SO_4^{2-} Anions Directed Hexagonal-Prismatic Cages *via* Cooperative C-H···O Hydrogen Bonds

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Supporting Information

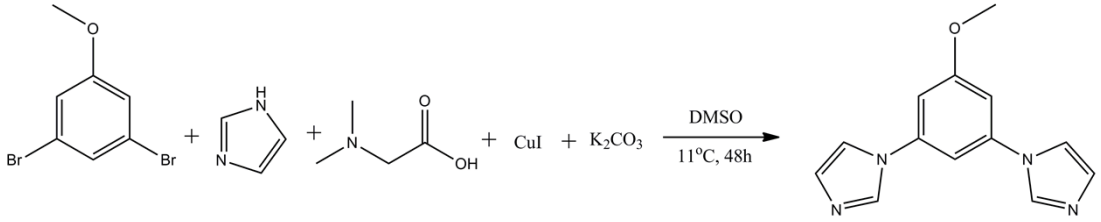
Experimental Section

Experimental Section

Materials and methods

All reactants were reagent grade and used as purchased without further purification. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. IR spectra were recorded in the range 4000–400 cm^{-1} with a Magna 750 FT0IR spectrometer using KBr pellets. The power X-ray diffraction (XRD) patterns were collected by a Rigaku DMAX2500 X-ray diffractometer using Cu Kα radiation (λ= 0.154 nm).

Synthesis of 1,1'-(5-methoxy-1,3-phenylene)bis(1H-imidazole)[2] (5-CH_3O-bib)



A Schlenk flask was charged with CuI (381mg, 2 mmol), N,N'-dimethylglycine (412mg, 4mmol), K_2CO_3 (5.53g, 40 mmol), 1,3-dibromo-5-methoxybenzene (2.66g, 10 mmol), and imidazole (2.72g, 40 mmol). The system was then evacuated twice and back filled with N_2, followed by addition of 40 mL of DMSO. The mixture was heated at 110 ^oC for 48 h before it was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO4, and concentrated in vacuo. The yellow residue was recrystallized from CH_3OH to afford the pure product. (1.25g, 5.2mmol, 52% yield based on 1,3-dibromo-5-methoxybenzene). ^1H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.13 (s, 2H), 7.24 (s, 2H), 7.57 (s, 1H), 7.92 (s, 2H), 8.43 (s, 2H).

Synthesis of complex 1

An aqueous (3 mL) of $NiSO_4 \cdot 6H_2O$ (28 mg, 0.1 mmol) was placed in the bottom of a test-tube, and a mixture (4 mL) of H_2O and MeOH (methanol) (V:V = 1:1) was carefully layered on the aqueous. Then a methanolic solution of bib (1,3-bis(1-imidazoly)benzene, 21 mg, 0.1 mmol) and tmp (2,4,6-trimethylpyridine, 20 μL) in methanol (3 mL) was layered on the top. A pale green needle crystalline precipitate formed on the shell of the tube after two weeks at room temperature (17 mg, 38%). Elemental analysis calcd(%) for compound **1**: C 32.36; H 4.38; N 12.49; found: C

31.72; H 4.26; N 12.45. IR (KBr disk, ν / cm^{-1}): 3392 (s), 3128 (m), 3084 (m), 1618 (m), 1519 (s), 1323 (w), 1296 (w), 1272 (m), 1122 (s), 1087 (s), 1074 (s), 999(w), 960 (w), 935 (w), 867 (w), 790 (m), 746 (m), 684 (m), 653 (m), 617 (m).

Synthesis of complex 2 and 3

An aqueous (3mL) of $NiSO_4 \cdot 6H_2O$ (28 mg, 0.1 mmol) was placed in the bottom of a test-tube, and a mixture (4 mL) of H_2O and MeOH (methanol) (V:V = 1:1) was carefully layered on the aqueous. Then a methanolic solution of 1,1'-(5-methyl-1,3-phenylene)bis(1H-imidazole) (5-CH_3-bib) (22.5 mg, 0.1 mmol) and tmp (2,4,6-trimethylpyridine, 20 μL) in methanol (3 mL) was layered on the top. Pale green needle crystals formed on the shell of the tube after two weeks. Single-crystal X-ray diffractions demonstrate that they are the mixture of the complexes $\{\{SO_4 \subset \{[Ni_4(\mu_3\text{-}OH)_4]_2(5\text{-}CH_3\text{-}bib)_6(\mu_2\text{-}SO_4)_2(H_2O)_8\}\}(SO_4)\}\{SO_4 \subset \{[Ni_4(\mu_3\text{-}OH)_4]_2(5\text{-}CH_3\text{-}bib)_6(\mu_2\text{-}SO_4)(SO_4)_2(H_2O)_8\}\} \cdot (H_2O)_{77}(CH_3OH)_5$ (**2**) and $\{\{\{SO_4 \subset \{[Ni_4(\mu_3\text{-}OH)_4]_2(5\text{-}CH_3\text{-}bib)_6(\mu_2\text{-}SO_4)(CH_3O)(H_2O)_7\}\}_2(\mu_4\text{-}SO_4)\}(SO_4)_2 \cdot xH_2O \cdot xCH_3OH$ (**3**). However, it is a pity that **2** and **3** can not be separated manually. Therefore, no further research is carried out.

Synthesis of complex 4

An aqueous (3 mL) of $NiSO_4 \cdot 6H_2O$ (28 mg, 0.1 mmol) was placed in the bottom of a test-tube, and a mixture (4 mL) of H_2O and MeOH (methanol) (V:V = 1:1) was carefully layered on the aqueous. Then a methanolic solution of 1,1'-(5-methoxy-1,3-phenylene)bis(1H-imidazole) (5-OCH_3-bib) (24 mg, 0.1 mmol) and tmp (2,4,6-trimethylpyridine, 20 μL) in methanol (3 mL) was layered on the top. A pale green crystalline precipitate formed on the shell of the tube after months at room temperature. **4** is very unstable and fragile. And it will turn into the green power quickly apart from the mother liquid.

Synthesis of complex 5

Complex **5** was prepared by a procedure similar to that of **1** with $Ni(ClO_4)_2 \cdot 6H_2O$ (35mg, 0.1mmol). The detailed discussion of **5** will be presented in the following work.

X-ray data collection and sructural determination

For the single crystal analysis of complex **1**, a pale-green needle crystal was taken directly from the mother liquor, transferred to oil and mounted into loop. The crystal was kept at 100 K during data collection on a supernova diffractometer equipped with a Multilayers mirror Cu-Kα radiation (λ = 1.5418 Å) by using a ω scan mode. Similarly, the same proceducures are for complex **2, 3**

and **4**. However, the data of complex **5** was collected on a Rigaku MM007 CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. The crystal structures were solved by direct method and refined by full-matrix least squares on F^2 using *SHELXTL* package.[1] All non-hydrogen atoms were refined with anisotropic thermal parameters except several solvent molecules. All the hydrogen atoms were located at geometrically calculated positions and refined by riding. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. In complex **3**, the free solvent molecules are highly disordered and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; structures were then refined again using the data generated. Complex **4** is very unstable and fragile. Though we tried our best the diffraction data is still poor. In **4**, the free solvent molecules are highly disordered and attempts to locate and refine the solvent peaks were unsuccessful. Only the metal ions are refined anisotropically. Additionaly, some balanced anions, which may be SO_4^{2-}, OH^- or CH_3O^- anions, can not found from the eletron density maps. Therefore, the diffused electron densities resulting from these solvent molecules or balanced anions were removed using the *SQUEEZE* routine of *PLATON*; structures were then refined again using the data generated. Nevertheless, in **4** the skeletons of the cages and the encapsulated SO_4^{2-} anions are undoutedly determined. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 1011630, 1011631, 1011632, 1011628 and 1011629 for complexes **1, 2, 3, 4** and **5** respectively.

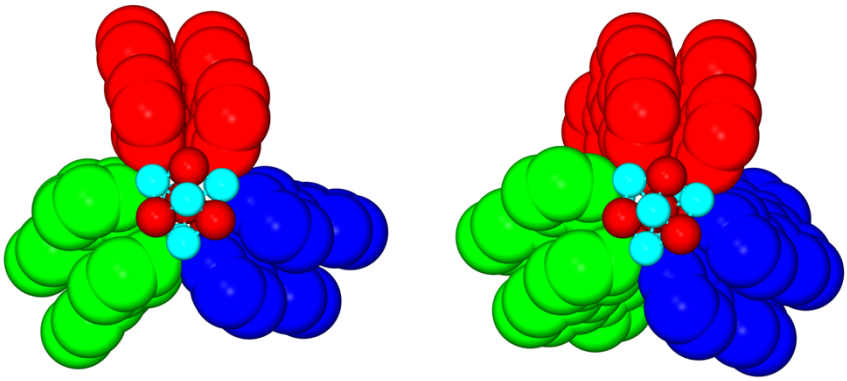


Figure S1 Three groups of bib ligands in each cage in **1**. Left: cage **A**; right: cage **B**.

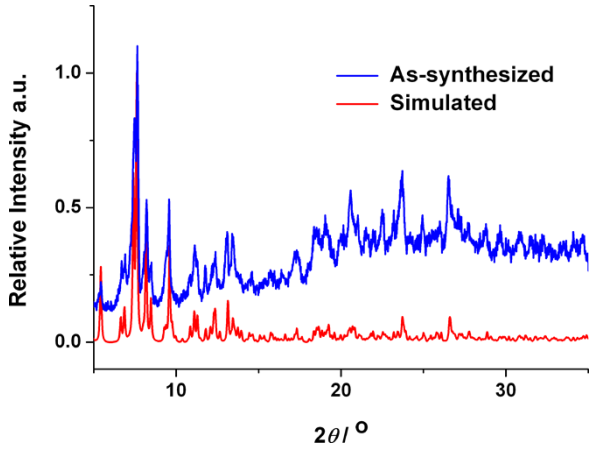


Figure S2 PXRD for complex **1**

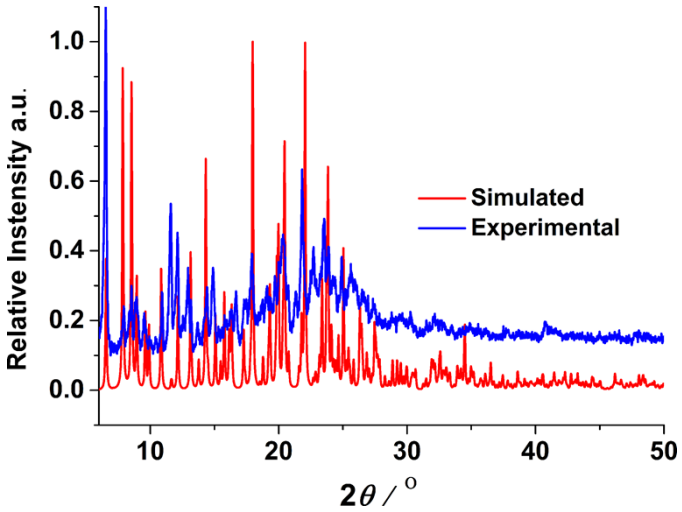


Figure S3 PXRD for complex 5.

Table S1. Crystal data and structure refinement for complex **1** and **2**:

Identification code	Complex **1**	Complex **2**
Empirical formula	$C_{145}H_{234}N_{48}Ni_{16}O_{96}S_8$	$C_{161}H_{363}N_{48}Ni_{16}O_{146}S_8$
Formula weight	5381.63	6503.81
Temperature	100(2) K	100(2) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$
Unit cell dimensions.	*a* = 44.0087(6) Å,	*a* = 20.55910(10) Å,
	b = 20.5888(3) Å,	*b* = 35.0164(2) Å,
	c = 26.8381(3) Å,	*c* = 39.4400(2) Å,
	β = 119.9980(10)°	*β* = 91.3010(10)°
Volume	21060.1(5) Å^3	28385.8(3) Å^3
Z	4	4
Density (calculated)	1.697 mg mm^{-3}	1.522 mg mm^{-3}
Absorption coefficient	3.164 mm^{-1}	2.583 mm^{-1}
F(000)	11136	13636
Crystal size	0.1×0.2×0.2 mm	0.1×0.1×0.1 mm
θ range for data collection.	3.320 to 73.102 °	3.316 to 73.580 °
Limiting indices	-54 <= *h* <= 35, -24 <= *k* <= 25, -28<= *l* <= 33	-15 <= *h* <= 25, -42 <= *k* <= 43, -48<= *l* <= 47
Reflections collected / unique	41765 / 24909 [*R*(int) = 0.0343]	55711 / 46658 [*R*(int) = 0.0347]
Completeness	99.7 %	99.8 %
Absorption correction	multi-scan	multi-scan
Data/restraints/params	41765 / 20 / 2820	55711 / 12 / 3594
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Goodness of fit on F^2	1.045	1.038
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0506, *wR*2 = 0.1358	*R*1 = 0.0674, *wR*2 = 0.1949
R indices (all data)	*R*1 = 0.0540, *wR*2 = 0.1405	*R*1 = 0.0794, *wR*2 = 0.2074

Table S2. Crystal data and structure refinement for complex **3** and **4**:

Identification code	Complex **3**	Complex **4**
Empirical formula	$C_{158}H_{190}N_{48}Ni_{16}O_{60}S_7$	$C_{314}H_{589}N_{96}Ni_{32}O_{224}S_{11}$
Formula weight	4885.35	11525.16
Temperature	100(2)K	100(2)K
Wavelength	1.54178 Å	1.54184 Å
Crystal system	tetragonal	triclinic
Space group	$P4_12_12$	*P*-1
Unit cell dimensions.	*a* = 31.2000(3) Å,	*a* = 20.5225(8) Å,
	b = 31.2000(3) Å,	*b* = 39.0486(5) Å,
	c = 25.3435(4) Å,	*c* = 39.0923(4) Å,
		α = 119.8440(10) °

		β = 91.894(2) °
		γ = 102.976(2) °
Volume	24670.4(6) Å^3	26087.7(11) Å^3
Z	4	2
Density (calculated)	1.315 mg mm^{-3}	1.467 mg mm^{-3}
Absorption coefficient	2.462 mm^{-1}	2.456 mm^{-1}
F(000)	10056	12018
Crystal size	0.12×0.08×0.06 mm	0.06×0.04×0.03 mm
θ range for data collection.	3.167 to 76.368 °	3.5480 to 51.2760 °
Limiting indices	-32 <= *h* <= 39, -38 <= *k* <= 38, -30<= *l* <= 30	-20 <= *h* <= 20, -39 <= *k* <= 39, -39<= *l* <= 38
Reflections collected / unique	59895 / 25295 [*R*(int) = 0.0448]	55850 / 30510 [*R*(int) = 0.1115]
Completeness	99.5%	98.2%
Absorption correction	multi-scan	multi-scan
Data/restraints/params	59895 / 44 / 1251	55850 / 0 / 5723
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Goodness of fit on F^2	1.172	1.882
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.1149, *wR*2 = 0.3125	*R*1 = 0.1773, *wR*2 = 0.4747
R indices (all data)	*R*1 = 0.1485, *wR*2 = 0.3425	*R*1 = 0.2198, *wR*2 = 0.5025

Table S3. Crystal data and structure refinement for complex **5**:

Identification code	Complex **5**
Empirical formula	$C_{37}H_{35}Cl_2N_{12}NiO_{10}$
Formula weight	937.38
Temperature	173(2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions.	*a* = 11.376(4) Å, *b* = 20.675(8) Å, *c* = 17.957(7) Å, β = 99.139(7) °
Volume	4170(3) Å^3
Z	4
Density (calculated)	1.515 mg mm^{-3}
Absorption coefficient	0.668 mm^{-1}
F(000)	1956
Crystal size	0.1×0.2×0.2 mm
θ range for data collection.	2.22 to 27.48 °
Limiting indices	-12 <= *h* <= 14, -26 <= *k* <= 26, -23<= *l* <= 23
Reflections collected / unique	33047 / 9387 [*R*(int) = 0.0821]
Completeness	99.2%
Absorption correction	multi-scan
Data/restraints/params	33047 / 0 / 569
Refinement method	Full-matrix least squares on F^2
Goodness of fit on F^2	1.087

Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0799, *wR*2 = 0.2099
R indices (all data)	*R*1 = 0.0957, *wR*2 = 0.2215

Table S4. The data of C-H⋯ O hydrogen bonds for complex **1**

D-H⋯A	*D* (H⋯O) Å	*θ* (∠C-H⋯O) º	D-H⋯A	*D* (H⋯O) Å	*θ* (∠C-H⋯O) º
Cage A			**Cage B**		
C58-H58⋯O65	2.397	167.95	C118-H118⋯O50	2.328	145.91
C57-H57⋯O65	2.450	176.13	C130-H130⋯O50	2.397	167.95
C49-H49⋯O65	2.493	154.71	C125-H125⋯O50	2.450	176.13
C61-H61⋯O65	2.749	153.89	C121-H121⋯O50	2.493	154.71
C70-H70⋯O65	2.751	148.58	C109-H109⋯O50	2.751	148.58
C64-H64⋯O65	2.882	156.86	C113-H113⋯O50	2.882	156.86
C34-H34⋯O66	2.328	145.91	C78-H78⋯O51	2.246	150.33
C37-H37⋯O66	2.359	158.42	C142-H142⋯O51	2.492	166.62
C13-H13⋯O66	2.433	158.51	C136-H136⋯O51	2.506	172.40
C13-H13⋯O67	2.192	155.81	C82-H82⋯O51	2.572	134.43
C2-H2⋯O67	2.392	136.09	C133-H133⋯051	2.622	151.03
C61-H61⋯O67	2.541	151.73	C142-H142⋯O52	2.433	166.28
C2-H2⋯O68	2.339	154.92	C82-H82⋯O52	2.552	155.64
C10-H10⋯O68	2.608	146.81	C94-H94⋯O52	2.608	146.81
C13-H13⋯O68	2.797	146.44	C118-H118⋯O53	2.359	158.42
C21-H21⋯O68	2.896	163.92	C106-H106⋯O53	2.433	158.51
C24-H24⋯O69	2.269	156.14	C94-H94⋯O53	2.797	146.44
C9-H9⋯O69	2.349	170.17	C106-H106⋯O54	2.192	155.81
C70-H70⋯O69	2.552	155.64	C85-H85⋯O54	2.269	156.14
C10-H10⋯O69	2.572	134.43	C101-H101⋯O54	2.392	136.09
C46-H46⋯O70	2.246	150.33	C98-H98⋯O54	2.541	151.73
C24-H24⋯O70	2.462	163.26	C88-H88⋯O54	2.896	163.92
C27-H27⋯O70	2.526	121.55	C98-H98⋯O55	2.339	154.92
C46-H46⋯O71	2.433	166.28	C85-H85⋯O55	2.349	170.17
C37-H37⋯O71	2.492	166.62	C73-H73⋯O55	2.526	121.55
C34-H34⋯O71	2.506	172.40	C73-H73⋯O56	2.462	163.26
C41-H41⋯O71	2.622	151.03	C133-H133⋯O56	2.648	164.77
C33-H33⋯O71	2.648	164.77	C121-H121⋯O56	2.749	153.89
C27-H27⋯O71	2.669	148.36			

Table S5. The data of C-H⋯ O hydrogen bonds for complex **2**

D-H⋯A	*D* (H⋯O) Å	*θ* (∠C-H⋯O) º	D-H⋯A	*D* (H⋯O) Å	*θ* (∠C-H⋯O) º
Cage A			**Cage B**		

C1-H1···O68	2.658	123.76	C79-H79···O57	2.510	155.11
C1-H1···O69	2.825	143.93	C79-H79···O63	2.533	152.79
C9-H9···O69	2.648	160.54	C87-H87···O57	2.535	155.42
C11-H11···O64	2.349	130.84	C89-H89···O57	2.503	168.77
C11-H11···O69	2.538	159.56	C89-H89···O59	2.670	139.14
C14-H14···O66	2.835	145.63	C92-H92···O58	2.415	153.74
C14-H14···O67	2.269	155.40	C92-H92···O63	2.357	136.55
C14-H14···O68	2.485	158.78	C100-H100···O58	2.282	176.58
C24-H24···O64	2.499	150.97	C102-H102···O58	2.377	163.84
C24-H24···O65	2.206	163.37	C102-H102···O59	2.307	144.57
C27-H27···O66	2.327	154.59	C105-H105···058	2.895	143.82
C27-H27···O67	2.349	138.49	C105-H105···O62	2.506	162.12
C31-H31···O66	2.337	157.84	C105-H105···O63	2.286	155.54
C37-H37···O65	2.300	153.30	C115-H115···O58	2.863	153.40
C37-H37···O66	2.435	165.40	C115-H115···O59	2.260	159.30
C40-H40···O67	2.467	148.78	C115-H115···O60	2.531	153.47
C40-H40···O70	2.684	155.51	C118-H118···O61	2.835	141.98
C44-H44···O70	2.857	150.76	C118-H118···O62	2.661	121.80
C50-H50···O65	2.715	140.61	C122-H122···O61	2.685	162.75
C50-H50···O70	2.637	167.01	C128-H128···O60	2.604	120.35
C53-H53···O70	2.594	148.33	C128-H128···O61	2.777	141.82
C57-H57···O70	2.502	165.95	C131-H131···O61	2.534	156.28
C63-H63···O70	2.455	160.43	C131-H131···O62	2.226	159.80
C66-H66···O68	2.316	159.66	C135-H135···O61	2.521	154.95
C66-H66···O69	2.620	152.67	C141-H141···O60	2.240	157.81
C70-H70···O69	2.504	154.54	C141-H141···O61	2.584	151.07
C76-H76···O64	2.251	152.79	C144-H144···O57	2.591	160.58
C76-H76···O69	2.368	165.68	C148-H148···O57	2.634	158.91
			C154-H154···O57	2.545	161.77

Table S6. The data of C-H··· O hydrogen bonds for complex **3**

D-H···A	*D* (H···O) Å	*θ* (∠C-H···O) °	D-H···A	*D* (H···O) Å	*θ* (∠C-H···O) °
C1-H1···O18	2.213	152.72	C44-H44···O19	2.836	153.87
C13-H13···O16	2.315	161.86	C50-H50···O16	2.811	125.00
C14-H14···O17	2.388	173.43	C50-H50···O19	2.562	175.52
C22-H22···O17	2.596	160.04	C53-H53···O19	2.768	142.49
C24-H24···O17	2.629	166.15	C57-H57···O19	2.373	165.61
C27-H27···O18	2.379	136.11	C64-H64···O19	2.181	174.89
C37-H37···O16	2.304	155.31	C66-H66···O17	2.600	144.51
C40-H40···O18	2.555	160.91	C70-H70···O17	2.467	161.19
C40-H40···O19	2.828	144.26	C75-H75···O17	2.485	173.44

Reference:

1. Sheldrick, G. M. *University of Göttingen: Germany*, **1997**.

2. S. Zhang, S. Yang, J. Lan, S. Yang, and J. You, *Chem. Comm.*, **2008**, 6170-6172.