2D and 1D Coordination Polymers with the Ability for Inclusion of Guest Molecules: Nitrobenzene, Benzene, Alkoxysilanes *

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Abstract

The complexation reactions of the electron rich, linear and bi-functional ligand, 9,10-bis(4-pyridyl)anthracene, with metal salts $Cd(NO_3)_2$, CdI_2, CoI_2 and CuI in the presence of guest molecules nitrobenzene, benzene and alkoxysilanes were studied. The single crystal analyses of the complexes reveal that an electron deficient guest molecule such as nitrobenzene consistently templated the open two-dimensional network with grid dimensions of *ca.* 15×15 Å. On the other hand the presence of benzene or alkoxysilane templated 1D-zigzag chains and/or 2D-grid layers. The crystal structures reveal the importance of host–guest interactions in tailoring the network architectures of coordination polymers.

Introduction

The field of crystal engineering enables us to create new materials with desired functional properties such as microporosity, molecular magnetism and nonlinear optical activity [1]. Currently coordination polymers occupy the major share in crystal engineering studies due to the stability and predictable formation of coordination bonds and also due to the veracity of coordination modes of transition metal atoms [2–13]. Using coordination bonds several open-framework materials with reasonably high empty space and stability even after removal of guest molecules were reported recently. Such network materials are expected to show interesting properties similar to zeolite-like and clay-like materials [2]. The utilization of the linear and bidentate ligand, 4,4′-bipyridine, and transition metal ions has thus far produced several novel networks with a high degree of porosity [3–11]. The topology of the networks formed in these systems were shown to depend on several factors such as the coordination geometry and oxidation state of the metal, the metal-to-ligand ratio and the 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 interest due to their predictable pore sizes and selective inclusion of guest molecules. We have shown recently that the ligand 9,10-bis(4pyridyl)anthracene **1** upon reaction with $Ni(NO_3)_2$ or $Cu(NO_3)_2$ can form 2D-layers containing square grids of dimension 15×15 Å and also 1D coordination polymers depending on the guest molecules

included [12, 13]. Interestingly, ligand **1** with $Ni(NO_3)_2$ or $Cu(NO_3)_2$ formed a non-interpenetrated square grid network only in the presence of an electron deficient guest molecules such as nitrobenzene or cyanobenzene. The formation of these non-interpenetrated 2D-layers was attributed to the strong host–guest interactions between the electron-rich anthracene moiety of ligand **1** and the electron deficient guest molecules. To verify further the role or robustness of host–guest interactions in the formation of the 15×15 Å square grid network we studied the reactions of ligand **1** with $Cd(NO_3)_2$, CdI_2, CoI_2 or CuI in the presence of nitrobenzene. The results indicate the consistent formation of non-interpenetrated two-dimensional networks probably due to the well optimised of host(donor)–guest(acceptor) interactions. We also present the inclusion of benzene and reactive alkoxysilanes in the coordination polymers formed by reaction of **1** with CdI_2.

Results and discussion

The reaction of **1** with $Cd(NO_3)_2$ in the presence of nitrobenzene is expected to form a structure similar to that of $Ni(NO_3)_2$ or $Cu(NO_3)_2$. As anticipated the reaction resulted in the complex $Cd(NO_3)_2$ **(1)**$_2$·2(nitrobenzene) **2** that contains open square grid network structure. On the other hand the reactions of **1** with CdI_2 and CoI_2 are difficult to predict as the MI_2 units are known to coordinate to the ligands in three bonding modes as shown in Scheme 1. However, in this particular case CdI_2 or CoI_2 is expected to bind in mode **I** to form a square grid network due to the donor–acceptor interactions between ligand and guest molecules. Indeed both CdI_2 and CoI_2 upon reaction with **1** in the presence of nitrobenzene formed complexes CdI_2**(1)**$_2$·2(nitrobenzene) **3**

I   **II**   **III**   **IV**
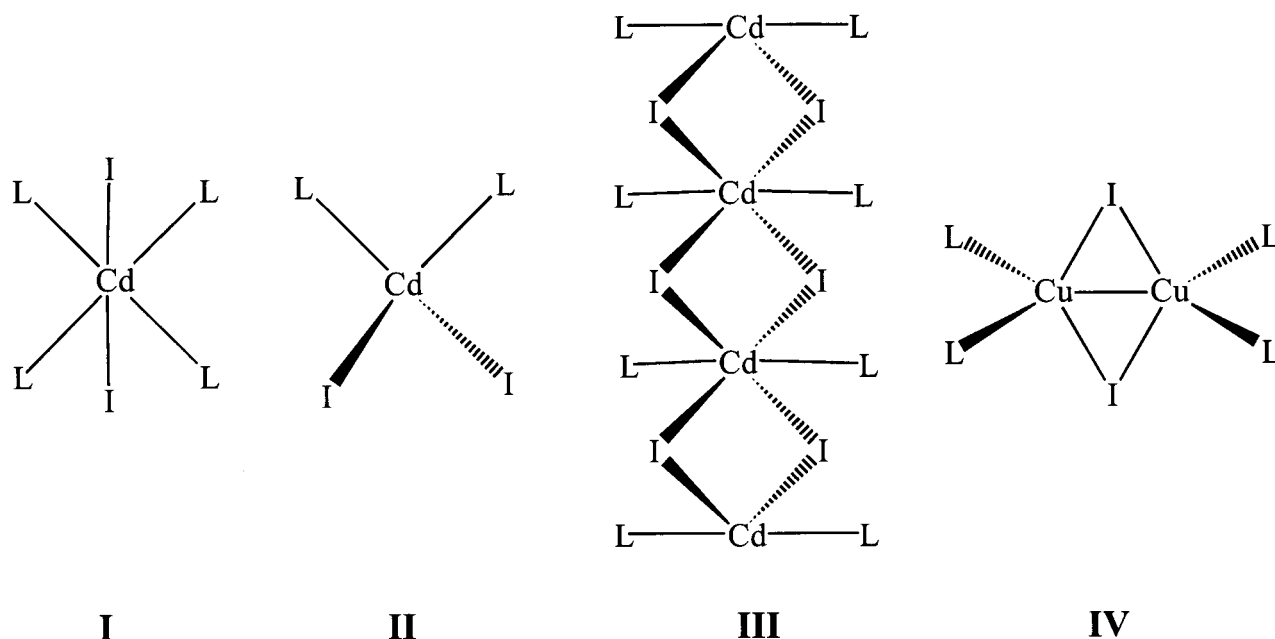
Scheme 1.

and $CoI_2(1)_2 \cdot 2$(nitrobenzene) **4** which have open square grid networks. The CuI is also anticipated to form an open square grid network with **1** in the presence of nitrobenzene by forming the self-dimer unit Cu_2I_2, **IV**. This reaction resulted in the crystals of a complex $Cu_2I_2(1)_2 \cdot 2$(nitrobenzene) **5** that also contains an open square grid network which is formed by the self assembly of Cu_2I_2 unit with ligand **1**.

We have shown previously that in the presence of a guest molecule like benzene ligand **1** forms a doubly interpenetrated square grid network with $Ni(NO_3)_2$ and two types of 1D-coordination polymers, zigzag chain without guest inclusion and linear chain with benzene inclusion, with $Cu(NO_3)_2$. Hence we tried the same reaction but with CdI_2 to see what type of structure would form. Interestingly the reaction resulted in only one 1D-coordination polymer $CdI_2(1) \cdot$benzene **6** with a zig-zag geometry that includes benzene molecules. Out of curiosity we tried the same reaction by replacing **1** with 4,4′-bipyridine. This reaction resulted in the complex $CdI_2(4,4′$-bipyridine) **7** in which the CdI_2 coordinates to the 4,4′-bipyridine in bonding mode **III** to form a two dimensional layer without inclusion of benzene.

The reactive alkoxysilanes such as $PhSi(OMe)_3$ and tetraethyl orthosillicate are considered as guest molecules knowing their potentiality to form silicon clusters in a ship in a bottle fashion [14]. Our strategy here is to react the encapsulated sililylalkoxy compounds with each other in the cavities of coordination polymers by treating the resulting crystals with water. Accordingly we reacted CdI_2 with **1** in the presence of $PhSi(OMe)_3$ or tetraethyl orthosilicate. The reaction in the presence of $PhSi(OMe)_3$ resulted in two complexes $CdI_2(1 \cdot PhSi(OMe)_3$ **8** and $CdI_2(1)_2 \cdot 2(PhSi(OMe)_3)$ **9** in same reaction flask whereas in the presence of tetraethyl orthosilicate resulted in $CdI_2(1) \cdot EtOH$, **10**. The pertinent crystallographic details of the crystal structures **2–10** are
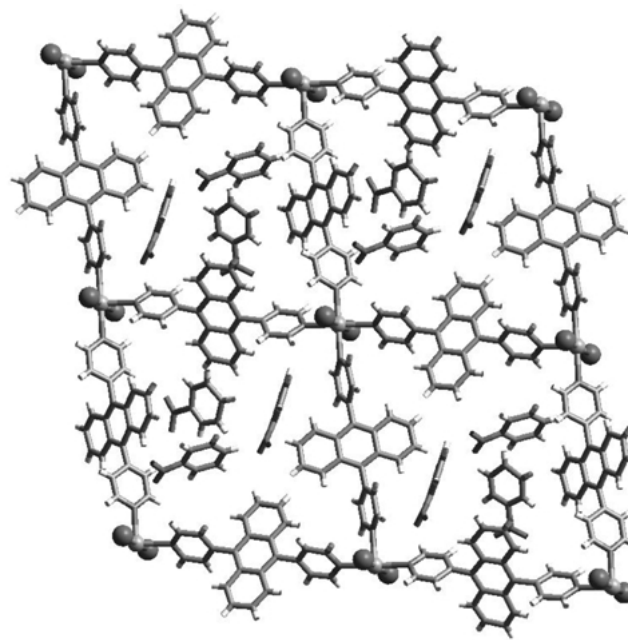

Figure 1. Representation of the square grid network exhibited by complex **3** (I = ball mode). Please note that the nitrobenzene molecule, disorder not shown, that is perpendicular to the plane of the grid is sandwiched between two anthracene moieties.

given in Table 1 and in the following sections the crystal structures will be described starting from **2** to **10**.

*Reactions of **1** with $Cd(NO_3)_2$, CoI_2 and CuI in the presence of nitrobenzene*

The crystal structures of complexes **2–4** are iso-structural in all aspects to those of the $Ni(NO_3)_2$ and $Cu(NO_3)_2$ square grid complexes of ligand **1**. In **2** the O-atoms of nitrate ions coordinate to apical positions of Cd-atoms (Cd—O: 2.348(6) Å) while the equatorial positions are occupied by

Table 1. Crystallographic parameters for complexes **2–10**

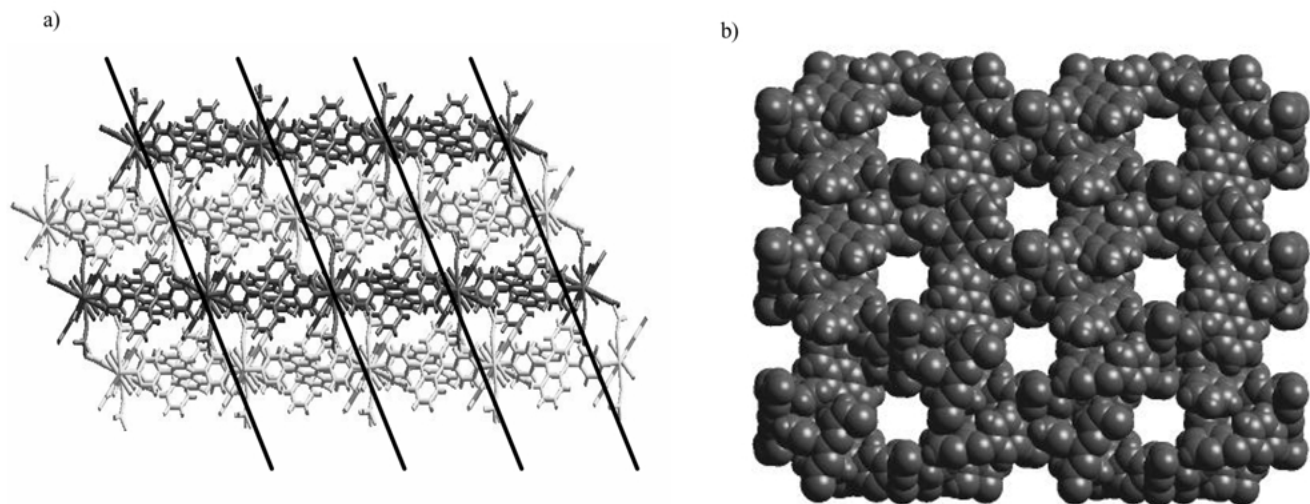|	2	3	4	5	6	7	8	9	10
Formula	$C_{50}H_{42}CdN_9O_{10}$	$C_{60}H_{42}CdI_2N_6O_4$	$C_{60}H_{42}CoI_2N_6O_4$	$C_{60}H_{42}Cu_2I_2N_6O_4$	$C_{30}H_{22}CdI_2N_2$	$C_{10}H_8CdI_2N_2$	$C_{33}H_{30}CdI_2N_2O_3Si$	$C_{66}H_{60}CdI_2N_4O_6Si_2$	$C_{24}H_{21}CdI_2N_2O$
Mol. Weight	1149.42	1277.20	1223.73	1291.88	776.70	522.38	896.8	1427.56	719.63
Temperature (K)	193 K	193 K	193 K	153 K	193 K	193 K	193 K	193 K	193 K
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	Cmcm	cmmm	Pbca	P-1	C2/c
a (Å)	13.696(1)	13.319(1)	13.323(2)	18.052(3)	9.820(1)	11.850(4)	12.543(5)	7.8702(6)	16.428(1)
b (Å)	25.900(3)	25.745(2)	24.943(4)	22.782(3)	12.618(1)	13.169(5)	21.774(10)	14.112(1)	7.0865(6)
c (Å)	14.951(2)	15.618(1)	15.615(3)	7.461(1)	21.990(2)	4.166(2)	24.837(8)	14.475(1)	23.269(2
α (°)	90	90	90	90	90	90	90	70.411(1)	90
β (°)	99.088(2)	96.499(2)	97.474(3)	102.507(3)	90	90	90	87.319(1)	105.632(2)
γ (°)	90	90	90	90	90	90	90	87.946(1)	90
V (Å³)	5236.7(10)	5320.9(8)	5144.9(15)	2995.5(8)	2724.7(5)	650.1(4)	6783(4)	1512.5(2)	2608(4)
Z	4	4	4	2	4	2	8	1	4
μ (mm⁻¹)	0.488	1.624	1.589	1.788	3.088	6.399	2.534	1.476	3.220
Measd reflns	16649	16851	15229	9663	8561	2064	15608	9833	8077
Unique reflns	6117	6206	5986	3572	1748	470	5814	6796	3060
	R(int) = 0.0710	R(int) = 0.0309	R(int) = 0.0262	R(int) = 0.1044	R(int) = 0.1680	R(int) = 0.4455	R(int) = 0.0118	R(int) = 0.0292	
R_1 ($I > 2\sigma(I)$)	0.559	0.0292	0.0326	0.0628	0.0457	0.0368	0.0760	0.0241	0.0301
wR2 (on F^2, all data)	0.1706	0.0733	0.0908	0.2332	0.0862	0.1026	0.2103	0.0783	0.0997

Figure 2. Packing of the grids exhibited by complex **2**. (a) side view, the line drawings show the direction of the channels. (b) Top view of packing in a space filling representation. Notice the uniform and continuous channels. Nitrobenzene molecules are not shown.

the N-atom of the ligand (Cd—N: 2.324(3), 2.317(4) Å). In **3** and **4** the I-atoms occupied the apical positions of Cd or Co-atoms (Cd—I: 2.9783(3); Co—I: 2.9377(4) Å) while the equatorial positions are occupied by ligand N-atoms (Cd—N: 2.361(2), 2.378(2) and Co—N: 2.155(2), 2.168(2) Å). The grid dimensions are 15.97×15.92, 16.06×16.15 and 15.69×15.76 Å in **2–4** respectively (Figure 1). The small differences in the dimensions of the grids are reflective of the differences in their M—N bond lengths. The diagonal-to-diagonal distances are 25.90×18.61, 25.75×19.34 and 24.94×19.16 Å in **2–4** respectively. These distances indicate that the grids are not exactly squaric but are of rhomboid-shape. The distortion from the squaric nature is due to the strong donor–acceptor interaction between the anthracene moiety and nitrobenzene at one of the corners of the grid: the distances between the C-atoms of the C_6-ring of the outer anthracene moiety and nitrobenzene are 3.3 to 4 Å. The cavities of the grid are occupied by three nitrobenzene molecules: one of them fully immersed in the grids, while the other two exist at the portals of the grids, only half of these molecules are within the grid. Interestingly the grids in all structures superimpose on each other in a slightly slipped manner on both edges (interlayer separation is *ca.* 5.4 Å) such that there are continuous channels of a dimension which is slightly less than the dimension of the grid (Figure 2). It is worth noting here that the anions have almost no role in the packing of the layers as they face into the channels that are formed across the layers. The square grid networks in **2–4** have guest available and accessible volumes of *ca.* 45% and 15%, respectively, of their crystal volume. A column of disordered nitrobenzene molecules occupied the channels that are formed across the packing of the grid layers.

Complex **5** also contains an open square grid network as expected proving the point further that the robustness of host–guest interactions can lead to the predictable formation of network structures. Here it is interesting to note that M^{1+} is serving the purpose of M^{2+} by forming the dimer to act
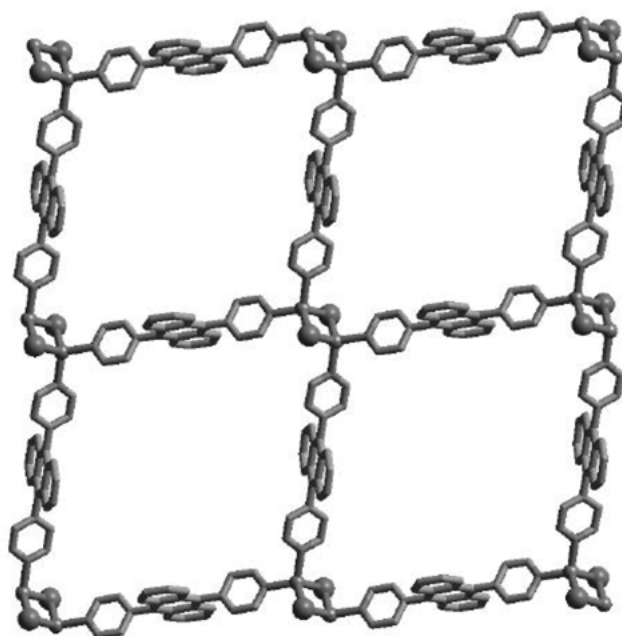

Figure 3. Representation of the square grid network exhibited by complex **5**. Note that Cu_2I_2 and anthracene moieties are perpendicular to the plane of the grids (I = ball mode).

as a four-connected node. This four-connected node can be regarded as a secondary building unit in the construction of coordination nets. We have previously reported its role in assembling 3,3′-5′,3‴-5″,3‴-quarterpyridine to form 2D and 3D-coordination polytubes [15]. In **5** each Cu_2I_2 unit coordinates to four ligands (Cu—N: 2.062(5) and Cu—I: 2.6408(8) Å) such that the Cu_2I_2 plane is perpendicular to the plane of the grids layer (Figure 3). This type of arrangement forced the planes of the pyridine and anthracene moieties to lie parallel and perpendicular, respectively, to the plane of the grids layer. Indeed in **5** the grid has six edges as four are formed by the ligand (15.60×15.61 Å) and two are formed by the Cu—Cu bond (2.772(2) Å). However, it can be regarded as a square grid complex due to the negligible
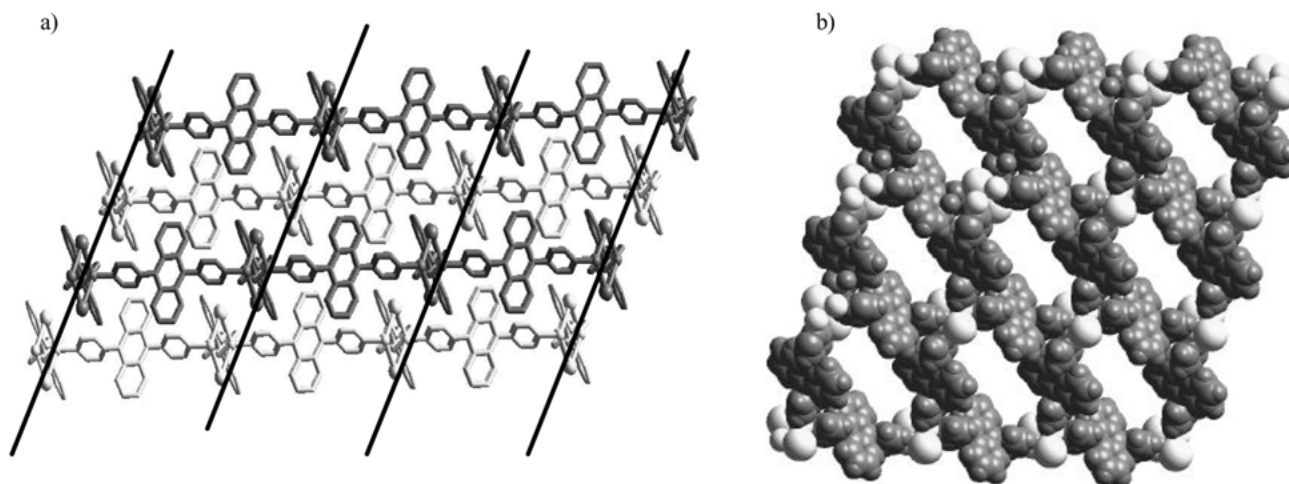
Figure 4. Packing of grids exhibited by complex **5**. (a) side view, the line drawings show the direction of the channels. (b) Top view of packing in a space filling representation. Nitrobenzene molecules are not shown. Compare with Figure 2.
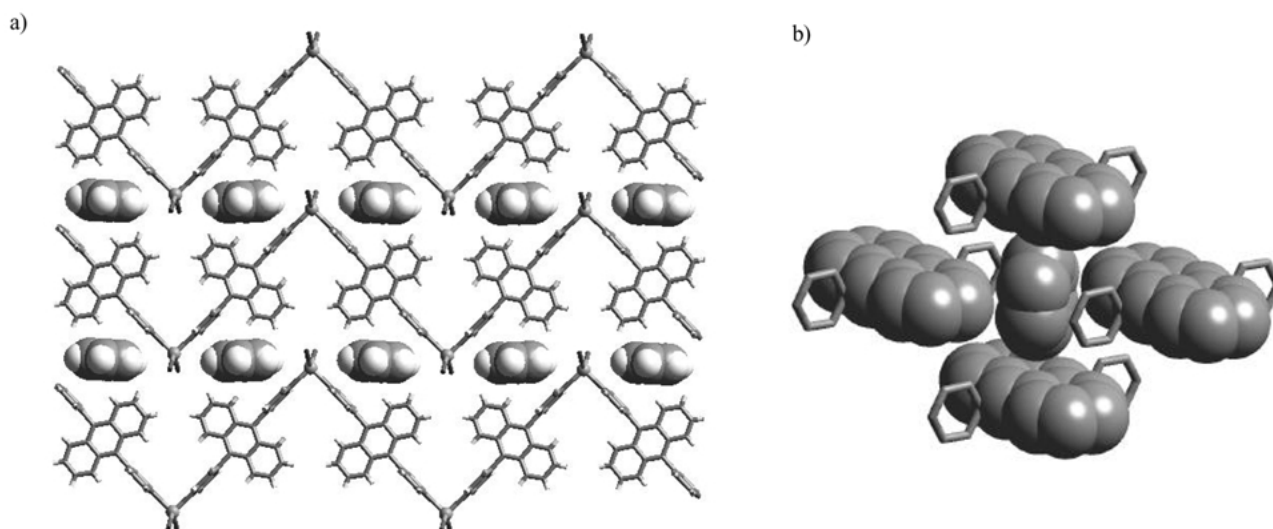

Figure 5. Illustrations of the crystal structure of complex **6**. (a) 2D-layer formed by zigzag chains and benzene molecules; (b) sandwiching of a benzene molecule by four moieties of **1**.

distance of the Cu—Cu bond when compared to 15.60 Å and the grids have a diagonal-to-diagonal distance of 20 × 26 Å. The packing of the grid layers is almost similar to that of the grid layers in **2–4** (Figure 4). However, in **5** the channels are rectangular while they are squaric in **2–4**. Further the nitrobenzene molecules have heavy disorder which is unresolved. Nevertheless the network has guest available and accessible volumes of 53% and 26%, respectively, of its crystal volume.

*Reactions of **1** with CdI$_2$ in the presence of benzene*

The crystal structure of complex **6** reveals the formation of a 1D-zigzag chain as CdI$_2$ adopts the coordination bonding mode **II**. Benzene molecules are included between the chains such that it leads to the formation of a 2D-layer in which the benzene molecules connect the chains through aromatic edge-face interactions (Figure 5). In fact the benzene molecules are sandwiched between four moieties of **1** as shown in Figure 5b. For example the closest distances

between the centers and edges of the anthracene moiety and benzene are 3.5 and 3.7 Å. Here it is interesting to note that benzene is not included in the zigzag chain polymer structure of ligand **1** [12] and Cu(NO$_3$)$_2$ (Figure 6). In that particular structure there is no room to include benzene as the chains are held together via C—H$\cdots$O hydrogen bonding between NO$_3$ ions and aromatic CH groups.

We studied a similar reaction with 4,4′bipyridine to differentiate from the above structure. However it resulted in a completely different crystal structure, **7**, without inclusion of benzene molecules. In **7** the CdI$_2$ adopts the bonding mode **III** to form a two dimensional layer in which the linear chains of **III** are interconnected by 4,4′-bipyridine (Figure 7). Here it is noteworthy that the pyrazine also forms a similar type of layer structure [16]. In **7** the 2D-layers contain rectangular grids of dimension 4.17 × 11.85 Å. These layers pack on each other with an interlayer separation of 6.5 Å.
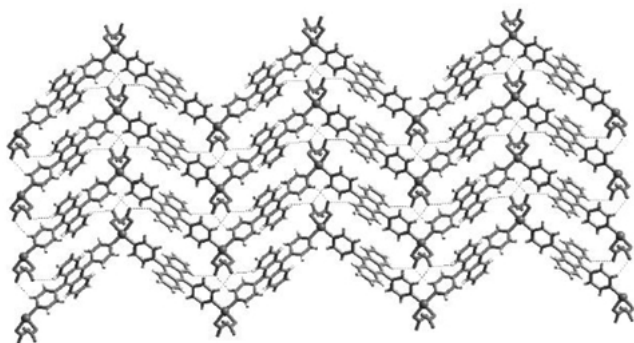
Figure 6. Representation of 2D-layer formed by **1** and Cu(NO$_3$)$_2$. Dotted lines represent C—H· · ·O hydrogen bonds.
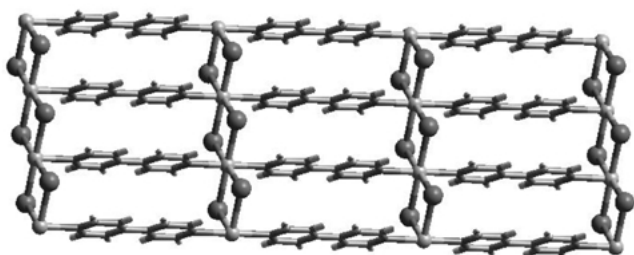

Figure 7. Representation of the 2D-layer formed via bonding mode **III** in the complex **7**.

Reactions of **1** with CdI$_2$ in the presence of alkoxysilanes

The reactions of **1** with CdI$_2$ in the presence of PhSi(OMe)$_3$ resulted first in single crystals of complex **8** in one day. Keeping the reaction for a further two more days without disturbing resulted in single crystals of complex **9** as the major product. The crystal structure of complex **8** reveals the formation of a zigzag linear chain that is similar to the structure of **6** (Figure 8). The PhSi(OMe)$_3$ molecules connect the 1D-chains via aromatic interactions such that it leads to the formation of the 2D-layer as shown in Figure 8a. However unlike in **8**, the guest molecules are not sandwiched by four moieties of **1** but by only three moieties as the C6-moiety of a guest has a Si(OMe)$_3$ substitution (Figure 8b). Due to this substitution the layers have an interesting packing arrangement in which the connection between the layers alternately contain either aromatic interactions or methyl-methyl interactions (Figure 9).

The anticipated 2D-grid layer formation was observed in the crystal structure of complex **9**. The grids in **9** are almost squaric, different from **2–4**, with dimensions of 16.15 × 16.40 Å and a diagonal-to-diagonal distance of 23.36 × 22.68 Å (Figure 10). Unlike the nitrobenzene molecules here the guest molecules are not sandwiched between the two anthracene moieties in the corner. Due to this reason the grids became more squaric in **9** than they are in **2–4**. Here it is interesting to note that a similar square nature of the grids was observed in the interpenetrated 2D-grids layers of **1** and Ni(NO$_3$)$_2$ [12]. In fact in **9** there are four guest molecules in each grid cavity but only half of each molecule actually lies in the cavity. The packing of the grid layers is almost similar to that of the grid layers in **2–4** (interlayer separation 5.7 Å). The PhSi(OMe)$_3$ molecules form columns that are fitted into

the channels which are formed across the packing of the layers (Figure 10b). Further **9** has slightly larger guest available and accessible volumes of 51% and 22% respectively (45% and 15% in **2–4**).

The crystal structure of complex **10**, which was prepared in the presence of tetraethyl orthosilicate, reveals the formation of a 1D-zigzag chain with just inclusion of EtOH but not the intended orthosilicate (Figure 11). We tried the similar reaction by considering Ni(NO$_3$)$_2$ and 4,4′-bipyridine. Interestingly this reaction resulted in bilayer structure of 4,4′-bipyridine with inclusion of EtOH but no inclusion of tetraethyl orthosilicate. A similar bilayer structure was reported with Co(NO$_3$)$_2$ and 4,4′-bipyridine by Kitagawa *et al.* [17]. This reaction indicates that aromatic substitution on alkoxysilanes is important to include them in these coordination polymers.

Treatment of crystals of **8** and **9** with H$_2$O

The crystals of **8** and **9** were heated at 100 °C in water for one day. Single crystal diffraction analyses of the crystals after heating in water revealed no change either in the network structure or in the guest molecules. The guest molecules neither reacted nor came out of the crystal indicating their stability in the cavities of the network. The observed non reaction between the alkoxysilanes could be due to the larger separation of the Si and O-atoms of the adjacent molecules in the crystals. For example the closest distance between the Si and O-atoms in **8** and **9** are 6.8 and 5.9 Å respectively.

Conclusion

The consistent formation of an open square grid coordination polymer in **2–5** by ligand **1** with various metal atoms in the presence of nitrobenzene indicates the importance of host-guest interactions in templating coordination polymeric networks. The guest molecule benzene showed inconsistency in templating the networks of **1** with various metal salts: with Ni(NO$_3$)$_2$ it formed a doubly interpenetrated grid layer, with Cu(NO$_3$)$_2$ it formed two types of 1D-chains [12] and with CdI$_2$ it formed only one type of 1D-chain. The crystal structures of complexes **8** and **9** reveal that the networks of **1** are capable of encapsulating alkoxysilanes. Further CdI$_2$ was shown to exhibit all three coordination bonding modes that were presented in Scheme 1.

Experimental

Synthesis of ligand **1**

Ligand **1** was prepared by Suzuki coupling of 9,10-dibromoanthracene with 4-pyridylboronic acid pinacol ester which was synthesized from 4-bromopyridine [18]. Compound **1** has good solubility in common organic solvents such as benzene, nitrobenzene, cyanobenzene, and CHCl$_3$.
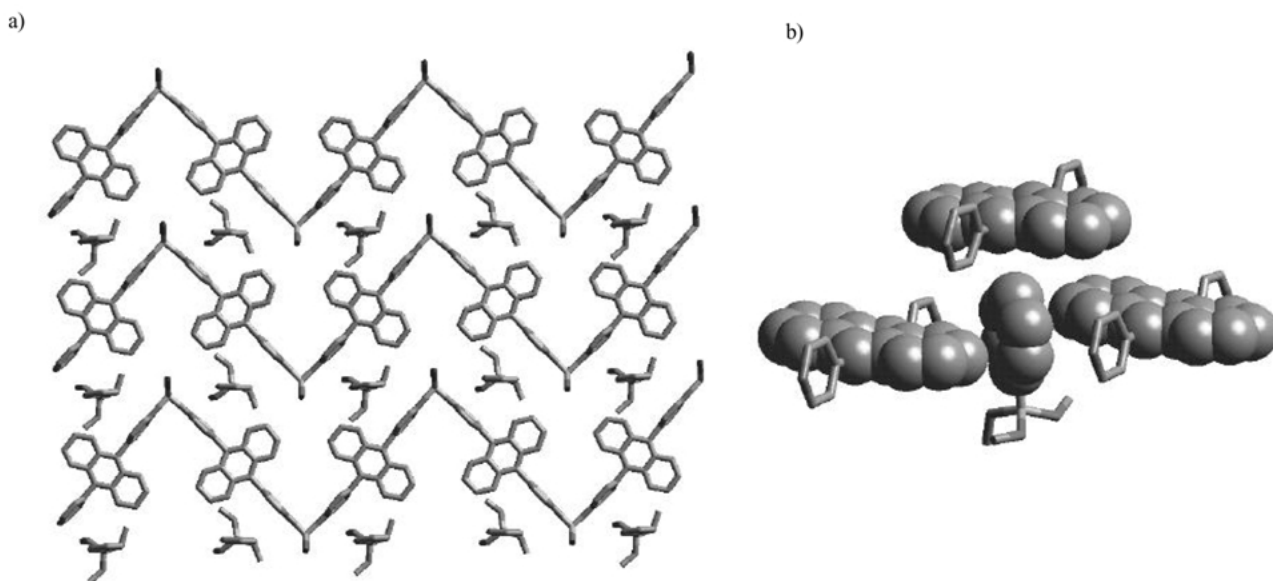
Figure 8. (a) The 2D-layer of 1D-zigzag chains and PhSi(OMe)$_3$ in the crystal structure of **8**; (b) sandwiching of Ph(Si(OMe)$_3$ between three moieties of **1**.

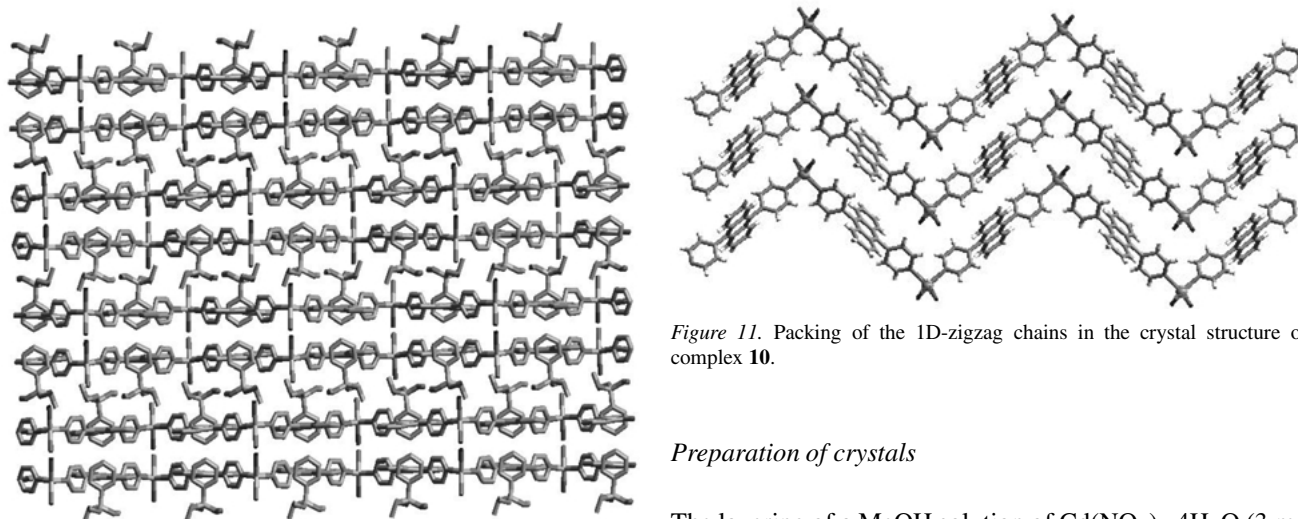*Figure 9.* Side view of the packing of the 2D-layers exhibited by **8**.

Figure 10. Illustrations of the crystal structure of complex **9**. (a) 2D-grid layer; (b) column of PhSi(OMe)$_3$ molecules.

Figure 11. Packing of the 1D-zigzag chains in the crystal structure of complex **10**.

Preparation of crystals

The layering of a MeOH solution of Cd(NO$_3$)$_2$·4H$_2$O (3 mg in 2 mL) onto the nitrobenzene solution of **1** (6.6 mg in 4 mL) resulted in single crystals of complex **2** in 64% yield after the solution was allowed to stand for 2 d. Similarly, the layering of the MeOH solution of CdI$_2$ or CoI$_2$ (3.7 mg of CdI$_2$ or 3.1 mg of CoI$_2$ in 2 mL) over the nitrobenzene solution of **1** (6.6 mg in 3 mL) resulted in single crystals of **3** and **4** in 58% and 37% yield in 4 d respectively. The crystals of complexes **5** were prepared by layering a CH$_3$CN solution of CuI (3.8 mg in 2 mL) over the nitrobenzene solution of **1** (6.6 mg in 4 mL). Crystals of complexes **6** and **7** were prepared similar to the crystals of complex **3** but by taking benzene instead of nitrobenzene and for **7**, 4,4′-bipyridine was used instead of ligand **1**. Crystals of complexes **8** and **9** formed in the same reaction flask when the MeOH solution of CdI$_2$ (3.7 mg in 2 mL) was layered onto the PhSi(OMe)$_3$ solution of ligand **1** (6.6 mg in 4 mL). Very tiny crystals of complex **8** were obtained in a day in 10% yield. Allowing the reaction to stand for four more days resulted in single crystals of complex **9** in 52% yield. Single crystals of complex **10** in 66% yield were prepared similar to the above but
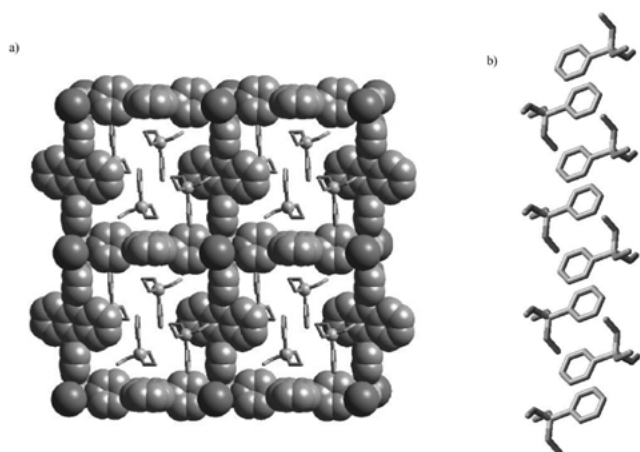
by using tetraethyl orthosilicate instead of PhSi(OMe)$_3$ and EtOH instead of MeOH.

X-Ray 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. Diffracted data were corrected for absorption using the SADABS [19] program. SHELXTL [20] was used for the structure solution and refinement was 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 Ueq (C)]. The H-atoms of nitrobenzene molecules **2–4** were not included in the calculations as these molecules are in disorder which was modeled in three different ways (**A**, **B** and **C**).
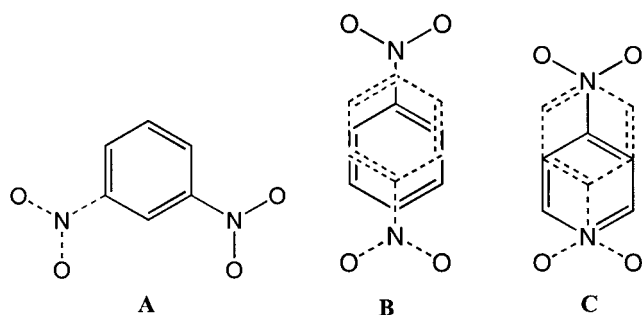
In **5** the nitrobenzene molecules are disordered heavily in an unresolvable manner and only some peaks corresponding to these molecules were located and refined isotropically by considering them as C-atoms. The crystals of complex **8** are tiny and diffracted very weakly that resulted in a high R-int value. As a result in **8** some of the atoms have non-positive definite U-values but as a whole the structure was refined with a good R-factor of 7.60%. Ethanol molecules in the crystal of complex **10** were disordered and refined isotropically. Pertinent crystallographic data are given in Table 1. The fractional coordinates, the full list of bond lengths and angles and the anisotropic displacement parameters have been deposited as supporting information. The distance between the appropriate metal atoms was indicated as grid dimensions and diagonal to diagonal distances. The distance between the two adjacent planes that are formed by metal atoms was represented as interlayer separations. The guest available and accessible volumes were calculated using the Cerius^2 4.0 program [21].

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