Supporting Information

A Novel Nanosized {Co_{16}} Metallamacrocycle Incorporating Four Linear {Co_4} Subunits Bridged by Polytriazolate Ligands †

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Experimental

Synthesis of complex **1**: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.056 g, 0.20 mmol), 3,5-H_2bptp (0.037g, 0.10 mmol) in MeOH (12 mL) was sealed in a 25 mL Teflon-lined, stainless-steel vessel and heated at 160 °C for 72 h, and then cooled to room temperature. The blue crystal were obtained. (yield ca. 40% based on 3,5-H_2bptp). C, H, N analysis calculated (%) for $C_{42}H_{36}N_{20}O_{10}Co_4(H_2O)_{1.5}(MeCN)_1$: C, 41.14; H, 3.29; N, 22.90. Found: C, 41.12; H, 3.25; N, 22.84. IR data (KBr), ν(cm^{-1}): 3428w, 2805m, 1610m, 1466w, 1437m, 1386s, 1301m, 1280m, 1119w, 1054m, 1018m, 812w, 747m, 718w, 481w.

Synthesis of complex **2:** A mixture of $CoCl_2 \cdot 6H_2O$ (0.048 g, 0.20 mmol), 1,3-H_2bptb (0.037 g, 0.05 mmol) and 3,5-H_3bptpt (0.037 g, 0.05 mmol) in MeOH/MeCN (V/V 1:1, 12 mL) was sealed in a 25 mL Teflon-lined, stainless-steel vessel and heated at 160 °C for 72 h, and then cooled to room temperature. The modena crystals were obtained (yield ca. 27% based on 1,3-H_2bptb). C, H, N analysis calculated (%) for $C_{204}H_{152}Co_{16}N_{76}O_{14}(H_2O)_{25}$: C, 46.60; H, 3.84; N, 20.05. Found: C, 46.56; H, 3.92; N, 20.14. IR data (KBr), ν(cm^{-1}): 3378w, 1607m, 1570s, 1519s, 1466m, 1436m, 1411w, 1327s, 1283s, 1255s, 1152vs, 1084s; 1049s; 1024s; 1006s; 805m; 740m; 694m; 662s; 636s; 445s; 415s.

Materials and Measurements. The commercially available chemicals and solvents were used and purified by standard procedures. The C, H and N microanayles were determined using an Elementar Vario-EL CHNS elemental anaylzer. IR spectra using KBr pellets were recorded on a Bio-Rad FTS-7 spectrometer. Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID. Polycrystalline samples of complex **1** and **2** were embedded in vaseline to prevent torqueing. All the ac susceptibility data were collected at zero dc field and 5 Oe ac amplitude. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

X-Ray Crystallography

Diffraction data for complex **1** were recorded on a Rigaku R-AXIS SPIDER IP diffractomer with Mo Kα radiation (λ = 0.71073 Å) at room temperature(298K) and complex **2** were recorded on a Bruker Apex CCD area detector diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The raw data frames were integrated with use of the Bruker SAINT package with a narrow frame algorithm.[1] An absorption correction based on symmetry equivalent reflections was applied using the SADABS program. The structures were solved with direct method and refined with full-matrix least-squares (SHELX-97).[2] All non-hydrogen atoms were refined anisotropically by full-matrix

least-squares on F^2 using the SHELXTL program. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms on organic ligands were generated by the riding mode.

The disordered solvent molecules could not be modelled properly; thus, the program SQUEEZE,[3] a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Selected bond distances and angles are listed in Table S1 in supporting information. The structure plots and space-filling diagram were produced with DIAMOND 3.1 and POV-Ray v3.62.[4]

Reference:

1 R.H. Blessing, *Acta Crystallogr.*, 1995, **A51**, 33.

2 G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112.

3 P. van der Sluis and A. L. Spek, *Acta Crystallogr.,* 1990, **A46**, 194.

4 W.T. Pennington, *J. Appl. Cryst*. 1999, **32**, 1028.

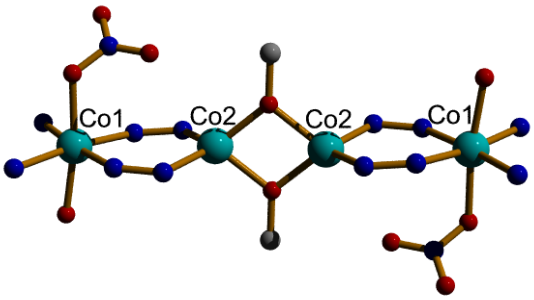


Fig. S1. The coordination environment of metal ions in complex **1**.

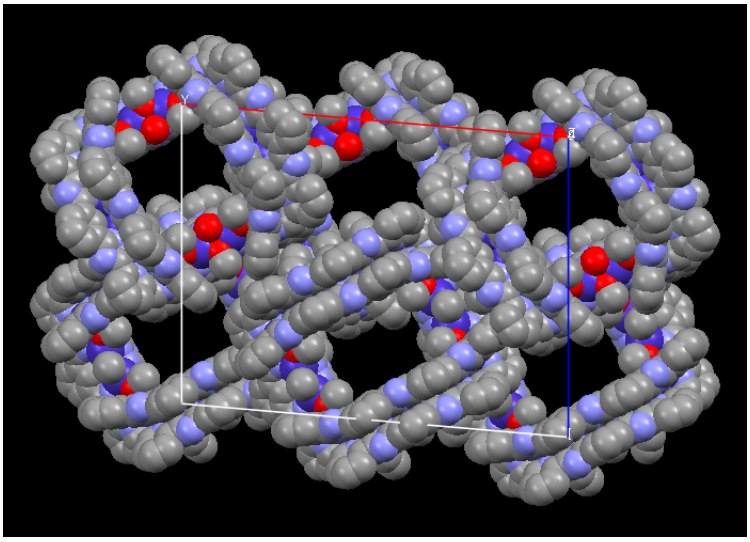


Fig. S2. Packing diagram of complex **2**.

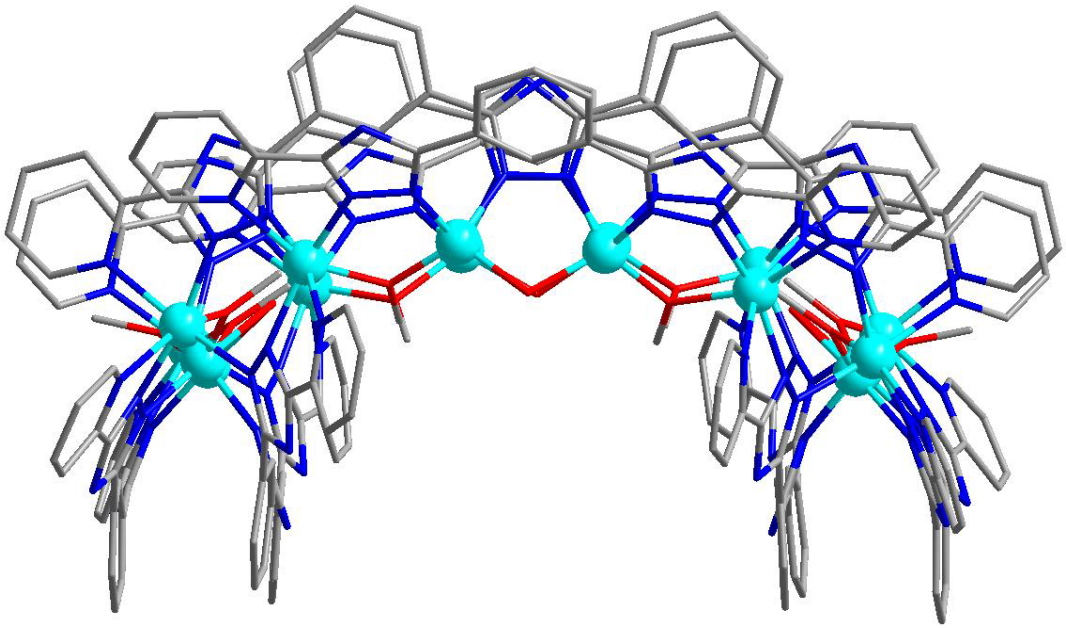


Fig. S3. Side view of the $\{Co_{16}\}$ mtallamacrocycle of complex **2**.

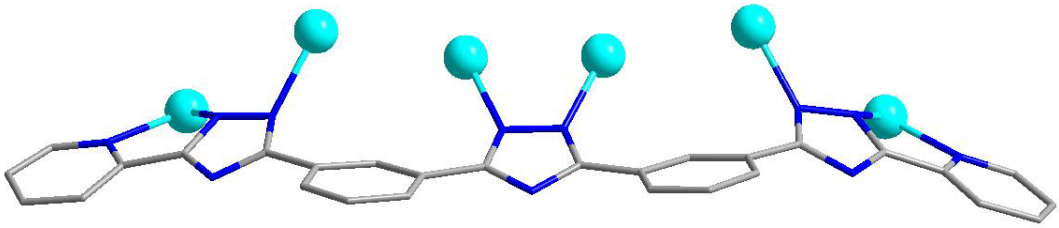


Fig. S4. Bridging mode of 3,5-bptpt^{3-} ligand.

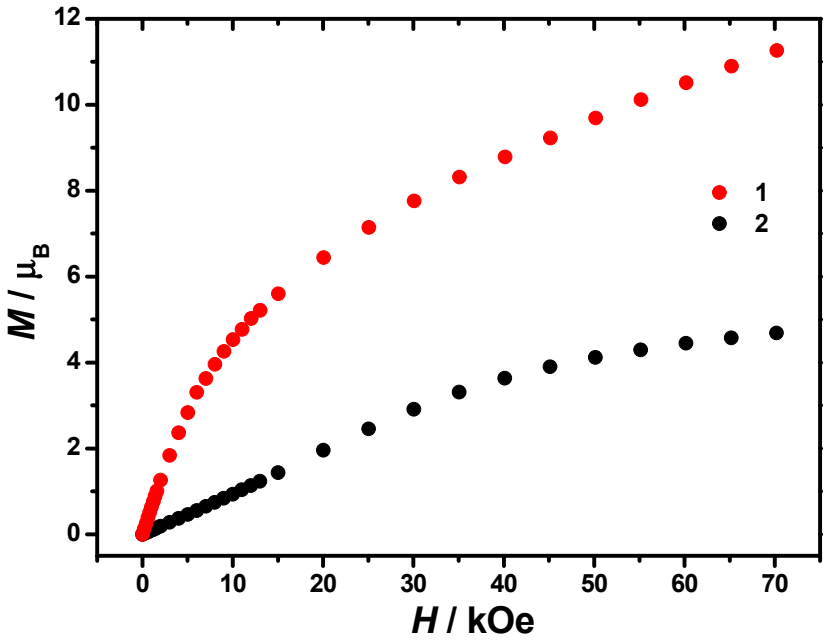


Fig. S5. Field-dependent magnetization plots at 2 K for **1** and **2**.

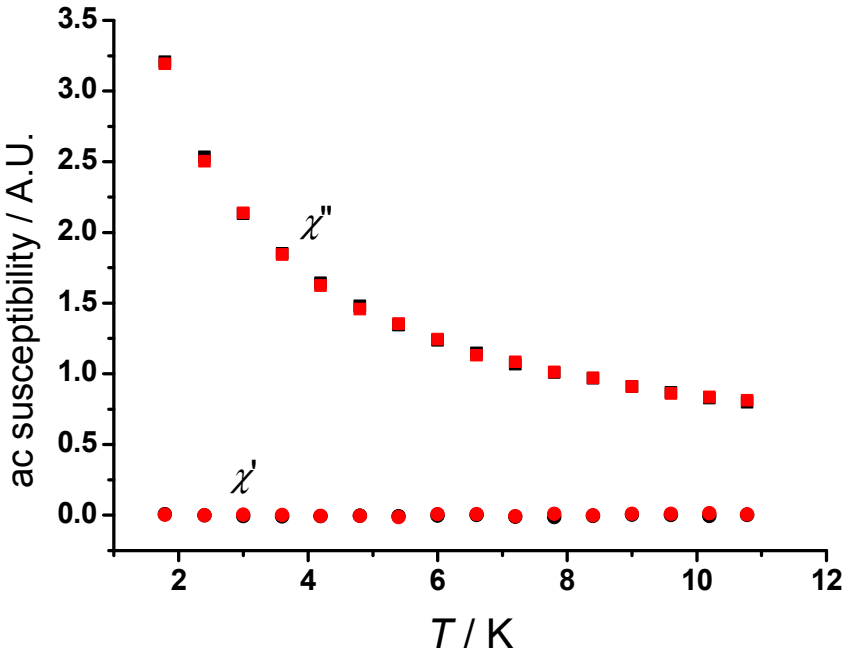
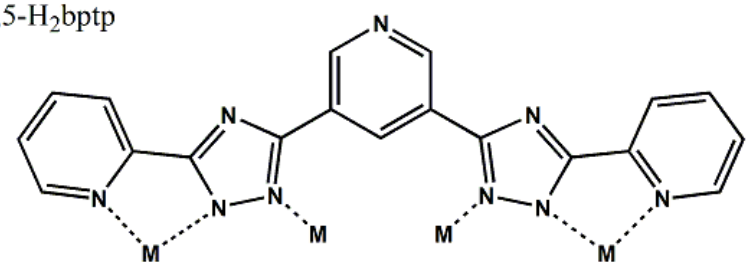
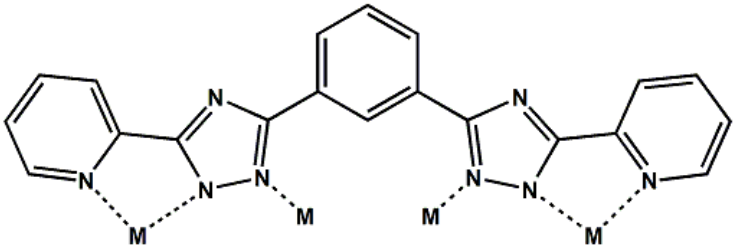


Figure S6. Temperature dependence of AC magnetic susceptibility at various frequency of **2**. Color code: black, 1 Hz; red, 1488 Hz.

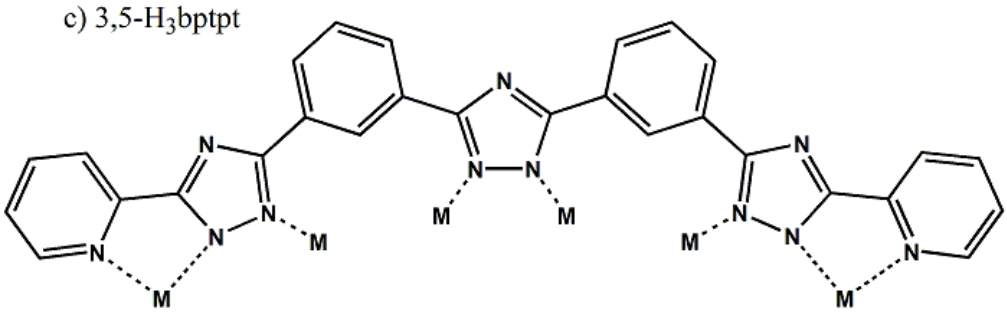
a) 3,5-H_2bptp



b) 1,3-H_2bptb



c) 3,5-H_3bptpt



Scheme S1. Coordination modes of the three polytriazolate ligands.

Table S1. Selected interatomic distances (Å) and angles (deg) for complex **2**.

Co1-O1	1.890(3)	Co3-O2	2.044(3)
Co1-O6^{i}	1.910(4)	Co3-N32	2.046(4)
Co1-N15	2.013(4)	Co3-N25	2.109(4)
Co1-N5	2.016(4)	Co3-N7	2.126(4)
Co2-O1	2.035(4)	Co3-N8	2.164(4)
Co2-N16	2.044(4)	Co3-N31	2.429(5)
Co2-N6	2.107(4)	Co4-O2	1.924(3)
Co2-N26	2.109(4)	Co4-O3	1.951(3)
Co2-N27	2.213(5)	Co4-N24	2.049(4)
Co2-N17	2.375(5)	Co4-N33	2.083(4)
Co5-O4	1.932(3)	Co7-O5	2.034(3)
Co5-O3	1.965(3)	Co7-N13^{i}	2.049(4)
Co5-N23	2.056(4)	Co7-N3^{i}	2.108(4)
Co5-N34	2.063(4)	Co7-N21	2.130(4)
Co6-N35	2.034(4)	Co7-N20	2.208(5)
Co6-O4	2.057(3)	Co7-N12^{i}	2.372(5)
Co6-N2^{i}	2.111(4)	Co8-O5	1.906(3)
Co6-N22	2.139(4)	Co8-O6	1.934(4)
Co6-N1^{i}	2.188(4)	Co8-N14^{i}	2.006(4)
Co6-N36	2.359(5)	Co8-N4^{i}	2.024(4)
O1-Co1-O6^{i}	116.17(15)	O2-Co3-N32	85.59(15)
O1-Co1-N15	97.99(17)	O2-Co3-N25	100.38(16)
O6^{i}-Co1-N15	120.73(18)	N32-Co3-N25	100.89(16)
O1-Co1-N5	124.39(16)	O2-Co3-N7	92.04(14)
O6^{i}-Co1-N5	97.82(17)	N32-Co3-N7	167.69(17)
N15-Co1-N5	100.48(17)	N25-Co3-N7	91.42(16)
O1-Co2-N16	85.97(16)	O2-Co3-N8	96.18(16)
O1-Co2-N6	98.29(16)	N32-Co3-N8	91.96(17)
N16-Co2-N6	104.67(17)	N25-Co3-N8	159.70(17)
O1-Co2-N26	92.99(15)	N7-Co3-N8	76.26(16)
N16-Co2-N26	161.41(18)	O2-Co3-N31	156.34(15)
N6-Co2-N26	93.86(17)	N32-Co3-N31	71.41(17)
O1-Co2-N27	91.25(17)	N25-Co3-N31	79.25(18)
N16-Co2-N27	85.54(18)	N7-Co3-N31	111.61(16)
N6-Co2-N27	166.41(18)	N8-Co3-N31	90.23(18)
N26-Co2-N27	75.91(18)	O2-Co4-O3	127.06(14)
O1-Co2-N17	156.69(14)	O2-Co4-N24	124.17(15)
N16-Co2-N17	72.19(17)	O3-Co4-N24	101.28(15)
N6-Co2-N17	80.01(16)	O2-Co4-N33	93.09(15)
N26-Co2-N17	110.31(16)	O3-Co4-N33	107.05(15)
N27-Co2-N17	95.00(18)	N24-Co4-N33	98.05(15)
O4-Co5-O3	128.77(14)	O5-Co7-N13i	85.30(16)

O4-Co5-N23	123.51(15)	O5-Co7-N3i	101.48(15)
O3-Co5-N23	101.93(15)	N13^{i}-Co7-N3i	105.95(17)
O4-Co5-N34	94.82(15)	O5-Co7-N21	89.83(15)
O3-Co5-N34	105.72(15)	N13^{i}-Co7-N21	162.47(17)
N23-Co5-N34	93.30(15)	N3^{i}-Co7-N21	91.52(16)
N35-Co6-O4	86.00(15)	O5-Co7-N20	97.94(15)
N35-Co6-N2^{i}	165.25(17)	N13^{i}-Co7-N20	88.01(17)
O4-Co6-N2^{i}	92.75(14)	N3^{i}-Co7-N20	156.85(17)
N35-Co6-N22	101.73(16)	N21-Co7-N20	75.98(16)
O4-Co6-N22	98.23(15)	O5-Co7-N12^{i}	156.25(15)
N2^{i}-Co6-N22	93.00(16)	N13^{i}-Co7-N12^{i}	71.51(17)
N35-Co6-N1^{i}	89.40(16)	N3^{i}-Co7-N12^{i}	80.70(16)
O4-Co6-N1^{i}	91.97(14)	N21-Co7-N12^{i}	113.85(16)
N2*i*-Co6-N1^{i}	75.95(16)	N20-Co7-N12^{i}	86.60(17)
N22-Co6-N1^{i}	165.35(16)	O5-Co8-O6	116.13(16)
N35-Co6-N36	72.46(17)	O5-Co8-N14^{i}	96.49(16)
O4-Co6-N36	156.69(15)	O6-Co8-N14^{i}	119.99(17)
N2^{i}-Co6-N36	110.35(17)	O5-Co8-N4^{i}	126.29(16)
N22-Co6-N36	78.10(15)	O6-Co8-N4^{i}	96.53(17)
N1^{i}-Co6-N36	96.52(16)	N14^{i}-Co8-N4^{i}	102.57(17)