

Entrapment of a Hexamer of Nitrobenzene Molecules between the Layers of (4,4)-Coordination Networks Containing Intra- β -Sheet Hydrogen Bonds

Madhushree Sarkar^[a] and Kumar Biradha^{*[a]}

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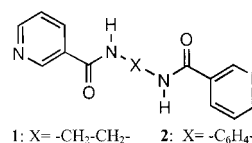
Two *exo*-bidentate pyridyl ligands containing diamides as spacers were shown to form non-interpenetrated 2D-coordination networks of (4,4)-geometry upon treatment with $\text{Cu}(\text{NO}_3)_2$ and NaSCN . The crystal structures reveal that both structures contain intralayer β -sheet hydrogen bonds. In one of these structures nitrobenzene occupies 60 % of the crystal

volume included between the coordination networks. The nitrobenzene molecules form a layer which has the hexameric $\text{C-H}\cdots\text{O}$ hydrogen bonded aggregate as a basic building block.

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The design and syntheses of novel coordination networks is currently an interesting area of research in chemistry as it offers novel materials with functional properties.^[1] One of the interesting aspects of coordination networks is that they offer intriguing possibilities for the inclusion and aggregation of guest molecules. The exploration of the geometry of such aggregates of small molecules in different surroundings is the most significant aspect as it helps in delineating and updating the principles of crystal engineering and supramolecular chemistry. The structure and characteristic properties of those aggregates are distinctly different from the properties of the parent molecules.^[2] There are several instances in which weak intermolecular interactions have led to the formation of a variety of aggregations of small molecules in different surroundings.^[2] We report here the $\text{C-H}\cdots\text{O}$ hydrogen-bonded hexameric aggregate of nitrobenzene that is trapped between the layers of a (4,4)-metal-organic network formed by Cu^{II} and bis(3-pyridyl-carboxamido)ethane (**1**). Ligand **1** contains two pyridine moieties for the formation of extended coordination networks, an alkyl moiety for providing the flexibility and two amide moieties for the formation of $\text{N-H}\cdots\text{O}$ hydrogen bonds.^[3] Recently, ligand **1** was shown by us to form doubly interpenetrated and non-interpenetrated (4,4)-coordination networks upon reaction with CuI .^[4] In both cases the networks are propagated by CuI clusters, secondary building units, and are joined together by β -sheet hydrogen bonds. Here we report another interesting variation of a (4,4)-network which is formed by the reaction of ligand **1** with $\text{Cu}(\text{SCN})_2$. The salient feature of the network is that the β -

sheet hydrogen bonds exist within the layer of the (4,4)-network but not between the layers. As a result, the (4,4)-networks have no cavities and the aromatic guest molecules are included between the layers. The Cambridge Structural Database (CSD)^[5] analysis on nitrobenzene complexes reveals that the $\text{C-H}\cdots\text{O}$ hydrogen-bonded nitrobenzene aggregate observed here is unique and unprecedented.



The careful layering of an MeOH solution of $\text{Cu}(\text{NO}_3)_2$ and NaSCN onto a nitrobenzene solution of ligand **1** resulted in single crystals of complex $\{\text{Cu}(\text{I})_2(\text{SCN})_2 \cdot 6(\text{nitrobenzene})\}_n$ (**3**). An X-ray structure analysis reveals that complex **3** exhibits a (4,4)-coordination network and includes six nitrobenzene molecules per metal atom. The asymmetric unit of **3** contains a Cu atom with half occupancy (on inversion center), two half units of **1**, one SCN anion (on inversion center) and three nitrobenzene molecules. Furthermore, the Cu atom has a highly distorted octahedral geometry as four units of **1** occupy the equatorial positions [Cu-N : 2.048(5) Å and 2.642(5) Å] and two SCN [Cu-N : 1.953(5) Å] anions occupy the axial positions. Each loop of the (4,4)-network has a rhomboidal shape with two Cu–Cu diagonal distances of 31.2 and 10 Å (Figure 1a). The ligands in the sheet recognize each other through β -sheet hydrogen bonds [$\text{N-H}\cdots\text{O}$: 2.989(7) Å, 164°; 2.933(7) Å, 157°] and edge-to-edge aromatic $\text{C-H}\cdots\pi$ interactions. The inter-layer separation between the coordination networks is as high as 11 Å as one layer of nitrobenzene molecules occupies the space between the layers (Figure 1b).

[a] Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, West Bengal, India
Fax: +91-3222-282252
E-mail: kbiradha@chem.iitkgp.ernet.in

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

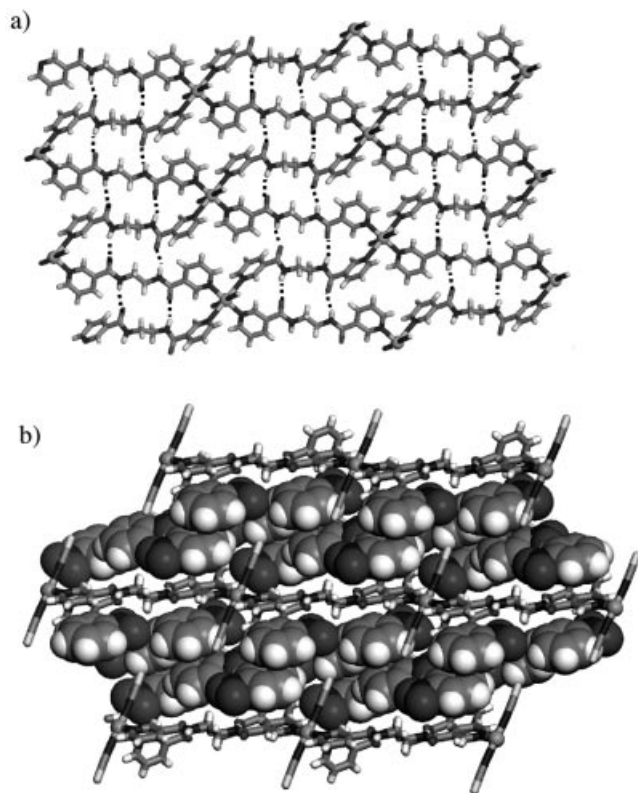


Figure 1. a) (4,4)-Network in the crystal structure of **3**. Note the intralayer β -sheet hydrogen bonds; b) entrapment of a nitrobenzene layer between (4,4)-coordination networks (view along the short diagonal).

The layer of nitrobenzene consists of C–H $\cdots$ O hydrogen-bonded hexameric aggregates of nitrobenzene molecules (Figure 2a). In the aggregate all the molecules lie in a plane and interact with each other through six C–H $\cdots$ O hydrogen bonds [C $\cdots$ O, C–H $\cdots$ O: 3.221(12) Å, 144°; 3.340(18) Å, 132°; 3.303(15) Å, 129°]. Furthermore, the aggregate has a distorted hexagon shape with the length and width dimensions of 25.8 and 11.4 Å, respectively. These aggregates stack on each other in a slipped fashion through aromatic π – π interactions to form a layer which interacts with the host framework through C–H $\cdots$ O hydrogen bonds and aromatic interactions (Figure 2b).

The repetition of the reaction by using other aromatic guests such as benzene, xylene, toluene, naphthalene and benzoic acid in place of nitrobenzene resulted in precipitates but not single crystals. Furthermore, the change of spacers from ethyl to butyl/hexyl/octyl did also not result in single-crystal formation. However, use of bromobenzene instead of nitrobenzene resulted in single crystals in very low yield (5%) which are very unstable for data collection.^[6]

In **3**, nitrobenzene occupies as much as 61% of the unit-cell volume. The analysis of the CSD shows that this aggregate is the first of its kind among the 135 nitrobenzene solvates that are present in the database. However, the structural motif **I**, which is part of the aggregate, was found to exist in 23 structures out of the 4607 structures of the nitroaromatic derivatives.

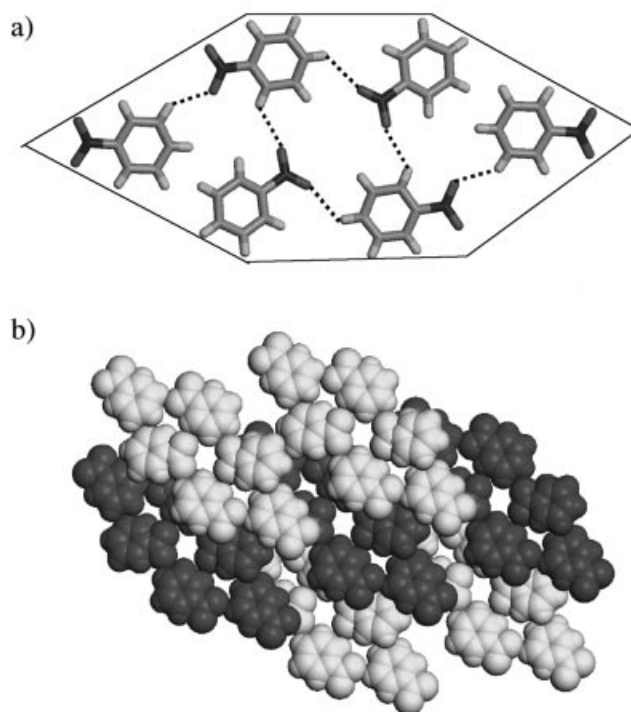
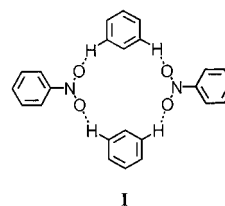


Figure 2. a) C–H $\cdots$ O hydrogen-bonded hexameric aggregate of nitrobenzene molecules; b) layer of hexameric aggregates formed through π – π interactions.



In TGA, a gradual weight loss (8%) of **3** occurred from 50–96 °C which may correspond to the loss of one of the nitrobenzene molecules bound by only one C–H $\cdots$ O hydrogen bond in the hexamer. From 90–141 °C, 40% weight loss occurred which corresponds to five nitrobenzene molecules. The network is stable up to 260 °C. Guest exchange reactions were tried by immersing crystals of **3** in benzene, toluene or naphthalene in CHCl₃. TLC of these crystals indicated the absence of nitrobenzene. From the elemental and powder X-ray diffraction analysis of the immersed crystals, it can be concluded that the nitrobenzene molecules are expelled, but the new guest molecules are not included. The TGA plots and XRPD spectra are included in the Supporting Information.

Ligand **2** was then considered as it has a phenyl spacer which makes the host network self-sufficient to interact with neighboring layers. The layering of an MeOH solution of Cu(NO₃)₂ and NaSCN onto a nitrobenzene solution of ligand **2** resulted in single crystals of the complex {Cu(**2**)₂(SCN)₂} (**4**). The X-ray diffraction analysis revealed that complex **4** also contains a (4,4)-network similar to **3**. The unit-cell contents are the same as for **3** but without nitrobenzene molecules, and the coordination geometry of the

Cu atom is a distorted octahedron [Cu–N: 2.060(4), 2.494(4) Å; Cu–NCS: 1.965(4) Å]. Within the (4,4)-network the ligands recognize each other through β -sheet hydrogen bonds [N–H $\cdots$ O: 2.924(5) Å, 150°; 3.154(5) Å, 152°] as well as aromatic edge-to-face interactions which form between the phenyl spacers and also between the pyridyl groups of adjacent ligands (Figure 3). The Cu atoms in the network are joined together by ligand **2** with a distance of 17.272 Å and each loop has a rhomboidal shape with diagonal-to-diagonal distances of 33.7 and 10.5 Å. These layers stack on each other with an interlayer separation of 5.2 Å which suggests strong aromatic edge-to-face interactions between the layers. The use of other solvents, such as CHCl₃ or toluene, in place of nitrobenzene also resulted in single crystals of complex **4**, which indicates that the crystallization of complex **4** does not depend on the nature of the solvents. These reactions emphasize the fact that the host–host (aromatic) interactions are robust enough to allow crystal formation of complex **4**.

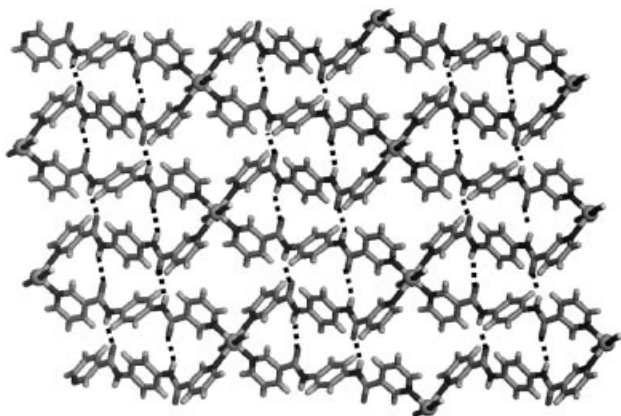


Figure 3. (4,4)-Coordination network of crystal structure **4**. Note the intralayer β -sheet hydrogen bonds and edge-to-face aromatic interactions between the ligands.

Experimental Section

General: FTIR spectra were recorded with an NEXUS-870 instrument, Thermo Nicolet Corporation. UV/Vis spectra were recorded with a Shimadzu UV-1601. Elemental analyses were obtained with a Perkin Elmer instrument, series II, CHNS/O analyzer 2400. TGA data were recorded with a Perkin Elmer instrument, Pyris Diamond TG/DTA (air). Powder XRD data were recorded with a Philips PW 1710 diffractometer.

Synthesis of Complex 3: Methanol (1.0 mL) was layered onto a nitrobenzene (5.0 mL) solution of *N,N'*-bis(3-pyridinecarboxamido)-1,2-ethane (**1**) (40.0 mg, 0.148 mmol). Onto this solution was layered a Cu(SCN)₂ solution, which was obtained by mixing a methanolic solution (0.5 mL) of Cu(NO₃)₂ (17.8 mg, 0.074 mmol) and a methanolic solution (0.5 mL) of NaSCN (11.9 mg, 0.148 mmol). Green crystals formed in 70% yield (300 mg) after 3–4 d. C₆₆H₅₈CuN₁₆O₁₆S₂ (1458.94): calcd. C 54.33, H 3.97, N 15.35; found C 53.48, H 3.71, N 15.02. IR: $\tilde{\nu}$ = 3317 (N–H stretch), 3071 (aromatic C–H stretch), 2064 (thiocyanate CN stretch), 1632 (amide C=O stretch), 1601 (amide II), 1519 (asym. N–O stretch),

1342 (sym. N–O stretch), 849.46 (C–N stretch) cm^{−1}. UV: λ_{max} (ϵ) = 205.67 (816097), 260.27 (616248 dm³ mol^{−1} cm^{−1}) nm.

Synthesis of Complex 4: A methanolic solution of Cu(SCN)₂, formed by addition of an MeOH (0.5 mL) solution of Cu(NO₃)₂ (15.2 mg, 0.063 mmol) to an MeOH (0.5 mL) solution of NaSCN (10.2 mg, 0.126 mmol), was carefully layered onto an ethanol (1 mL)/CHCl₃ (5.0 mL) solution (6 mL) of 1,4-bis(3-pyridinecarboxamido)benzene (**2**) (40.0 mg, 0.126 mmol). Light-green crystals formed in 20% yield (40.8 mg) after a week. C₃₈H₂₈CuN₁₀O₄S₂ (816.36): calcd. C 55.9, H 3.4, N 17.1; found C 55.0, H 2.9, N 16.8. IR: $\tilde{\nu}$ = 3326 (N–H stretch), 3066 (aromatic C–H stretch), 2068 (thiocyanate, CN), 1645 (C=O stretch), 1610 (amide) cm^{−1}. UV: λ_{max} (ϵ) = 204 (45314), 295.71 (27043 dm³ mol^{−1} cm^{−1}) nm.

X-ray Structure Analysis of Complexes 3 and 4: The single-crystal data sets were collected at room temperature for both complexes with a Bruker-Nonius Mach3 CAD4 X-ray diffractometer using graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) in the ω -scan mode. The crystals of complex **3** were immersed in oil and covered with glue in order to prevent loss of guest molecules. The structure was solved by direct methods and refined by least-squares methods on *F*² using SHELX-97.^[7] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. In complex **4**, the S atom of the NCS anion was disordered over two sites and hence the occupancies were refined (61 and 39%). Crystal data for **3**: Triclinic, *P* $\bar{1}$, *a* = 9.967(2), *b* = 12.950(3), *c* = 14.945(3) Å, α = 106.90(3), β = 102.94(3), γ = 102.11, *V* = 1718.9(6) Å³, *Z* = 1, *D*_{calcd.} = 1.409 g cm^{−3}, 3111 reflections out of 5858 unique reflections with *I* > 2 σ (*I*), 1.50° < θ < 25.06°, final *R* values: *R*₁ = 0.0778, *wR*₂ = 0.1724. Crystal data for **4**: Triclinic, *P* $\bar{1}$, *a* = 8.259(2), *b* = 9.613(2), *c* = 12.656(3) Å, α = 85.70(3), β = 74.66(3), γ = 71.18, *V* = 917.1(3) Å³, *Z* = 1, *D*_{calcd.} = 1.478 g cm^{−3}, 2292 reflections out of 3231 unique reflections with *I* > 2 σ (*I*), 1.67° < θ < 25.00°, final *R* values: *R*₁ = 0.0522, *wR*₂ = 0.1177. CCDC-286845 (**3**) and -286846 (**4**), 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): Preparative procedures for **1–4**, TGA measurement of **3**, powder spectra of guest-exchanged materials of **3**, ORTEP drawings of **3** and **4**, and IR and UV spectra of complexes and ligands.

Acknowledgments

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