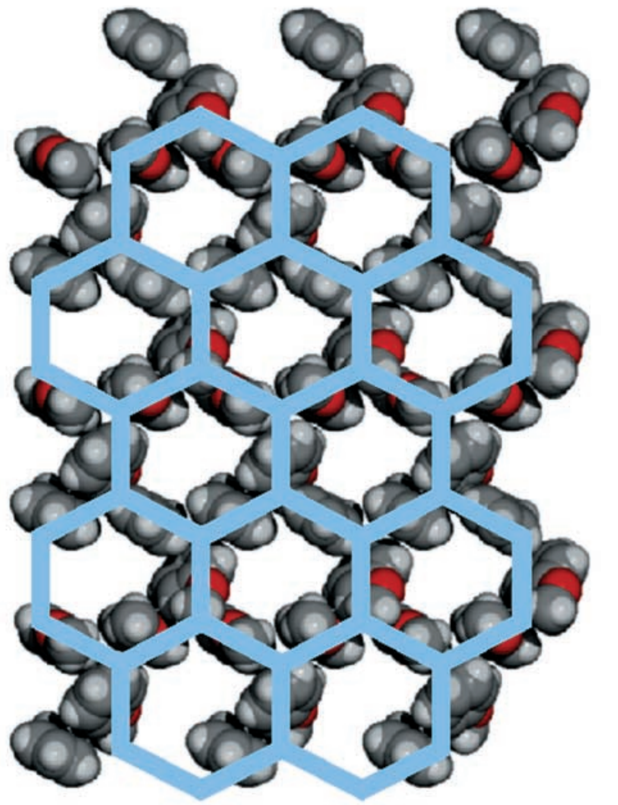


Fig. 4 An illustration of how a honeycomb network overlays onto the honeycomb (6,3) network of anisole molecules in compound **2**·3PhOMe.

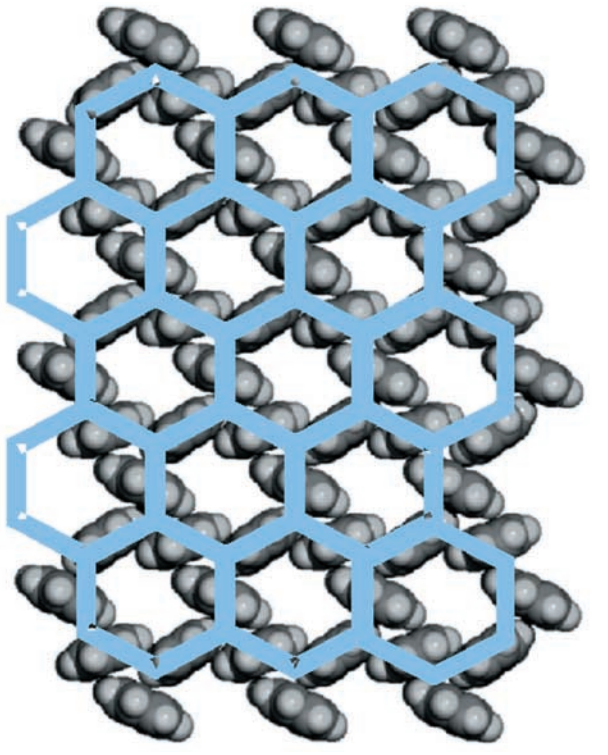


Fig. 5 An illustration of how a honeycomb network overlays onto the honeycomb (6,3) network of naphthalene molecules in compound **2**·3naphthalene.

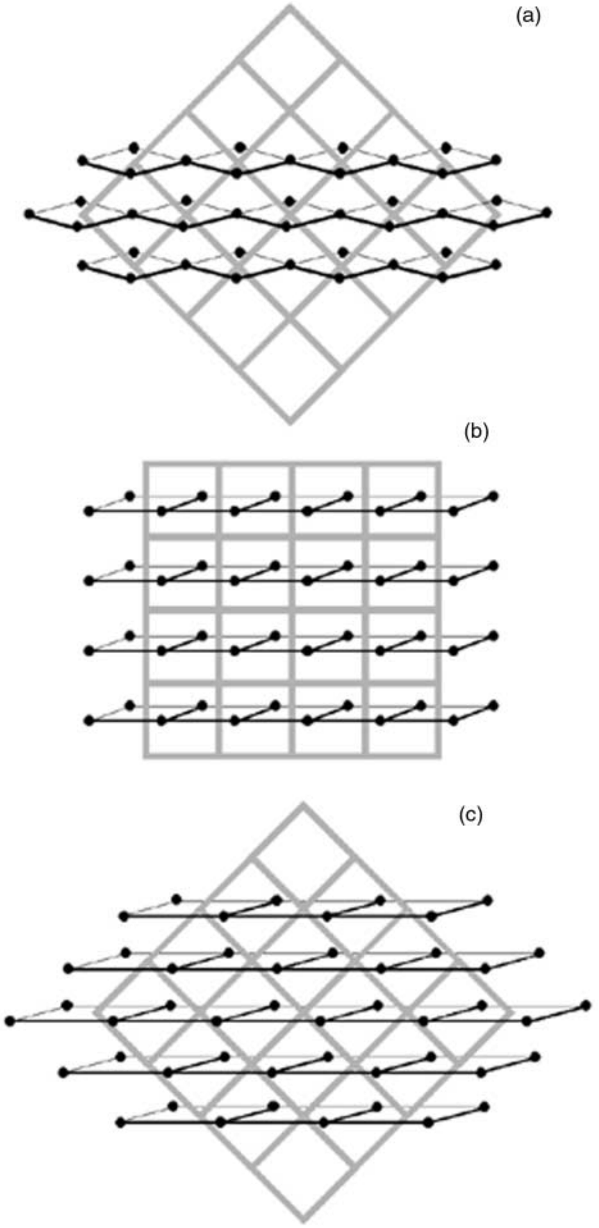
array as a (6,3) network is based upon the assumption that the node of the network is the centre of gravity of three neighboring molecules (Fig. 5). The closest C · · · C contacts between the hydrocarbon molecules are in the range 3.416–3.820 Å and are consistent with edge-to-face interactions, being comparable with those seen in pure aromatic compounds.[18]

Interpenetration of networks

As noted earlier in this contribution, both (4,4) and (6,3) networks are complementary from a topological sense with (4,4) square grid coordination polymer network. In coordination polymers in which (4,4) networks that are planar and identically interpenetrate two types of interpenetration have thus far been observed, both of which are examples of *inclined interpenetration*.[8] The most commonly encountered form might be described as *diagonal/diagonal inclined interpenetration* and was observed in the prototypal $[M(bipy)_2X_2]_n$ compound, $[Zn(bipy)_2(H_2O)_2]SiF_6$.[3a] The other mode might be described as *parallel/parallel inclined interpenetration* and to our knowledge has only been reported for two compounds.[3c,d] These types of interpenetration are illustrated in Schemes 3(a) and 3(b), respectively, and differ in how the networks orient and cut through each other. *Parallel* refers to the structure in which a "spacer" ligand from one network threads through the cavity of the other, *diagonal* to the structure in which a "node" from one network (*e.g.* the metal moiety) is within the cavity of the other. One would anticipate that the structure that is adopted by a particular compound would be influenced by several geometric factors: the relative size of the cavity; the distance between adjacent nodes within a network; the thickness of the layers and how this limits the interlayer separation of adjacent networks and the steric bulk of the node. In this context, it is important to note that, with all other things equal, the diagonal/diagonal mode of interpenetration facilitates an interlayer separation that is 41.4% greater than that of the parallel/parallel mode. Furthermore, the diagonal/diagonal mode ensures a staggered orientation of parallel layers whereas an eclipsed orientation is necessary if the parallel/parallel structure is present. Therefore, in terms of steric considerations, the diagonal/diagonal mode would appear to be most likely to be favored. However, circumstances where the interlayer separation would ideally be shorter, or where the metal atoms in adjacent layers would be eclipsed (*e.g.* to maximize interlayer interactions), could favor the parallel/parallel mode.

The ten structures reported herein that are based upon complementary (4,4) networks exhibit a new mode of inclined interpenetration that is a hybrid of the modes described above: *parallel/diagonal inclined interpenetration*. The non-covalent (4,4) arene networks exhibit parallel inclined interpenetration with respect to the (4,4) metal–organic coordination networks, whereas the covalent coordination networks demonstrate diagonal inclined interpenetration with respect to the arene networks (Scheme 3c). This salient structural feature means that the nitrate groups of adjacent parallel coordination polymer grids are staggered (Figs. 2a, 2b and 2c) and that the interlayer separation is a consequence of the size of the arene network. It should therefore be unsurprising that type A grids result when templated by the smallest arenes (benzene and derivatives) as they exhibit smaller interlayer separations than type B and C packing. Grid types B and C occur in the presence of larger or more arenes. Although the interlayer separations are similar (7.5–8.0 Å), the salient difference between type B and C packing is the angle at which the two types of network interpenetrate. It seems likely that this hybrid mode of interpenetration is an artifact of the chemical and structural differences of the two (4,4) networks and is less likely to occur when identical networks interpenetrate. For the case of (4,4) and (6,3) inclined interpenetration, there are two likely variants: the (6,3) network is parallel or diagonal to the (4,4) network. The former is observed in the compounds reported herein and it results in the same orientation of adjacent (4,4) networks as in the diagonal/diagonal mode of interpenetration observed for two (4,4) networks.

In type B structures, the arene networks interpenetrate at an angle of 90°, whereas for type C grids the arene network interpenetrates at an oblique angle. The orientation of the



Scheme 3 A representation of the modes of inclined interpenetration by complementary (4,4) networks: (a) diagonal/diagonal, (b) parallel/parallel, and (c) parallel/diagonal.

axial nitrate ligands appears to be affected by the angle of interpenetration. A compound in which (6,3) and (4,4) coordination polymers interpenetrate was recently reported[3d] but it is not directly relevant to our study because the cavity sizes are mismatched and two (4,4) networks are needed to fill the cavity in the (6,3) network. Such a structure is perhaps best described as a triply interpenetrated parallel/parallel/diagonal structure.

Given that cavity size within the aromatic networks is complementary with the width and height of a single aromatic ring, the self-assembly of aromatic molecules in the compounds reported herein is readily sustained by edge-to-face and face-to-face interactions with the hydrocarbon portion of the bipy moieties. These interactions are presumably a primary driving force for the clathration of the guests and a mitigating factor against interpenetration. Indeed, it is interesting that none of the compounds reported herein displays interpenetration of coordination polymer networks and that stacking interactions are seen in all compounds. It is also relevant that only three packing modes are observed in 13 compounds of similar composition. However, a question that cannot be answered from this study concerns whether or not the non-covalent networks of aromatic molecules can exist in the absence of the coordination polymers. In this context, the 1 : 1 binary compound between ferrocene and pyrene[11] represents an important prototype since pairs of ferrocene molecules are stacked inside a pyrene 2-D network that is sustained by non-covalent C–H···π interactions.

In summary, we believe that interpretation of the crystal structures of $\{[M(bipy)_2(NO_3)_2]\cdot arene\}_n$ as interpenetrating covalent and non-covalent networks is potentially important in the context of understanding the structure and stoichiometry of host–guest compounds that are based upon square grid coordination polymers. In particular, it seems that complementary topology plays an important role in influencing several parameters, including stoichiometry and overall crystal packing. Furthermore, when coupled with a study on the structure of the cocrystals formed between ferrocene and pyrene, it seems that certain non-covalent networks can exist in the absence of covalent networks. We therefore now appear to be in position rationally to generate 3-D architectures from planar networks of very different composition and use this information to use the concepts of topology to design binary compounds that are sustained by a diverse range of molecular components. Further studies will explore a wider range of square grid coordination polymers by expanding the selection of metal ions, anions and ligands in $[M(bipy)_2(X)_2]_2$. In this context, it should be noted that inclusion compounds of general formula $[M(py)_4(NO_3)_2]$ have been studied for a wide range of transition metals,[19] and that anions can also cross-link metal centers in order to form planar networks.[20]

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