Electronic supplemental information

A disc like Co_7 cluster with solvent dependent catecholase activity

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Experimental Section

Materials and methods

All experiments were carried out under aerobic conditions. The ligand (ampdH_2), NaSCN, $Co(NO_3)_2$ and $Co(OAc)_2$ were used as received. The solvents used in the reactions were reagent grade and used without further purification.

Physical methods

FTIR spectra were recorded on a Perkin-Elmer spectrum GX automatic recording spectrophotometer with sample prepared as KBr discs. Melting point was determined by open capillary method and is uncorrected. Absorption spectroscopic measurements were carried out at room temperature; using a Perkin-Elmer Lambda-25 UV-visible spectrophotometer in 10^{-3} M solution in CH_3OH, cu-vettes of 1 cm path length. PXRD patterns have been recorded by ''MiniflexII X-ray diffractometer'' with Cu-$K\alpha$ radiation. Molar conductivity of 10^{-3} M aqueous solution was recorded on Systronics-305 digital conductivity bridge at room temperature. Thermal gravimetric analysis (TGA) data were recorded from room temperature up to 700 °C at a heating rate of 20 °C/min. The data were obtained using a Shimadzu TGA-50H instrument. Magnetic susceptibility was measured by using a Quantum Design MPMS-XL7 SQUID magnetometer. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

X–ray crystal structure determination and refinements

Single-crystal X-ray data of **1** were collected at 296(2) K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X–ray Crystallography [1]. The data integration and reduction were processed with SAINT Software [2]. An empirical absorption correction was applied to the collected reflections with SADABS [3] and the space group was determined using XPREP [4]. The structure was refined using full-matrix least-squares techniques on F^2 using the OLEX-2 program package [5a] and version 2017/1 of ShelXL program package [5b]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. Electron density contributing to the disordered solvent water molecules was masked using Olex-2 (Table 4S). CCDC reference number for **1** is 1570038.

Synthesis of 1

The slow stirring of ampdH_2 (5 mmol) and 10 mmol NaSCN for ten minutes in methanol produces a clear clolourless solution. To this solution was added dropwise methanolic solution (5 ml) of 10 mmol $Co(NO_3)_2$ or $Co(OAc)_2$ under aerobic conditions. After 2 hr stirring the brown solution was kept overnight which afforded reddish brown crystals of **1**.

[Yield: 56%, m.p. = 270 C, Molar conductance, Λ_m (10^{-3} M, methanol): 65 $\Omega^{-1}cm^2mol^{-1}$. Anal. Calcd. (%) for $C_{30}H_{62}Co_7N_{12}O_{20}S_6$: C 23.77; H 4.12; N 11.09, S = 12.69. Found (%): C 23.33; H 4.57; N 11.14, S = 12.87. Molar conductance, Λ_m (10^{-3} M, methanol): 65 $\Omega^{-1}cm^2mol^{-1}$. IR spectra (KBr pellets, cm^{-1}): ν(O–H): 3448, ν(C–H): 2877, 2950, 2962, ν(C–O): 990, 1012, ν(C–N): 1125, 1260, ν(NH_2): 3293, 3236, υ(SCN): 2079.

References

1 J. A. Ibers and W. C. Hamilton, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 1974, vol. IV.

2 SMART & SAINT Software Reference manuals, Version 6.45, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2003.

3 G. M. Sheldrick, SADABS, software for empirical absorption correction, Ver. 2.05, University of Go¨ttingen, Go¨ttingen, Germany, 2002.

4 XPREP, version 5.1, Siemens Industrial Automation Inc., Madison, WI, 1995.

5 (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339 (b) G.M. Sheldrick, , *Acta Cryst.*, 2015, **C27**, 3-8.

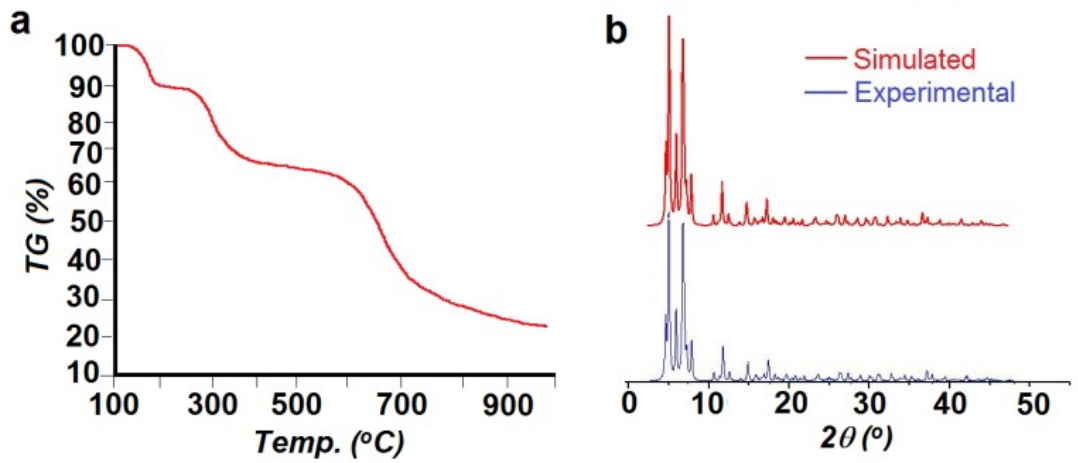

Fig. 1S. (a) Thermogram of the **1**. (b) Simulated and as-synthesized PXRD patterns of **1**.

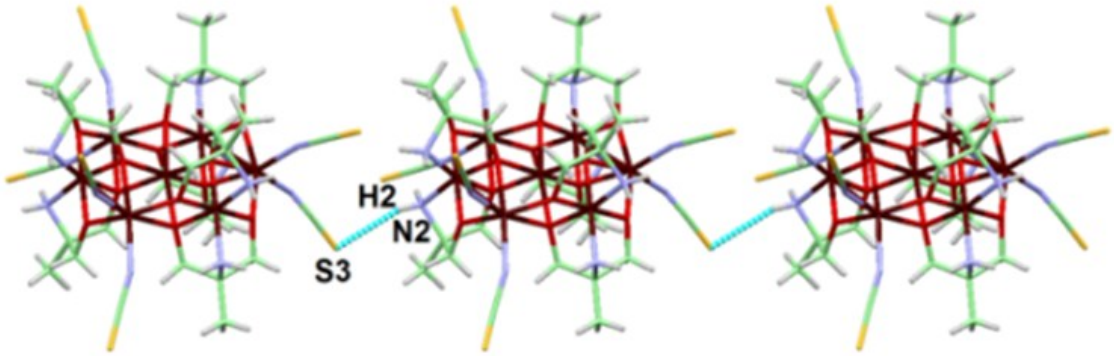

Fig. 2S. Existence of 1D chain as a result of S···H interactions.

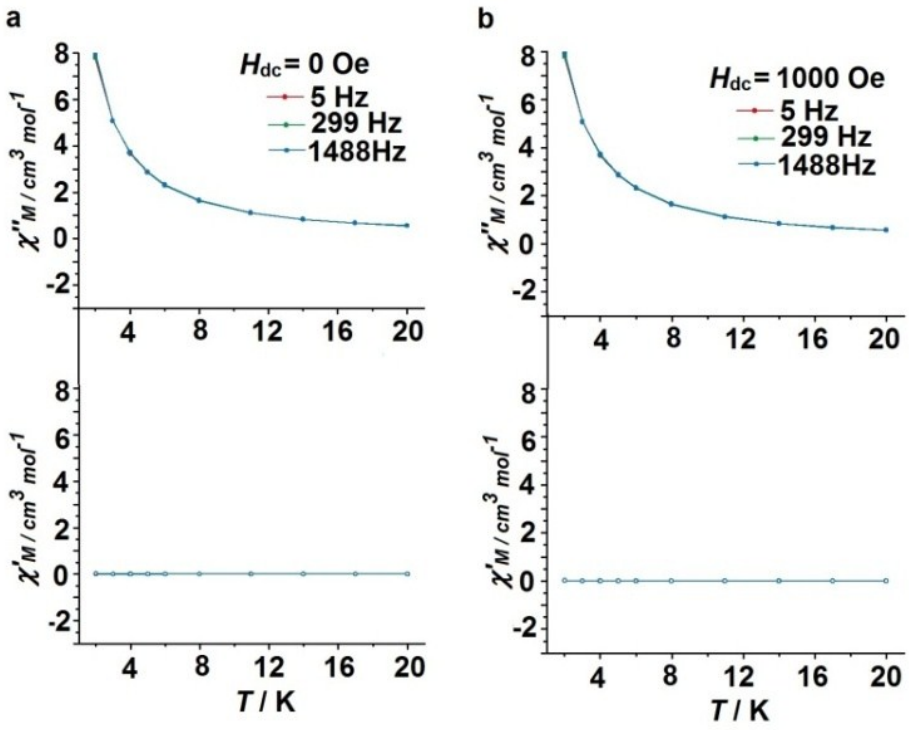

Fig. 3S. In-phase (χ') and out-of-phase (χ'') AC susceptibility measurements at different frequencies and applied dc fields for **1**.

Table 1S. Crystal data for **1**.

Compound	**1**
Formula	$C_{30}Co_7H_{74}N_{12}O_{22}S_6$
$D_{calc.}$/ g cm^{-3}	1.656
μ/mm^{-1}	2.084
Formula Weight	1559.88
Colour	Red
Shape	block
Size/mm^3	0.28×0.19×0.14
T/K	296(2)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	22.4034(16)
b/Å	14.9191(16)
c/Å	20.435(2)
α/°	90
β/°	113.618(4)
γ/°	90
V/Å^3	6258.1(10)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	2.731
Θ_{max}/°	24.997
Measured Refl.	47412
Independent Refl.	5494
Reflections Used	2976
R_{int}	0.1051
Parameters	307
Restraints	0
Largest Peak	0.810
Deepest Hole	-0.684
GooF	1.027
wR_2 (all data)	0.1793
wR_2	0.1514
R_1 (all data)	0.1268
R_1	0.0664

Table 2S. Selected bond lengths (Å) and bond angles (°) of **1**.

Atom	Atom	Length/Å
Co1	Co2[1]	2.9836(11)
Co1	Co2	2.9837(11)
Co1	Co3	2.974(2)
Co1	O4	2.091(4)
Co1	O4[1]	2.091(4)
Co1	O5	2.086(5)
Co1	O5[1]	2.086(5)
Co1	O1[1]	2.106(4)
Co1	O1	2.106(4)
Co2	O4	1.901(4)
Co2	O2	1.874(5)
Co2	O1	1.898(4)
Co2	O3	1.878(5)
Co2	N2	1.929(5)
Co2	N1	1.931(6)
Co3	O5[1]	1.900(5)
Co3	O5	1.900(5)
Co3	O6[1]	1.877(5)
Co3	O6	1.877(5)
Co3	N3[1]	1.936(6)
Co3	N3	1.936(6)
Co4	O1[1]	2.261(4)
Co4	O1	2.262(4)
Co4	O3[1]	2.027(4)
Co4	O3	2.027(4)
Co4	N4[1]	2.062(7)
Co4	N4	2.062(7)
Co5	O4	2.265(4)
Co5	O5[1]	2.273(4)
Co5	O2	2.008(5)
Co5	O6	2.000(5)
Co5	N6	2.058(8)
Co5	N5	2.061(7)
S2	C14	1.589(9)
S1	C13	1.647(11)
O4	C8	1.451(7)
O5	C11	1.440(7)
O2	C4	1.421(8)
O1	C3	1.430(7)
O3	C7	1.431(8)
O6	C12	1.401(9)
S3	C15	1.646(12)
N2	C6	1.499(8)
N1	C2	1.540(9)
N6	C15	1.100(11)
N3	C10	1.521(10)
N5	C14	1.141(9)
C3	C2	1.514(10)
C8	C6	1.494(10)
C6	C7	1.520(11)
C6	C5	1.518(9)
C11	C10	1.506(11)
N4	C13	1.143(10)
C4	C2	1.529(11)
C2	C1	1.510(10)
C12	C10	1.538(11)
C10	C9	1.505(10)

Symmetry code: [1]1-x, +y, 3/2-z

Table 2S. continued…..

Atom	Atom	Atom	Angle/˚
Co2[1]	Co1	Co2	120.27(6)
Co3	Co1	Co2[1]	119.87(3)
Co3	Co1	Co2	119.87(3)
O4[1]	Co1	Co2	134.98(13)
O4[1]	Co1	Co2[1]	39.25(12)
O4	Co1	Co2	39.25(12)
O4	Co1	Co2[1]	134.99(13)
O4[1]	Co1	Co3	93.88(13)
O4	Co1	Co3	93.88(13)
O4	Co1	O4[1]	172.2(3)
O4[1]	Co1	O1[1]	78.47(16)
O4[1]	Co1	O1	95.98(16)
O4	Co1	O1[1]	95.98(16)
O4	Co1	O1	78.47(16)
O5[1]	Co1	Co2	93.74(12)
O5[1]	Co1	Co2[1]	134.77(12)
O5	Co1	Co2	134.78(12)
O5	Co1	Co2[1]	93.73(12)
O5	Co1	Co3	39.42(13)
O5[1]	Co1	Co3	39.41(13)
O5[1]	Co1	O4[1]	95.76(16)
O5	Co1	O4[1]	90.24(17)
O5[1]	Co1	O4	90.24(17)
O5	Co1	O4	95.77(16)
O5	Co1	O5[1]	78.8(3)
O5[1]	Co1	O1	95.76(17)
O5	Co1	O1	172.16(17)
O5[1]	Co1	O1[1]	172.16(17)
O5	Co1	O1[1]	95.76(17)
O1	Co1	Co2[1]	94.10(12)
O1[1]	Co1	Co2	94.10(12)
O1	Co1	Co2	39.22(11)
O1[1]	Co1	Co2[1]	39.22(11)
O1	Co1	Co3	134.92(12)
O1[1]	Co1	Co3	134.92(12)
O1	Co1	O1[1]	90.2(2)
O4	Co2	Co1	44.11(12)
O4	Co2	N2	83.8(2)
O4	Co2	N1	167.6(2)
O2	Co2	Co1	89.22(15)
O2	Co2	O4	85.3(2)
O2	Co2	O1	93.83(19)
O2	Co2	O3	178.9(2)
O2	Co2	N2	95.0(2)
O2	Co2	N1	85.4(2)
O1	Co2	Co1	44.57(13)
O1	Co2	O4	88.68(18)

O1	Co2	N2	167.8(2)
O1	Co2	N1	83.8(2)
O3	Co2	Co1	89.84(14)
O3	Co2	O4	93.7(2)
O3	Co2	O1	85.84(19)
O3	Co2	N2	85.1(2)
O3	Co2	N1	95.6(2)
N2	Co2	Co1	127.22(17)
N2	Co2	N1	105.2(2)
N1	Co2	Co1	127.57(17)
O5	Co3	Co1	44.20(14)
$O5^{1}$	Co3	Co1	44.20(13)
$O5^{1}$	Co3	O5	88.4(3)
$O5^{1}$	Co3	$N3^{1}$	83.7(2)
$O5^{1}$	Co3	N3	167.8(2)
O5	Co3	$N3^{1}$	167.8(2)
O5	Co3	N3	83.7(2)
O6	Co3	Co1	89.52(17)
$O6^{1}$	Co3	Co1	89.52(17)
$O6^{1}$	Co3	$O5^{1}$	93.2(2)
$O6^{1}$	Co3	O5	86.1(2)
O6	Co3	O5	93.2(2)
O6	Co3	$O5^{1}$	86.1(2)
O6	Co3	$O6^{1}$	179.0(3)
O6	Co3	$N3^{1}$	95.4(3)
$O6^{1}$	Co3	$N3^{1}$	85.1(3)
$O6^{1}$	Co3	N3	95.4(3)
O6	Co3	N3	85.1(2)
N3	Co3	Co1	127.3(2)
$N3^{1}$	Co3	Co1	127.3(2)
$N3^{1}$	Co3	N3	105.4(4)
$O1^{1}$	Co4	O1	82.5(2)
O3	Co4	$O1^{1}$	93.87(17)
O3	Co4	O1	73.44(17)
$O3^{1}$	Co4	O1	93.87(17)
$O3^{1}$	Co4	$O1^{1}$	73.44(17)
O3	Co4	$O3^{1}$	163.4(3)
$O3^{1}$	Co4	$N4^{1}$	94.1(2)
$O3^{1}$	Co4	N4	96.7(2)
O3	Co4	$N4^{1}$	96.7(2)
O3	Co4	N4	94.1(2)
$N4^{1}$	Co4	$O1^{1}$	165.2(2)
N4	Co4	O1	165.2(2)
N4	Co4	$O1^{1}$	90.6(2)
$N4^{1}$	Co4	O1	90.6(2)
$N4^{1}$	Co4	N4	98.8(4)
O4	Co5	$O5^{1}$	81.39(15)
O2	Co5	O4	73.25(17)
O2	Co5	$O5^{1}$	92.64(18)
O2	Co5	N6	95.4(3)
O2	Co5	N5	95.3(2)
O6	Co5	O4	93.30(19)
O6	Co5	$O5^{1}$	73.89(18)
O6	Co5	O2	162.47(19)
O6	Co5	N6	95.9(3)

O6	Co5	N5	96.5(2)
N6	Co5	O4	165.6(3)
N6	Co5	O5[1]	90.5(2)
N6	Co5	N5	97.4(3)
N5	Co5	O4	92.6(2)
N5	Co5	O5[1]	168.2(2)
Co1	O4	Co5	94.24(16)
Co2	O4	Co1	96.64(18)
Co2	O4	Co5	95.62(17)
C8	O4	Co1	134.2(4)
C8	O4	Co2	109.1(4)
C8	O4	Co5	119.1(4)
Co1	O5	Co5[1]	94.13(16)
Co3	O5	Co1	96.39(18)
Co3	O5	Co5[1]	94.77(18)
C11	O5	Co1	132.8(4)
C11	O5	Co3	109.7(4)
C11	O5	Co5[1]	120.9(4)
Co2	O2	Co5	105.8(2)
C4	O2	Co2	111.8(5)
C4	O2	Co5	132.4(5)
Co1	O1	Co4	93.66(15)
Co2	O1	Co1	96.21(17)
Co2	O1	Co4	95.85(17)
C3	O1	Co1	132.0(4)
C3	O1	Co2	109.7(3)
C3	O1	Co4	121.7(4)
Co2	O3	Co4	104.9(2)
C7	O3	Co2	109.9(5)
C7	O3	Co4	134.3(4)
Co3	O6	Co5	105.2(2)
C12	O6	Co3	111.1(5)
C12	O6	Co5	134.2(5)
C6	N2	Co2	98.5(4)
C2	N1	Co2	97.6(4)
C15	N6	Co5	153.0(10)
C10	N3	Co3	98.0(5)
C14	N5	Co5	167.1(7)
O1	C3	C2	110.4(5)
O4	C8	C6	109.9(5)
N2	C6	C7	102.8(6)
N2	C6	C5	112.7(6)
C8	C6	N2	105.3(6)
C8	C6	C7	111.1(6)
C8	C6	C5	111.3(7)
C5	C6	C7	113.1(7)
O5	C11	C10	110.1(6)
O3	C7	C6	109.7(6)
C13	N4	Co4	155.3(8)
O2	C4	C2	108.5(6)
C3	C2	N1	103.8(6)
C3	C2	C4	110.9(7)
C4	C2	N1	103.5(6)
C1	C2	N1	112.9(7)
C1	C2	C3	112.5(7)

	C1	C2	C4	112.5(7)	
	O6	C12	C10	109.6(6)	
	N5	C14	S2	178.0(9)	
	N6	C15	S3	172.8(11)	
	N4	C13	S1	177.5(9)	
	N3	C10	C12	102.1(7)	
	C11	C10	N3	105.1(6)	
	C11	C10	C12	110.5(7)	
	C9	C10	N3	111.9(7)	
	C9	C10	C11	113.2(7)	Symmetry code: [1]1-x,+y,3/2-
z	C9	C10	C12	113.2(7)	

Table 3S. Bond valence summation (BVS) parameters for **1**.

Atom	Co(II)	Co(III)
Co1	**1.9420**	1.7592
Co2	3.5164	**3.1093**
Co2	3.5164	**3.1093**
Co3	3.4092	**2.8726**
Co4	**2.0268**	1.7936
Co5	**2.1102**	1.8675
Co5	**2.1102**	1.8675

Table 4S: Solvent masking information for **1**.

No	**x**	**y**	**z**	**V**	**e**	**Content**
1	0.255	0.250	0.505	912.2	198.4	$5H_2O$
2	-0.285	0.750	-0.535	912.2	198.4	$5H_2O$