Hydrogen bond directed honeycomb-like porous network structure of tris(bipyridyl-glycoluril)cobalt(III) chloride

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Supporting Information:

Solution and refinement of the X-ray structure

The structure of **1** was solved in the trigonal space group $P\bar{3}1c$ by direct methods and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, G. M., University of Göttingen, Germany, 1997). Systematic absences do not allow to distinguish between the space groups $P\bar{3}1c$ and P31c and the structure can be equally well solved in P31c. The space group $P\bar{3}1c$ was chosen based on the MISSYM check carried out for the structure solution in the acentric space group (Y. Le Page, *J. Appl. Cryst.* 1987, **20**, 264; *J. Appl. Cryst.* 1988, **21**, 983; A. L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005). The water molecules of crystallization were found to be severely disordered. Site occupancy factors of 0.5, 0.4, 0.2, 0.35, 0.15 , 0.2 and 0.4 were assigned to the oxygens O1W, O3W, O4W, O5W, O6W, O7W, and O8W on the basis of the peak heights in the difference map. All water oxygens were refined isotropically. Disorder was also observed for N2, N3, C7 and O1 of the glycouril entity N2, N3, C7 and O1 are disordered over two positions with site occupancies of 0.5 each as determined from the heights of the difmap peaks.

Synthesis of ligand and complex. The bpg ligand was synthesized according to the reported procedure.[1] The complex **1** was synthesized by the bpg ligand (0.2 g, 0.68 mmol) and anhydrous cobalt chloride (0.029 g, 0.23 mmol) in methanol (50 mL) reflux for 1 h. During the reaction yellow solution turned to dark brown. It was cooled in ice, chlorine gas (generated by mixing potassium permanganate and concentrated hydrochloric acid)[2] was passed through it. The dark brown solution turned to violet and a solid precipitated, which was filtered. The precipitate was then dissolved in 10^{-3} M hydrochloric acid (50 mL) by warming at 60 °C for 30 min. The violet colored product obtained on keeping in the refrigerator overnight was separated by filtration, washed with diethyl ether and dried in vacuum. Elemental analysis of the complex **1** correlated well with the calculated values and confirmed the stoichiometry (Found: C, 37.25, H, 4.60, N, 18.57. Calcd for $CoC_{42}H_{56}N_{18}O_{19}Cl_3$: C, 39.33, H, 4.40, N, 19.66). The UV-visible spectrum of complex **1** in water exhibits weak absorption in the visible region 425–475 nm which is due to d-d transition and ligand based π–π* transitions in the UV region 210–332 nm. The IR spectrum exhibit a broad band at 3447 cm^{-1}, which may be assigned to O–H stretching frequency of water and $\nu_{C=O}$, 1697 cm^{-1}; ν_{N-H}, 3098 cm^{-1} of bpg ligand.

1 (*a*) J.A.A.W. Elemans, R. D. Gelder, A. E. Rowan and R.J.M. Nolte, *Chem. Commun.* 1998, 1553; (*b*) A.A.W.E. Johannes, E. R. Alan and R.J.M. Nolte, *J. Am. Chem. Soc.* 2002, **124**, 1532.

2 S. Ghosh, A. C. Barve, A. A. Kumbhar, A. S. Kumbhar, V. G. Puranik, P. A. Datar, U. B. Sonawane and R. R. Joshi, *J. Inorg. Biochem*. 2006, **100**, 331.

Table S1 Crystal data and structure refinement for complex **1**

	Complex **1**
Formula	$C_{42}H_{56}Cl_3CoN_{18}O_{19}$
M_r	1282.38
Wavelength	0.71073 Å
Temperature	293K
Crystal size (mm)	0.40 × 0.40 × 0.30
Crystal system	trigonal
Space group	$P\bar{3}1c$
Unit cell dimensions	a =18.870(2) Å, α = 90°
	b =18.870(2) Å, β = 90°
	c =9.747(1) Å, γ = 120°
V [Å^3]	3005.7(6)
Z	2
D_{calc} (g cm^{-3})	1.477
μ(Mo K_α) (mm^{-1})	0.501
F(000)	1388
2θ range (°)	6.5 – 50.6
No. measd. reflections	19574
No. unique reflections (R_{int})	1826 (12.1 %)
No. of observed reflections	1453 ($I > 2\sigma(I)$)
No. of parameters	164
Final R_1, wR_2 (observed reflections) [a]	R_1 = 10.1%, wR_2 = 25.7%
Goodness-of-fit(observed reflections)	1.156

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; $P = (F_o^2 + 2F_c^2)/3$.

Table S2 Selected geometry parameters [Å°] of **1**

Co1–N1^{i}	1.944 (4)	N1^{i}–Co1–N1^{ii}	84.1 (2)
N1^{i}–Co1–N1^{iii}	93.7 (2)	N1^{ii}–Co1–N1^{iv}	176.9 (2)
N1^{ii}–Co1–N1^{iii}	88.7 (2)		

Symmetry code(s): (i) $-x+y$, y, $-z+3/2$; (ii) $-y+1$, $x-y+1$, z; (iii) $-x+y$, $-x+1$, z; (iv) x, $x-y+1$, $-z+3/2$.

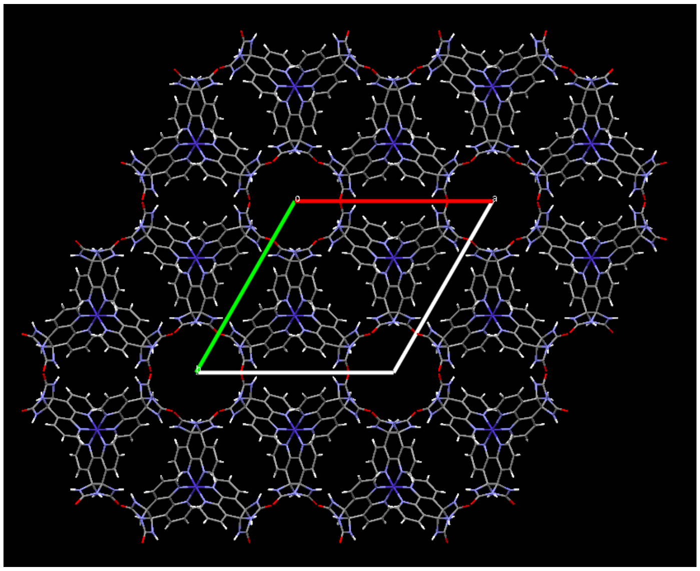

Fig. S1 View along the *c*-axis, showing the hexagonal pores in complex **1**.

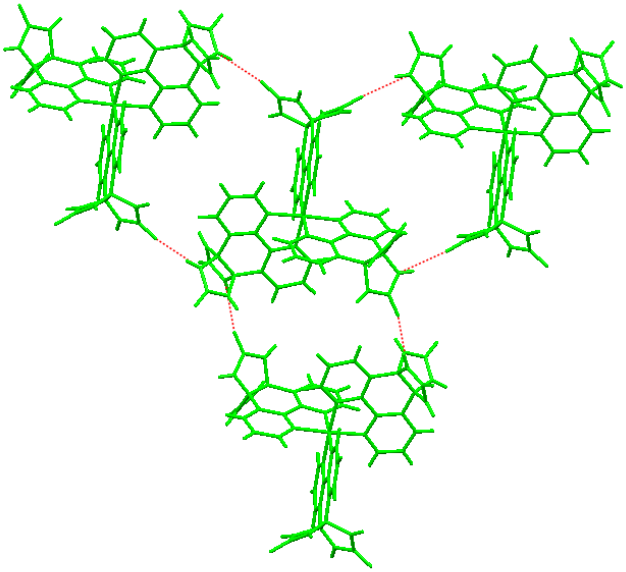

Fig. S2 Structure of complex **1** showing the intermolecular hydrogen bonding (N–H, C=O) interaction of bpg ligand.

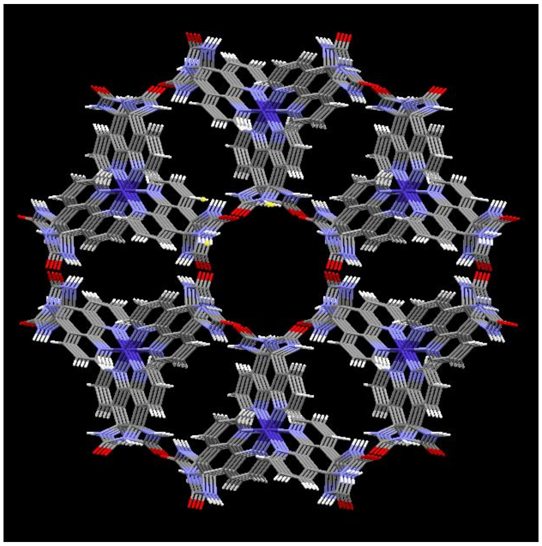

Fig. S3 Multilayered hexagonal sheets of the complex **1** (the water molecules and Cl^{-} anions are omitted for clarity).

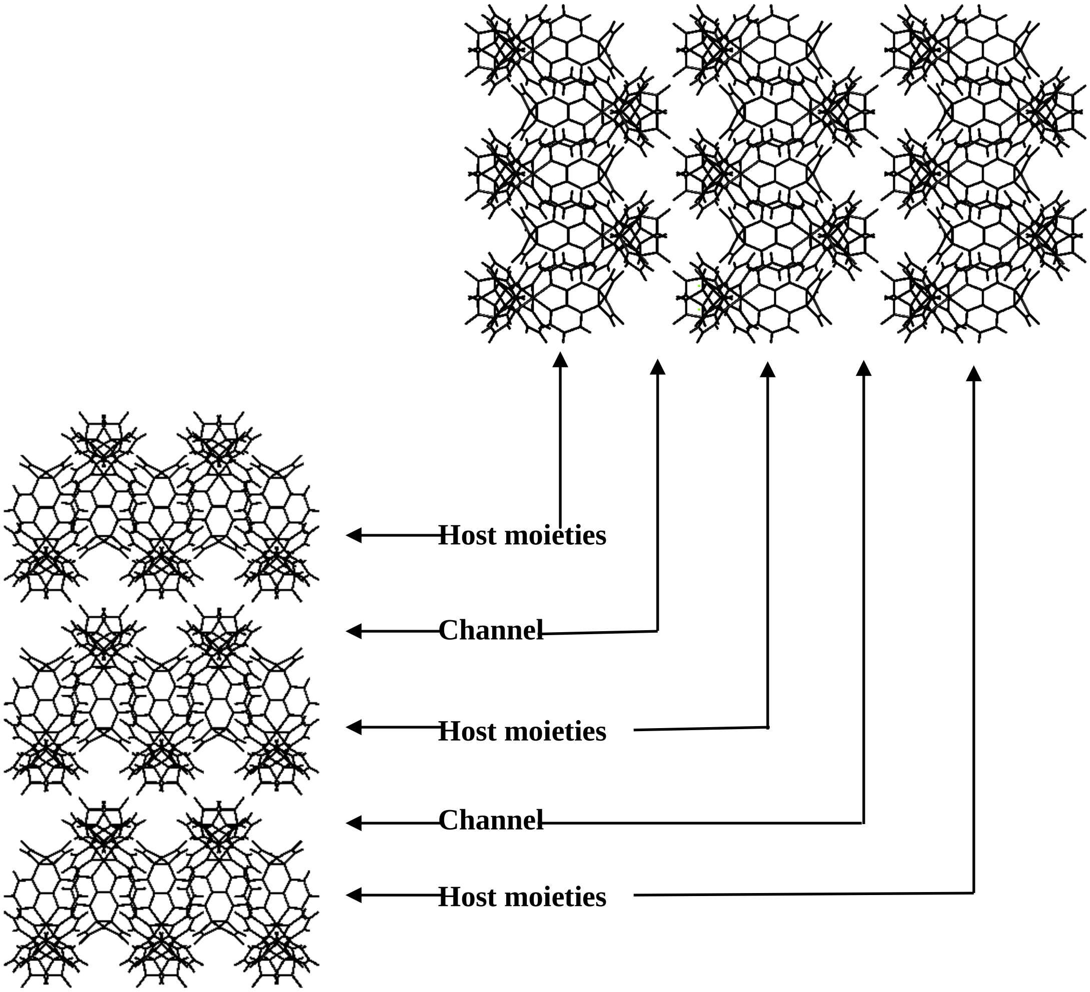

Fig. S4 Packing diagram of complex **1** on *a*- and *b*-axis (the water molecules and Cl^{-} ions are omitted for clarity).

H_2 and CO_2 adsorption measurements. Hydrogen adsorption-desorption experiments were conducted at 77 K using Quantachrome Quadrasorb automatic volumetric instrument. Ultrapure H_2 (99.95 %) was purified further by using calcium aluminosilicate adsorbents to remove trace amounts of water and other impurities before introduction into the system. For measurements at 77 K, a standard low-temperature liquid nitrogen dewar vessel was used. CO_2 adsorption-desorption measurements were done at room temperature (293 K). Before gas adsorption measurements, as-synthesized complex **1** was immersed in dry chloroform for 3 days and evacuated at ambient temperature for 72 h and then at elevated temperature (85°C) under ultrahigh vacuum (10^{-8} mbar) overnight. About 75 mg of samples were loaded for gas adsorption, and the weight of each sample was recorded before and after out gassing to confirm complete removal of all guest H_2O molecules from framework.