Supporting information

A sequentially assembled grid composed of supramolecular meso-helical nodes

Miguel Martínez-Calvo,[a] Rosa Pedrido,*[a] Ana M. González-Noya,*[b] María J. Romero,[a] Magdalena Cwiklinska,[a] Guillermo Zaragoza[c] and Manuel R. Bermejo[a]

S.1. Materials

All solvents, 1,3-diacetylbenzene, 4-methoxyphenyl-isothiocyanate, hydrazine monohydrate and the cobalt plate are commercially available and were used without further purification.

S.2 Physical Measurements

Elemental analyses of C, H and N were performed on a Carlo Erba EA 1108 analyser. ^{1}H NMR spectra were recorded on Bruker DPX-250 and Varian Inova 500 spectrometers, using DMSO-d_6 and CD_3CN as solvents. Infrared spectra were measured with KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000-600 cm^{-1}. Electrospray ionization (ESI) mass spectra were registered on an API4000 Applied Biosystems mass spectrometer. Matrix Assisted Laser Desorption Ionisation Time of Flight (MALDI-TOF) mass spectra were registered on a Bruker Autoflex spectrometer using DCTB as matrix. Room temperature magnetic susceptibility was measured using a Digital Measurement system MSB-MKI, calibrated using mercury *tetrakis*(isothiocyanato) cobalt(II). Molar conductivity value was obtained at 25 °C from a 10^{-3} M solution in acetone on a Crison micro CM 2200.

S.3. Synthesis

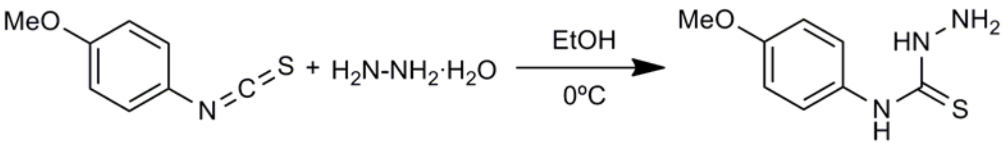

Chart S1

S.3.1. 4-N-(4-metoxyphenyl)-3-thiosemicarbazide (H_2PhOMe)

To a solution of 4-methoxyphenyl-isothiocyanate (2.47 g, 15 mmol) in 20 mL of absolute ethanol was added hydrazine monohydrate (1.48 mL g, 30 mmol) in small portions and stirring at 0 ºC (Chart S1). After one hour, the white solid formed was filtered, washed with diethyl ether and dried under *vacuum*.

H_2PhOMe: Yield: 2.55 g (85%). Anal. $C_8H_{11}N_3SO$ requires: C, 48.7; H, 5.6; N, 21.3; S, 16.2. Found: C, 48.6; H, 5.6; N, 21.3; S, 16.2. MS ESI (m/z) 196.1 [H_2PhOMe-H]$^-$; IR (KBr, cm^{-1}): ν(NH) 3321 (m), 3275 (w), 3167 (m), ν(C=N+C-N) 1529 (vs), 1512 (s), 1491 (m), ν(C=S) 1105 (w), 833 (w), ν(N-N) 1034 (m); ^{1}H NMR δ_H(dmso-d_6): 9.51 (s, 1H), 8.97 (s, 1H), 7.42 (s, 2H, J=8.4 Hz), 6.84 (d, 2H, J=8.4 Hz), 4.72 (s, 2H), 3.73 (s, 3H).

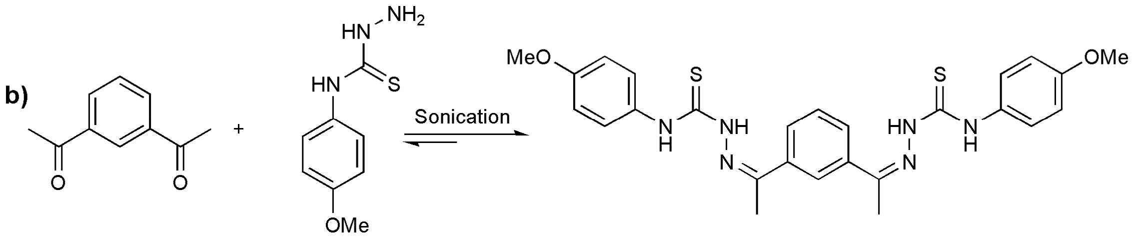

Chart S2

S.3.2. Synthesis of H_2L^b

1.12 g (9 mmol) of 4-*N*-(4-metoxyphenyl)-3-thiosemicarbazide and 0.73 g (0.45 mmol) of 1,3-diacetylbenzene were mixed in an agate mortar until homogeneous mixture. The mixture was sonicated at 55ºC for six hours. The yellow oil obtained was treated with 20 mL of absolute ethanol, giving rise to a white solid, which was filtered, washed with diethyl ether and dried under *vacuum* (Chart S2).

H_2L^b: Yield: 1.27, 85 %. Anal. $C_{26}H_{28}N_6S_2O_2$ requires: C, 60.0; H, 5.0; N, 16.1; S, 12.3. Found: C, 59.9; H, 5.1; N, 16.0; S, 12.1. MS ESI (m/z) 519.2 $[H_2L^b\text{-}H]^-$; IR (KBr, cm^{-1}): ν(NH) 3307 (w), 3242 (w), ν(C=N+C-N) 1595 (w), 1544 (s), 1521 (s), 1477 (m), ν(C=S) 1111 (m), 800 (w), ν(N-N) 1030 (m); ^{1}H NMR δ_H(dmso-d_6): 10.53 (s, 2H), 10.01 (s, 2H), 8.38 (s, 1H), 8.03 (d, 2H, J=7.7 Hz), 7.44 (t, 1H, J=7.7 Hz), 7.34 (d, 4H, J=8.8 Hz), 6.90 (d, 4H, J=8.8 Hz), 3.77 (s, 6H), 2.42 (s, 6H).

S.3.3. Synthesis of $[Co_2(L^b)_2]\cdot H_2O$ (**1**$\cdot H_2O$).

The compound was obtained by means of an electrochemical procedure.[i,ii] An acetonitrile solution of the ligand H_2L^b, in the presence of a supporting electrolyte, was electrolyzed using a platinum wire as cathode and a cobalt plate as anode. The cell can be summarised as: Pt(–)|H_2L^b + MeCN|Co(+).

A solution of the ligand (0.1 g, 0.19 mmol) in acetonitrile (80 cm^3), containing 10 mg of tetraethylammonium perchlorate (CAUTION: although no problem has been encountered in this work, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care), was electrolyzed for 62 minutes using a current of 10 mA. The resulting green solid was filtered off, washed with diethyl ether and dried *in vacuo*.

The complex, $[Co_2(L^b)_2]\cdot H_2O$ (**1**$\cdot H_2O$), was characterised by elemental analysis, mass spectrometry (MALDI-TOF), ^{1}H NMR, infrared spectroscopy and magnetic and conductivity measurements. Slow evaporation from the mother liquors allow us to obtain green crystals of $[Co_2(L^b)_2]$ **1**, studied by X-ray diffraction.

$[Co_2(L^b)_2]\cdot H_2O$: Yield: 0.084 g (74 %). Anal. $Co_2C_{52}H_{54}N_{12}S_4O_5$ requires: C, 53.2; H, 4.6; N, 14.3; S, 10.9. Found: C, 53.1; H, 4.6; N, 14.3; S, 10.8. MS MALDI-TOF (m/z) 578.2 [ML], 1155.1 $[M_2L_2]$; IR (KBr, cm^{-1}): ν(OH) 3417 (w), ν(NH) 3317 (m), ν(C=N+C-N) 1593 (w), 1509 (s), 1483 (m), ν(C=S) 1100 (w), 798 (w), ν(N-N) 1044 (m); ^{1}H NMR δ_H(CD_3CN): 140.36, 118.00, 108.63, 78.88, 62.00, 32.92, 31.16, 20.91, 19.55, 17.04, 16.00, 11.28, 10.00, 9.23, 7.62, 6.91, 6.23, 5.93, 3.16, 0.63, -16.63, -23.01, -31.10, -35.45, -48.40, -61.50; Λ_M ($\mu S\cdot cm^2$)= 5.6; μ (B. M.) = 4.1.

S.4. X-Ray Crystallographic Studies

Crystals of **1,** suitable for X-ray diffraction studies, were ground as previously described. Crystallographic data were collected on a Bruker Appex-II CCD

Diffractometer, using graphite-monocromated $Mo\text{-}K_{\alpha}$ radiation (λ = 0.71073 Å) from a fine focus sealed tube source. The structures were solved by direct methods [iii] and finally refined by full-matrix, least-squares based on F^2 by SHELXL.[iv] An empirical absorption correction was applied using SADABS.[v] All non hydrogen atoms were anisotropically refined and the hydrogen atoms positions were included in the model by electronic density or were geometrically calculated and refined using a riding model.

Bond distances and angles are summarized in Tables S1 and S2, while hydrogen bond parameters are listed in Table S3.

CCDC 828824 contains 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.

Table S1 Bond lengths (Å) for [$Co_2(L^b)_2$] **1**

Bond lengths (Å)			
C1—O1	1.419 (3)	C18—N4	1.297 (3)
C2—C7	1.375 (3)	C19—N5	1.307 (3)
C2—C3	1.380 (3)	C19—N6	1.362 (3)
C2—O1	1.380 (3)	C19—S2	1.757 (2)
C3—C4	1.379 (3)	C20—C25	1.393 (3)
C4—C5	1.384 (3)	C20—C21	1.397 (3)
C5—C6	1.378 (3)	C20—N6	1.417 (3)
C5—N1	1.429 (3)	C21—C22	1.381 (3)
C6—C7	1.400 (3)	C22—C23	1.390 (3)
C8—N2	1.299 (3)	C23—O2	1.376 (3)
C8—N1	1.364 (3)	C23—C24	1.389 (3)
C8—S1	1.755 (2)	C24—C25	1.392 (3)
C9—C10	1.499 (3)	C26—O2	1.428 (3)
C10—N3	1.296 (3)	N2—N3	1.399 (2)
C10—C11	1.479 (3)	N3—Co1	2.034 (2)
C11—C16	1.392 (3)	N4—N5	1.404 (2)
C11—C12	1.397 (3)	N3—Co1	2.034 (2)
C12—C13	1.384 (3)	S1—Co1	2.268 (1)
C13—C14	1.383 (3)	N4—Co1^{i}	2.045 (2)
C14—C15	1.405 (3)	S2—Co1^{i}	2.241 (1)
C15—C16	1.393 (3)	Co1—N4^{i}	2 .045 (2)
C17—C18	1.501 (3)	Co1—S2^{i}	2.241 (6)
Symmetry transformations: (i) 2-x, -y, 1-z			

Table S2 Bond angles (°) for [Co$_2$(L^b)$_2$] **1**

Bond Angles (º)			
C7—C2—C3	120.2 (2)	C25—C20—C21	119.1 (2)
C7—C2—O1	124.7 (2)	C25—C20—N6	123.9 (2)
C3—C2—O1	115.2 (2)	C21—C20—N6	117.0 (2)
C2—C3—C4	120.1 (2)	C22—C21—C20	120.5 (2)
C3—C4—C5	120.6 (2)	C21—C22—C23	120.5 (2)
C6—C5—C4	119.0 (2)	O2—C23—C24	125.1 (2)
C6—C5—N1	121.9 (2)	O2—C23—C22	115.7 (2)
C4—C5—N1	119.0 (2)	C24—C23—C22	119.2 (2)
C5—C6—C7	120.6 (2)	C23—C24—C25	120.6 (2)
C2—C7—C6	119.4 (2)	C24—C25—C20	120.0 (2)
N2—C8—N1	116.6 (2)	C8—N1—C5	124.8 (2)
N2—C8—S1	127.4 (2)	C8—N2—N3	114.6 (2)
N1—C8—S1	116.0 (2)	C10—N3—N2	113.6 (2)
N3—C10—C11	118.4 (2)	C10—N3—Co1	127.7 (2)
N3—C10—C9	122.9 (2)	N2—N3—Co1	117.7 (2)
C11—C10—C9	118.6 (2)	C18—N4—N5	117.8 (2)
C16—C11—C12	119.6 (2)	C18—N4—Co1^{i}	122.9 (1)
C16—C11—C10	121.3 (2)	N5—N4—Co1^{i}	119.1 (1)
C12—C11—C10	119.0 (2)	C19—N5—N4	113.1 (2)
C13—C12—C11	120.2 (2)	C19—N6—C20	130.6 (2)
C14—C13—C12	119.9 (2)	C2—O1—C1	117.6 (2)
C13—C14—C15	121.0 (2)	C23—O2—C26	117.6 (2)
C16—C15—C14	118.5 (2)	C8—S1—Co1	93.6 (7)
C14—C15—C18	117.4 (2)	C19—S2—Co1^{i}	95.1 (7)
C11—C16—C15	120.7 (2)	N3—Co1—N4^{i}	128.8 (7)
N4—C18—C15	127.2 (2)	N3—Co1—S2^{i}	119.6 (5)
N4—C18—C17	116.5 (2)	N4^{i}—Co1—S2^{i}	85.6 (5)
C15—C18—C17	116.3 (2)	N3—Co1—S1	86.4 (5)
N5—C19—S2	126.8 (2)	N4^{i}—Co1—S2^{i}	85.6 (5)
N6—C19—S2	112.8 (2)	N3—Co1—S1	86.4 (5)
S2^{i}—Co1—S1	117.3 (2)	N4^{i}—Co1—S1	122.9 (5)

Symmetry transformations: (i) 2-*x*, -*y*, *1-z*

Table S3 Hydrogen bond parameters [Å] for $[Co_2(L^b)_2]$ **1**

Parameter	**D–H···A**	**D–H**	**H···A**	**∠DHA**
N1—H1N···O2^{ii}	0.77 (3)	2.54 (3)	3.222 (3)	149 (3)
N6—H6N···S2^{iii}	0.81 (3)	2.68 (3)	3.415 (2)	152 (2)

Symmetry transformations: (ii) 1-*x*, -*y*, 2-*z*; (iii) 2-*x*, -1-*y*, 1-*z*

S.5 Additional figures

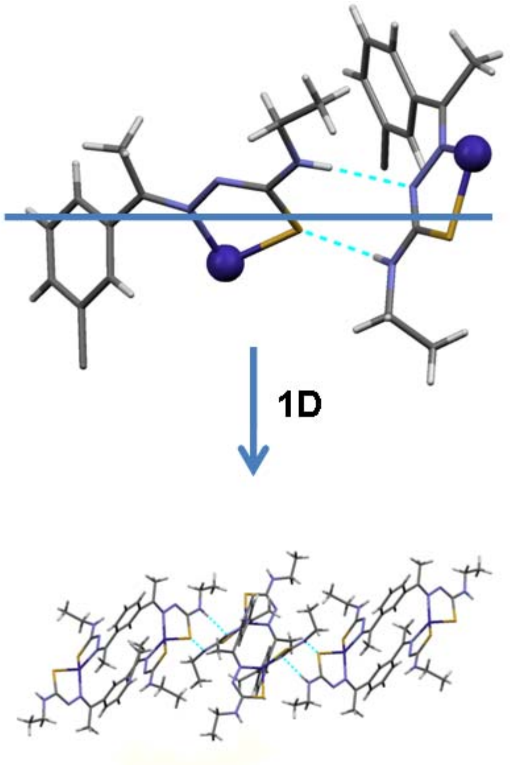

Figure S1 1D chains assembled by the cobalt mesocate $[Co_2(L^b)_2]$.

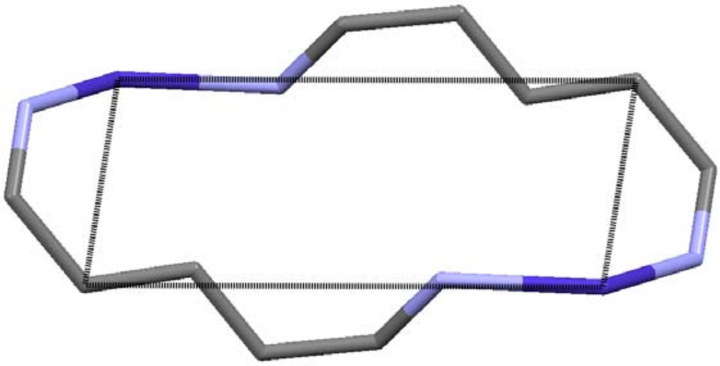

Figure S2 Metallomacrocyclic cavity exhibit by the cobalt mesocate [Co$_2$(L^b)$_2$].

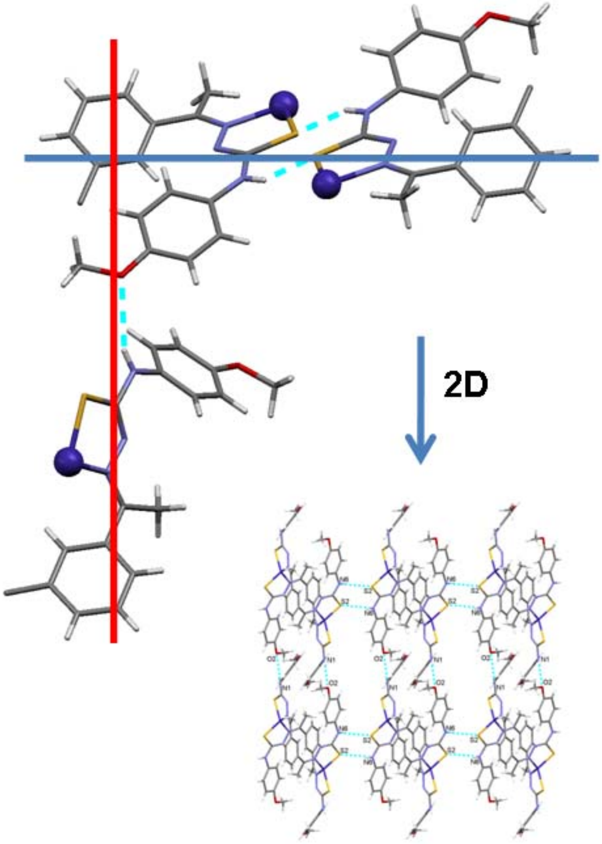

Figure S3 2D grid assembled by $[Co_2(L^b)_2]$, in which the nodes are mesocate-type units.

References

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