Encapsulation of Two Types of Chloroform Dimers in the Cavities of a Coordination Polymer

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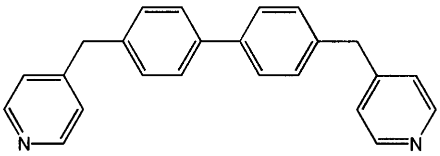
$CHCl_3$ molecules were found to form two types of dimers via C-H···Cl and C-Cl···Cl-C interactions in the cavities of a coordination polymer. The Cambridge Structural Database studies indicated that the Cl···Cl dimer is the first example of $CHCl_3$ with Cl to Cl distance (3.478(4), 3.501(3) Å) below the sum of the van der Waals radii of two Cl-atoms.

Designing coordination polymers using exobidentate ligands and transition metal moiety received significant recent attention due to their important functional properties such as guest inclusion, catalytic activity, porosity and conductivity.[1] However, the flexible and nonlinear ligands have not been much explored compared to rigid and linear ligands.[2] The interesting feature of the networks with flexible ligands is that the guest molecules determine the shape and size of the cavity and also the topology of the network.[3] Further, due to the variety of options for guest inclusion, the guest molecules can be included as adducts of dimers, trimers, tertramers and so on. Here we present one such example where the flexible ligand **1** reacts with $Ni(NO_3)_2$ in presence of $CHCl_3$ to form a open 2D-framework coordination polymer, $[Ni(\mathbf{1})_2(NO_3)_2]$, **2**, with guest accessible cavities. Interestingly, the cavities are occupied by two types of $CHCl_3$ dimers: Cl···Cl dimer (**I**) and C-H···Cl dimer (**II**). Cambridge Structural Database (CSD) analysis revealed that **I** is the first example of Cl···Cl dimer of $CHCl_3$ with Cl···Cl distance (3.478(4), 3.501(3) Å) below the sum of the van der Waals radii of two Cl-atoms.[4]



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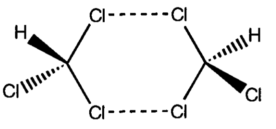
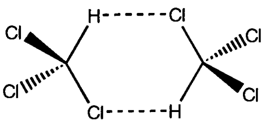


I



II

Single crystals of **2** were grown by layering CH_3OH solution of $Ni(NO_3)_2$ onto the $CHCl_3$ solution of **1.** The crystal structure analysis of **2** revealed that it contains a non-interpenetrated and corrugated 2D-network with large loops that are formed by four metal atoms and four ligands (Figure 1).[5] Each loop has the cavity of dimension ca. 35.0 x 13.6 Å. Part of the cavity was filled by two centrosymmetric $CHCl_3$ dimers, **I** and **II**, while the remaining part filled by neighboring layers as each loop has the non-coplanar geometry.

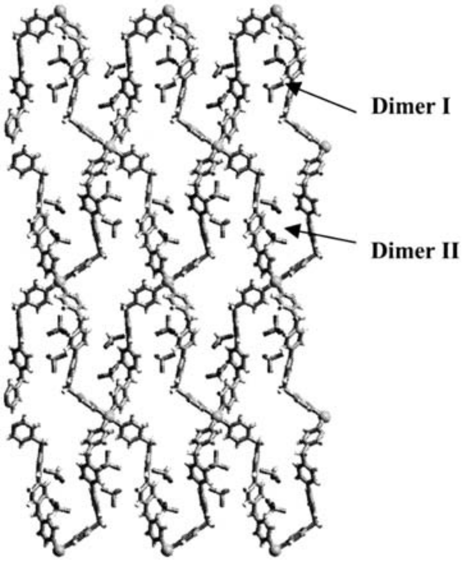


Figure 1. The 2D layer exhibited by the complex **2**. Note the inclusion of two types of $CHCl_3$ dimers in each loop.

The Ni-atom has distorted octahedral geometry with the four-pyridyl groups at equatorial positions and with two NO_3 anions at apical positions. The networks pack on top of each other in an offset fashion such that the crests of one layer will pack in troughs of the adjacent layer. The pyridyl rings in ligand **1** make interplanar angles of 75º-85º with the central C_6H_4 rings. The non bonded torsion angles of the N(pyridyl)-C(methyl)-C(methyl)-N(pyridyl) are 119.7º and 130.0º indicating the approximate *trans* geometry of pyridyl rings.

The asymmetric unit contains two molecules of $CHCl_3$ (**A** and **B**). The molecule A forms Cl···Cl dimer, **I**, (3.501(3) Å) because of the fact that the C-H group of **A** is already involved in a C-H···O [C···O 3.20(1) Å; H···O 2.347 Å and C-H···O 142.9°] hydrogen bond with nitro group (Figure 2a). Exactly opposite happened in case of molecule **B**, that is the C-H group of **B** is involved in C-H···Cl dimer, **II**, (C···Cl 3.748 Å; H···Cl 2.967 Å; C-H···Cl 135.6°), while one of the other two Cl-atoms forms O···Cl interaction (2.949(5) Å) with NO_3 group (Figure 2b).[6] Interestingly in **I**, Cl-atoms of one of the diagonal also interact with each other with a short Cl···Cl distance of 3.478(4) Å. In effect **I** is constituted by three Cl···Cl interactions whereas **II** is constituted by two C-H···Cl interactions. Furthermore, two of the Cl···Cl contacts in **I** are of type **II** category with two C-Cl···Cl angles of 94° and 141°, while the diagonal contact is of type **I** with one C-Cl···Cl angle of 96°.[7]

The occurrence of two types of $CHCl_3$ dimers prompted us to check how many $CHCl_3$ solvates in the CSD contain **I** and

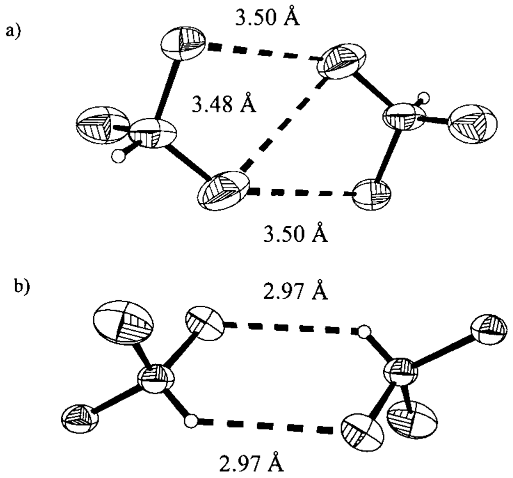


Figure 2. Representation of CHCl$_3$ dimers of in crystal structure of **2**: a) dimer of molecule **A** (**I**); b) dimer of molecule **B** (**II**). Ellipsoids were drawn with 50% probability.

II. The CSD search on the CHCl$_3$ solvates revealed the presence 433 crystal structures.[8] To our surprise, among 433 structures none of the structures were found to contain **I** with the Cl···Cl distance below 3.52 Å, the sum of the Cl-atoms van der Waals radii. However, 26 structures were found for **I** when the Cl···Cl distance relaxed up to 3.8 Å. Among these 26, the most shortest Cl···Cl distance is 3.575 Å in dicyano-pthalocyaninato-*N,N',N'',N'''*)cobalt(III) radical chloroform solvate,[9] while the next shortest is 3.618 Å. Interestingly, in the above mentioned compound also the C-H of CHCl$_3$ is already involved in a C-H···N hydrogen bond (C···N 3.072 Å; H···N 1.966 Å; C-H···N 169.3°). Whereas the dimer **II** found in six structures out of 433 with H···Cl distance below 3.0 Å. Although rather extensive literature exists on the intermolecular interactions involving halogen atoms, the nature of these interactions is matter of further interest and debate.[10]

References and Notes

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5 Crystal Data: Size = 0.20 x 0.15x 0.15 mm^3, monoclinic, space group = P2$_1$/n, a = 10.188(2), b=13.832(3), c = 34.714(8) Å, β = 96.90°, V = 4856.3(2) Å^3, Z = 4, D_c = 1.497 g cm^{-3}, 8539 unique reflections out of 25296 (2θmax = 50°) with $I > 2\sigma(I)$, completeness of data = 99.99%, final R-factors R$_1$ = 0.0705; wR$_2$ = 0.1874, S = 0.987, μ = 0.787 mm^{-1}, largest diffraction peak and hole = 1.160 and –1.388 e.Å^3. Ueq values of Cl-atoms 0.039(1), 0.079(1), 0.083(1), 0.062(1), 0.050(1) and 0.066(1) Å^2. Diffraction data were collected on a Siemens SMART/CCD diffractometer at 193 K with MoK$_\alpha$ radiation and corrected for absorption using the SADABS program. SHELXTL was used for the structure solution and refinement was based on F^2.

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7 A halogen(X)···halogen(X) contact C-X···X-C is defined as type **I** if the C-X···X angle θ$_1$ is equal or nearly equal to the X···X-C angle θ$_2$. If θ$_1$ ≈ 180° and θ$_2$ ≈ 90°, the contact is defined as type II. See: N. Ramasubbu, R. Parthasarathy, and P. Murray-Rust, *J. Am. Chem. Soc.*, **108**, 4308 (1986).

8 Database Analysis: CSD, April 1999 release with 197481 entries was used for these studies. Only the structures with following features were considered: error-free, ordered, atom coordinates present, perfect match between crystallographic and chemical connectivity and R-factor ≤10%. The crystallographic data for 136 structures found to be collected at low temperatures out of total 433 structures. While calculating C-H···Cl interactions the –C-H distances are normalized to neutron derived values.

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