Electronic Supporting Information (ESI)

Synthesis and Ferrimagnetic Properties of an Unprecedented Polynuclear Cobalt Complex Composed of [Co_{24}] Macrocycles

Song-De Han,[a] Wei-Chao Song,[a] Jiong-Peng Zhao,[a,b] Qian Yang,[a] Sui-Jun Liu,[a] Yue Li[a] and Xian-He Bu*[a]

[a]*Department of Chemistry, and TKL of Metal- and Molecule-Based Material Chemistry, Nankai University, Tianjin 300071, P. R. China.*

[b]*School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China.*

*Corresponding author. E-mail: buxh@nankai.edu.cn. Fax: +86-22-23502458

Experimental Section

Materials and methods.

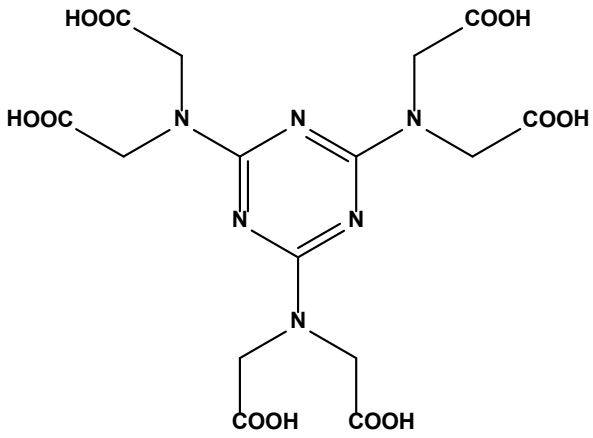
All chemicals were reagent grade and used as purchased without further purification.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were measured on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. UV-VIS absorption spectra were measured with a UV-3600 (SHIMADZU) spectrophotometer. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 FOCUS diffractometer equipped with a SOL-X Si(Li) detector using Cu Kα radiation (40kV, 40mA). Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. The magnetic measurements were performed by using an MPMS XL-5 SQUID magnetometer with polycrystals of **1**. With the assistance of a ^{3}He system (at Tianjin Normal University), measurements can be manipulated at 0.5 K. Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

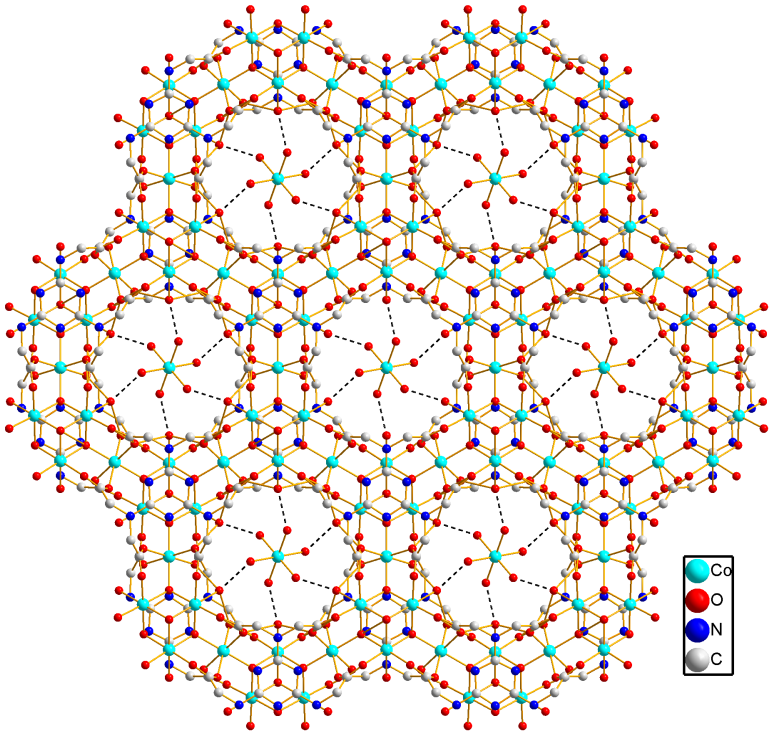
X-ray Crystallography.

The crystallographic data of **1** was collected on a Rigaku Saturn724+ diffractometer at 113 K with Mo-Kα radiation (λ = 0.71073 Å). The program SAINT[1] was used for integration of the diffraction profiles. The crystal data of **1** was solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[2] Anisotropic thermal parameters were used to refine all the non-H atoms and solvent O4w molecules. Full crystallographic data for **1** has been deposited with the CCDC (868337). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

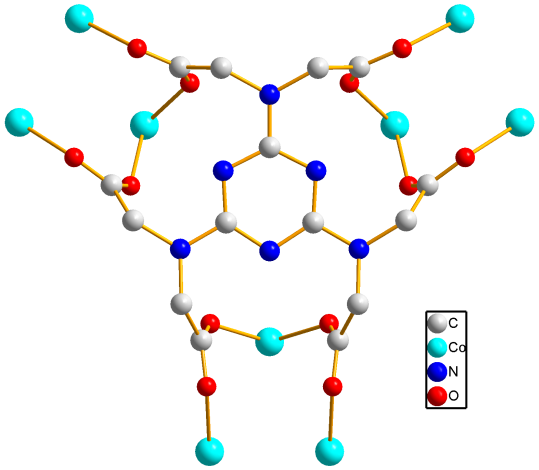
via www.ccdc.cam.ac.uk/data_request/cif.



Scheme S1 1,3,5-triazine-2,4,6-triamine hexaacetic acid (H_6TTHA)



Scheme S2 The 2D layer of **1** along the *c* axis.



Scheme S3 The bridging mode of the ligand.

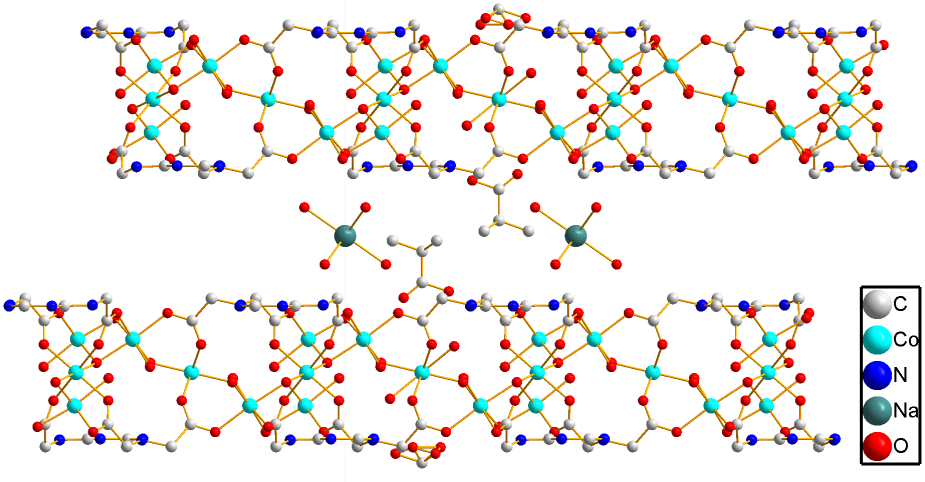


Fig. S1 $(CH_3)_3CCOO^-$ and $[Na(H_2O)_6]^+$ located among the 2D layers of **1** along the *b* axis.

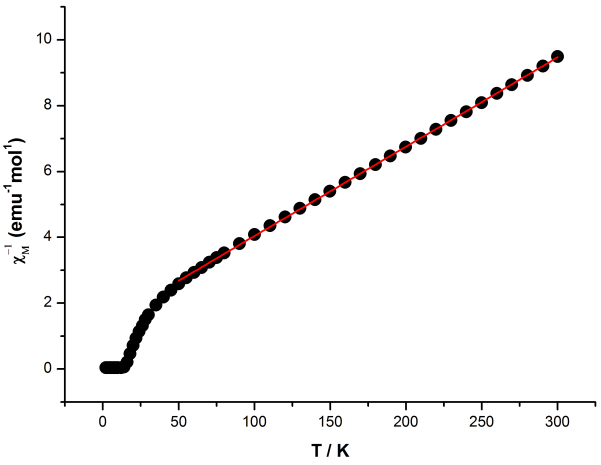


Fig. S2 The Curie-Weiss plot of **1**. Solid line represents the best fit.

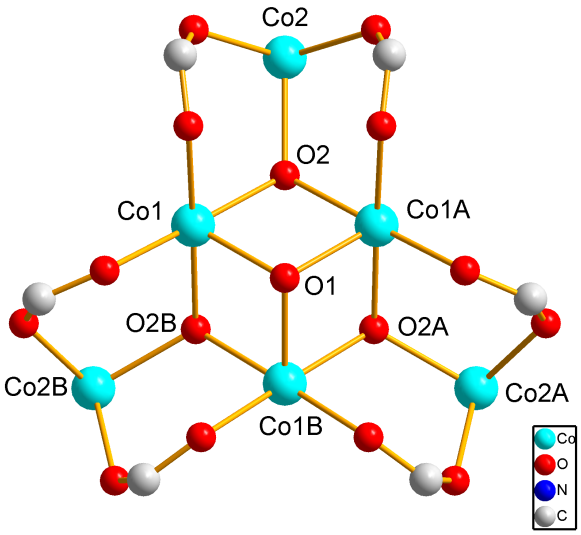


Fig. S3 Magnetic exchange ways between the Co^{II} ions in **1**.

Table S1 The number and type of the exchange ways between the Co^{II} ions and the interactions of the macrocycle.

Coupling	Metal ions	Number of bridges		M-μ_3-O-M(°)	Interactions	Ref:
		syn-syn	μ_3-O			
J_1	Co1-Co1A		2	97.5(2) / 94.80(15)	F	3,4,5
J_2	Co1-Co1B		2	97.5(2) / 94.80(15)	F	3,4,5
J_3	Co1A-Co1B		2	97.5(2) / 94.80(15)	F	3,4,5
J_4	Co2-Co1	1	1	121.11(12)	AF	3,4,5
J_5	Co2-Co1A	1	1	121.11(12)	AF	3,4,5
J_6	Co2A-Co1A	1	1	121.11(12)	AF	3,4,5
J_7	Co2A-Co1B	1	1	121.11(12)	AF	3,4,5
J_8	Co2B-Co1	1	1	121.11(12)	AF	3,4,5
J_9	Co2B-Co1B	1	1	121.11(12)	AF	3,4,5

The *syn-syn* carboxylate conduct strong antiferromagnetic interactions between metal ions, while the interactions conducted by the μ_3-O atom depend on the Co-O-Co angle. Large Co-O-Co angles lead to antiferromagnetic interactions while small ones induce ferromagnetic couplings. As reported by Zeng, the intracube Co-μ_3-O-Co angles ranging from 94.5 to 102.1°, should favor ferromagnetic interactions for the significant orbital orthogonality between the metal centers and the bridging atom. So, the coupling of the intra-trimeric units is ferromagnetic and the coupling between the trimeric units and neighbouring monomeric units is antiferromagnetic.

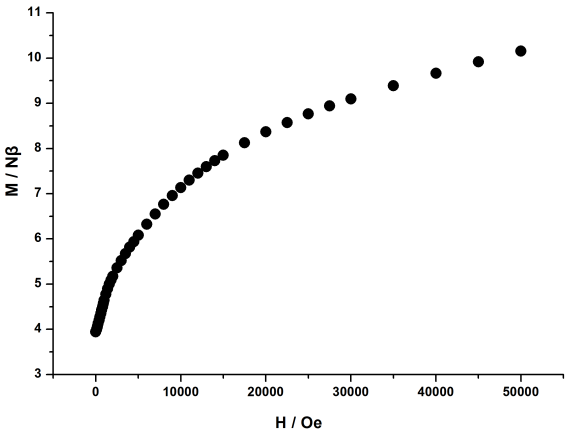


Fig. S4 Field dependence of the magnetization (*M*) of **1** at 2 K.

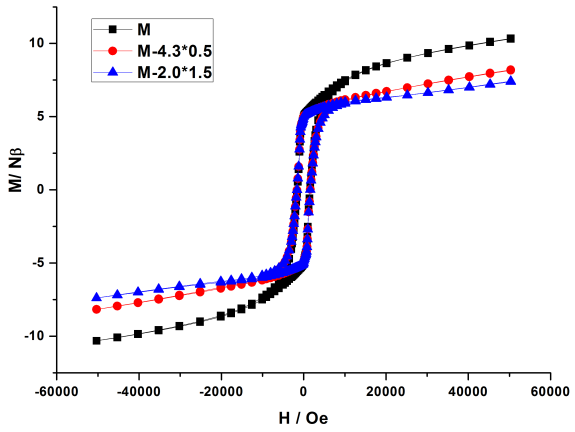


Fig. S5 Plots of hysteresis loop of **1** (black squares) and the anionic network $[Co_9(OH)_7(H_2O)_7(TTHA)_2]^-$ (blue triangles with S= 3/2 and g = 2.0 for one $[Co(H_2O)_6]^{2+}$ ion; red circles with S = 1/2 and g = 4.3 for one $[Co(H_2O)_6]^{2+}$ ion) at 2 K.

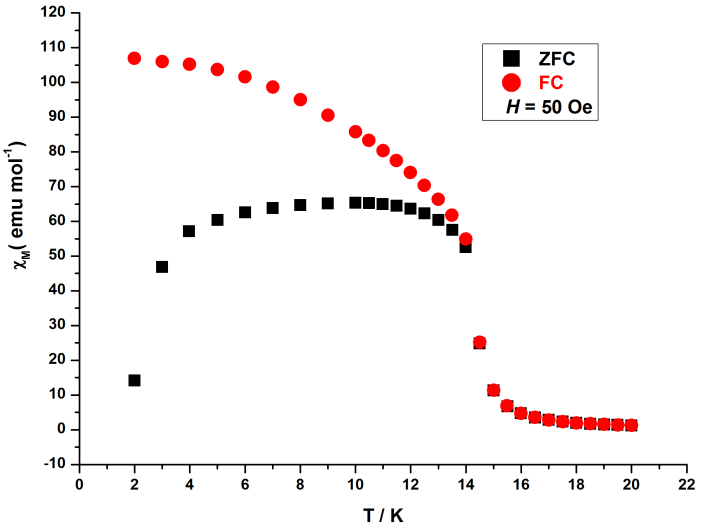


Fig. S6 FC and ZFC magnetization of **1** in the dc field of 50 Oe.

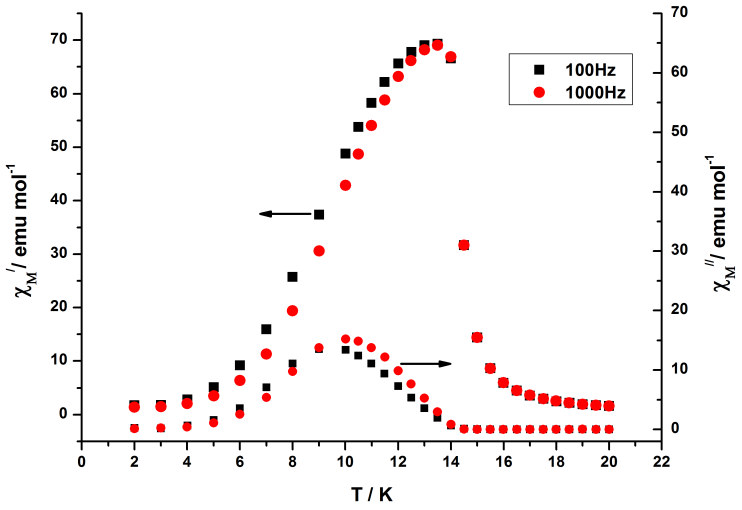


Fig. S7 Plot of the in-phase (χ'_M) and out-of-phase (χ''_M) ac susceptibility signals for complex **1.**

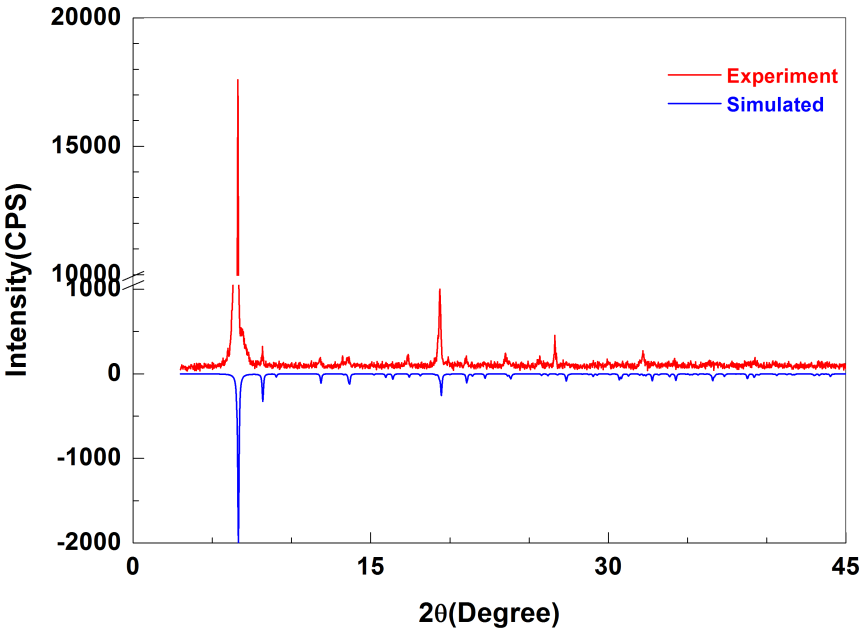


Fig. S8 RXPD patterns of **1**.

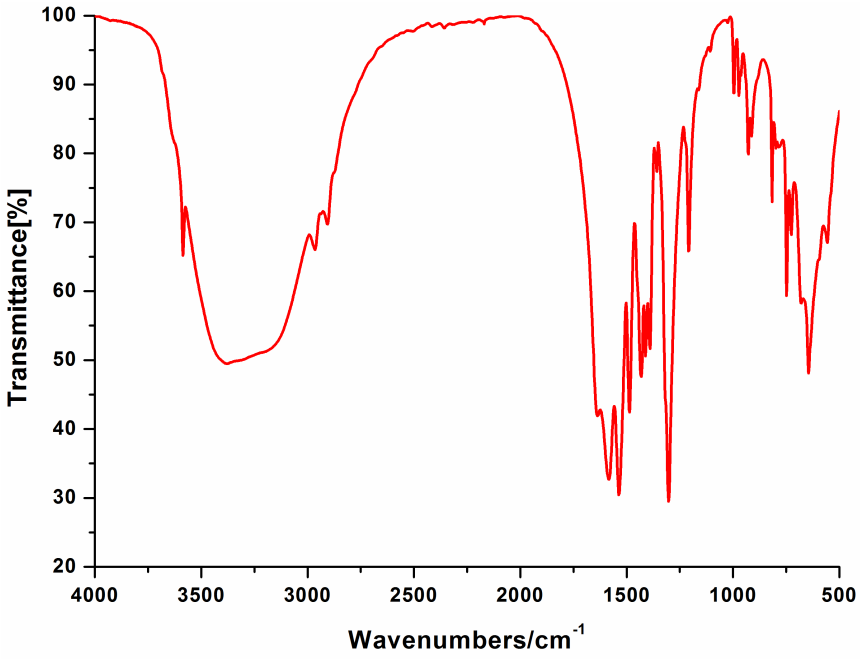


Fig. S9 IR spectra of **1**.

The presence of a broadband centered at 3380 cm^{-1} and the small sharp band at 3586 cm^{-1} may imply the stretching vibrations of water molecules, and its intensity and complexity reflects the intricate and extensive system of hydrogen bond found in **1**.[6] The weak bands at 2964 and 2906 cm^{-1} may be ascribe to the C-H stretching vibrations.[7] The bands at about 1636, 1583 and 1536 cm^{-1} may be attributed to the carboxylate groups.[8] No strong absorption peaks around 1700 cm^{-1} for -COOH are observed, indicating that carboxylic groups of organic moieties in **1** are completely deprotonated.[9] The expected characteristic band at about 1303 cm^{-1} for the C-N bond also appeared in **1**.[8b,8c,10]

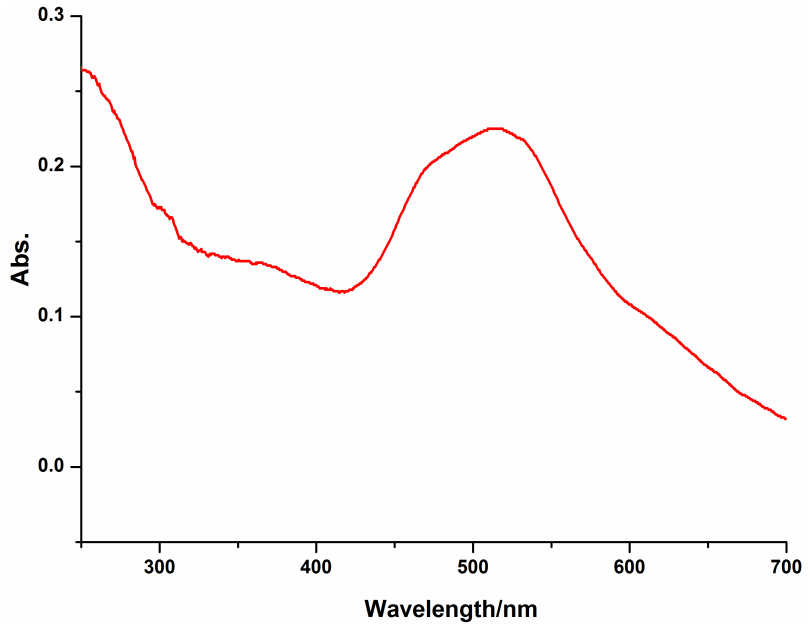


Fig. S10 UV-VIS spectra of **1**.

Table S2 The selected bond lengths [Å] and angles [º] of compound **1**.

Co(1)-O(1)	2.064(3)	Co(1)-O(2)#1	2.108(2)
Co(1)-O(2)	2.108(2)	Co(1)-O(5)#2	2.113(2)
Co(1)-O(5)	2.113(2)	Co(1)-O(3W)	2.133(3)
Co(2)-O(2)	2.050(3)	Co(2)-O(2)#3	2.050(3)
Co(2)-O(3)#4	2.111(2)	Co(2)-O(3)#5	2.111(2)
Co(2)-O(3)#3	2.111(2)	Co(2)-O(3)	2.111(2)
Co(3)-O(1W)	2.095(5)	Co(3)-O(1W)#4	2.095(5)
Co(3)-O(1W)#6	2.095(5)	Co(3)-O(1W)#7	2.095(5)
Co(3)-O(1W)#8	2.095(5)	Co(3)-O(1W)#9	2.095(5)
Co(3)-O(1W)#10	2.095(5)	Co(3)-O(1W)#11	2.095(5)
Co(3)-O(1W)#12	2.095(5)	Co(3)-O(1W)#13	2.095(5)
Co(3)-O(1W)#14	2.095(5)	Co(3)-O(1W)#15	2.095(5)
O(1)-Co(1)#1	2.064(3)	O(1)-Co(1)#16	2.064(3)
O(2)-Co(1)#16	2.108(2)		
O(1)-Co(1)-O(2)#1	83.78(13)	O(1)-Co(1)-O(2)	83.78(13)
O(2)#1-Co(1)-O(2)	91.5(2)	O(1)-Co(1)-O(5)#2	94.21(14)
O(2)#1-Co(1)-O(5)#2	92.08(12)	O(2)-Co(1)-O(5)#2	175.70(12)
O(1)-Co(1)-O(5)	94.21(14)	O(2)#1-Co(1)-O(5)	175.70(12)
O(2)-Co(1)-O(5)	92.08(12)	O(5)#2-Co(1)-O(5)	84.26(14)
O(1)-Co(1)-O(3W)	170.71(19)	O(2)#1-Co(1)-O(3W)	89.75(10)

O(2)-Co(1)-O(3W)	89.75(10)	O(5)#2-Co(1)-O(3W)	92.67(10)
O(5)-Co(1)-O(3W)	92.67(10)	O(2)-Co(2)-O(3)#4	93.84(10)
O(2)#3-Co(2)-O(3)#4	86.17(10)	O(2)-Co(2)-O(3)#5	86.16(10)
O(2)#3-Co(2)-O(3)#5	93.83(10)	O(2)-Co(2)-O(3)#3	86.16(10)
O(2)#3-Co(2)-O(3)#3	93.83(10)	O(3)#4-Co(2)-O(3)#3	86.50(13)
O(3)#5-Co(2)-O(3)#3	93.50(13)	O(2)-Co(2)-O(3)	93.84(10)
O(2)#3-Co(2)-O(3)	86.17(10)	O(3)#4-Co(2)-O(3)	93.50(13)
O(3)#5-Co(2)-O(3)	86.50(13)	O(1W)-Co(3)-O(1W)#4	30.9(3)
O(1W)-Co(3)-O(1W)#6	149.1(3)	O(1W)#4-Co(3)-O(1W)#7	149.1(3)
O(1W)#6-Co(3)-O(1W)#7	30.9(3)	O(1W)-Co(3)-O(1W)#8	93.42(19)
O(1W)#4-Co(3)-O(1W)#8	118.4(3)	O(1W)#6-Co(3)-O(1W)#8	61.6(3)
O(1W)#7-Co(3)-O(1W)#8	86.58(19)	O(1W)-Co(3)-O(1W)#9	86.58(19)
O(1W)#4-Co(3)-O(1W)#9	61.6(3)	O(1W)#6-Co(3)-O(1W)#9	118.4(3)
O(1W)#7-Co(3)-O(1W)#9	93.42(19)	O(1W)-Co(3)-O(1W)#10	93.42(19)
O(1W)#4-Co(3)-O(1W)#10	77.7(3)	O(1W)#6-Co(3)-O(1W)#10	102.3(3)
O(1W)#7-Co(3)-O(1W)#10	86.58(19)	O(1W)#8-Co(3)-O(1W)#10	86.58(19)
O(1W)#9-Co(3)-O(1W)#10	93.42(19)	O(1W)-Co(3)-O(1W)#11	86.58(19)
O(1W)#4-Co(3)-O(1W)#11	102.3(3)	O(1W)#6-Co(3)-O(1W)#11	77.7(3)
O(1W)#7-Co(3)-O(1W)#11	93.42(19)	O(1W)#8-Co(3)-O(1W)#11	93.42(19)
O(1W)#9-Co(3)-O(1W)#11	86.58(19)	O(1W)-Co(3)-O(1W)#12	118.4(3)
O(1W)#4-Co(3)-O(1W)#12	93.42(19)	O(1W)#6-Co(3)-O(1W)#12	86.58(19)
O(1W)#7-Co(3)-O(1W)#12	61.6(3)	O(1W)#8-Co(3)-O(1W)#12	102.3(3)
O(1W)#9-Co(3)-O(1W)#12	77.7(3)	O(1W)#10-Co(3)-O(1W)#12	30.9(3)

O(1W)#11-Co(3)-O(1W)#12	149.1(3)	O(1W)-Co(3)-O(1W)#13	77.7(3)
O(1W)#4-Co(3)-O(1W)#13	93.42(19)	O(1W)#6-Co(3)-O(1W)#13	86.58(19)
O(1W)#7-Co(3)-O(1W)#13	102.3(3)	O(1W)#8-Co(3)-O(1W)#13	30.9(3)
O(1W)#9-Co(3)-O(1W)#13	149.1(3)	O(1W)#10-Co(3)-O(1W)#13	61.6(3)
O(1W)#11-Co(3)-O(1W)#13	118.4(3)	O(1W)#12-Co(3)-O(1W)#13	86.58(19)
O(1W)-Co(3)-O(1W)#14	102.3(3)	O(1W)#4-Co(3)-O(1W)#14	86.58(19)
O(1W)#6-Co(3)-O(1W)#14	93.42(19)	O(1W)#7-Co(3)-O(1W)#14	77.7(3)
O(1W)#8-Co(3)-O(1W)#14	149.1(3)	O(1W)#9-Co(3)-O(1W)#14	30.9(3)
O(1W)#10-Co(3)-O(1W)#14	118.4(3)	O(1W)#11-Co(3)-O(1W)#14	61.6(3)
O(1W)#12-Co(3)-O(1W)#14	93.42(19)	O(1W)-Co(3)-O(1W)#15	61.6(3)
O(1W)#4-Co(3)-O(1W)#15	86.58(19)	O(1W)#6-Co(3)-O(1W)#15	93.42(19)
O(1W)#7-Co(3)-O(1W)#15	118.4(3)	O(1W)#8-Co(3)-O(1W)#15	77.7(3)
O(1W)#9-Co(3)-O(1W)#15	102.3(3)	O(1W)#10-Co(3)-O(1W)#15	149.1(3)
O(1W)#11-Co(3)-O(1W)#15	30.9(3)	O(1W)#13-Co(3)-O(1W)#15	93.42(19)
O(1W)#14-Co(3)-O(1W)#15	86.58(19)		
Symmetry transformations used to generate equivalent atoms: #1: -y+1, x-y+1, z; #2: -y+1,-x+1,z; #3: -x+1,-y+2, -z; #4: -x+y, y, z; #5: x-y+1, -y+2, -z; #6: x-y, -y, -z; #7: -x, -y, -z; #8: x-y, x, -z; #9: -x+y, -x, z; #10: y, -x+y, -z; #11: -y, x-y, z; #12: y, x, -z; #13: -x, -x+y, -z; #14: x, x-y, z; #15: -y, -x, z; #16: -x+y, -x+1, z.			

Reference

1. *Bruker AXS, SAINT Software Reference Manual*, Madison, WI, 1998.

2. (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

3. M.-H. Zeng, M.-X. Yao, H. Liang, W.-X. Zhang, and X.-M. Chen, *Angew. Chem., Int. Ed.,* 2007, **46**, 1832.

4. E. C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezmagairaud, and G. Christou, *J. Appl. Phys.*, 2002, **91**, 7382.

5. W. E. Hatfield in *Magneto-Structural Correlations in Exchange Coupled Systems* (Eds.: R. D. Willet, D. Gatteschi, O. Kahn), Reidel, Dordrecht, The Netherlands, 1984, p. 555.

6. (a) J.-G. Wang, C.-C. Huang, X.-H. Huang, and D.-S. Liu, *Cryst. Growth Des.*, 2008, **8**, 795; (b) D. Dobrzyńska, L. B. Jerzykiewicz, J. Jezierska, and M. Duczmal, *Crystal Growth & Design*, 2005, **5**, 1945.

7. C.-R. Li, S.-L. Li, and X.-M. Zhang, *Cryst. Growth Des.,* 2009*,* **9**, 1702.

8. (a) H. Y. Wang, S. Gao, L. H. Huo, S. W. Ng, J. G. Zhao, *Cryst. Growth Des.,* 2008, **8**, 665; (b) Q. Zhu, T. Sheng, R. Fu, S. Hu, J. Chen, S. Xiang, C. Shen and X. Wu, *Cryst. Growth Des.,* 2009, **9**, 5128; (c) Q. Zhu, T. Sheng, R. Fu, S. Hu, C. Shen, X. Ma and X. Wu, *CrystEngComm*, 2011, **13**, 2096;

9. L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley: New York, 1958.

10. (a) X. Zhu, C. Tian, S. M. Mahurin, S. H. Chai, C. Wang, S. Brown, G. M. Veith, H. Luo, H. Liu, and S. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 10478; (b) P. Kuhn, M. Antonietti, and A. Thomas, *Angew. Chem. Int. Ed.,* 2008, **47**, 3450.