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Supporting information for article:

Targeted synthesis of a polypyridyl polyoxometalate coordination complex using microwave-assisted reaction conditions

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Materials, Instrumentation, and Methods

Chemicals

4,4’-Dipyridyl (Sigma), 4-Aminopyridine (Sigma), methanol (Chem supply), acetonitrile (Unilab), hexane (ACI Labscan), ethyl acetate (EMSURE), Deuterium oxide (Sigma).

Bond Valence Sum Calculations

Bond valence sum calculations were performed using the bond valence calculator, version 2.00 February 1993, written by C. Hormillosa, S. Healy and revised by T. Stephen. [1]

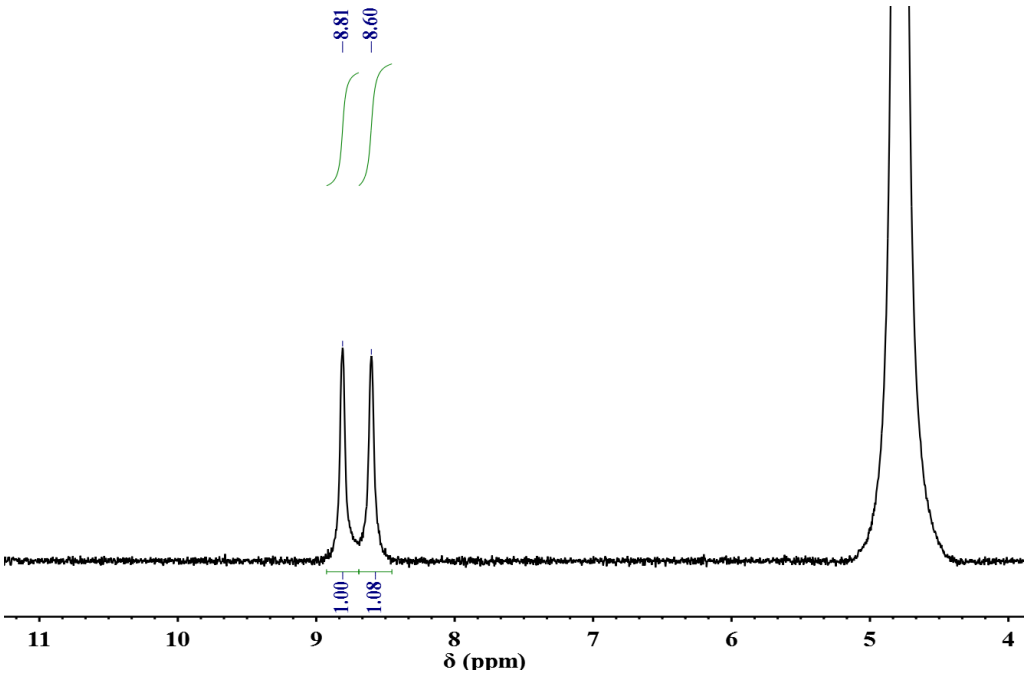
Synthesis and Analysis

Microwave experiments were conducted using a Biotage Initiator Classic, using 2-5 mL reaction vessels.

Materials and chemicals

$K_8[BW_{11}O_{39}H]\cdot 13H_2O$ was prepared as described in literature.[2] 2,4,6-tri(4-pyridyl)-1,3,5-triazine was prepared as described in literature.[3] 4,4'-azopyridine was prepared as described in the literature.[4] All other materials were prepared by modification of literature procedures or used as purchased where stated.

^{1}H NMR



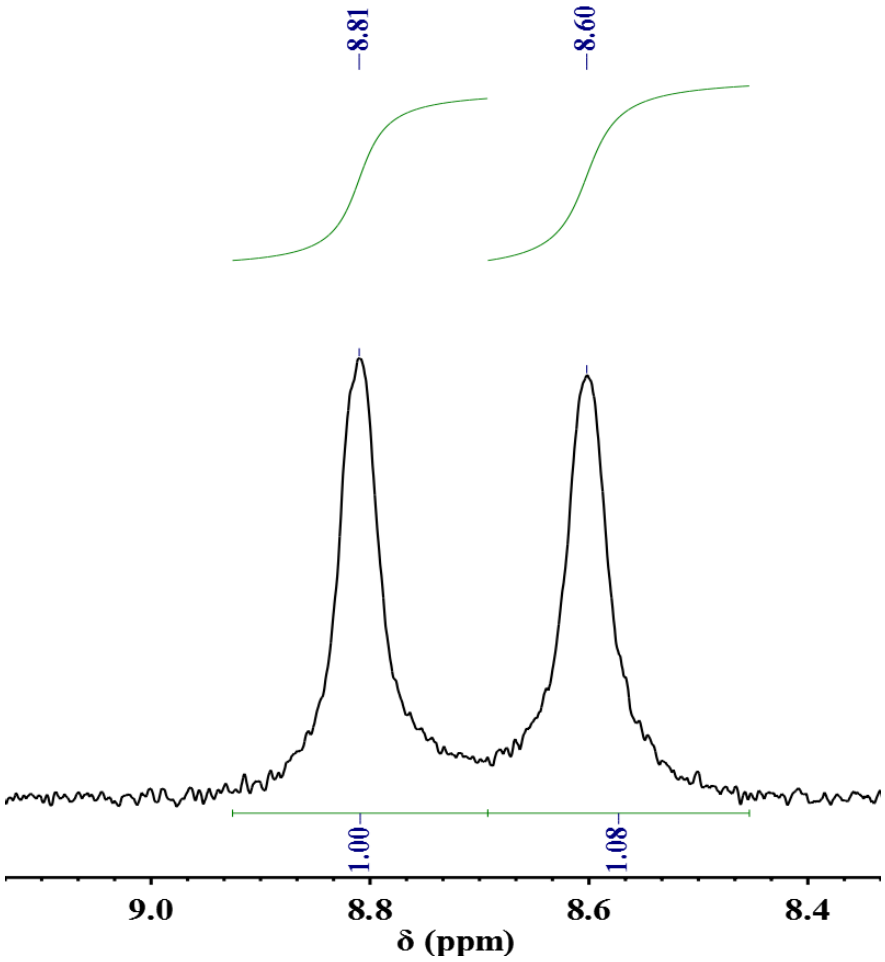


Figure S1. ^{1}H NMR spectrum of compound **(1)**.

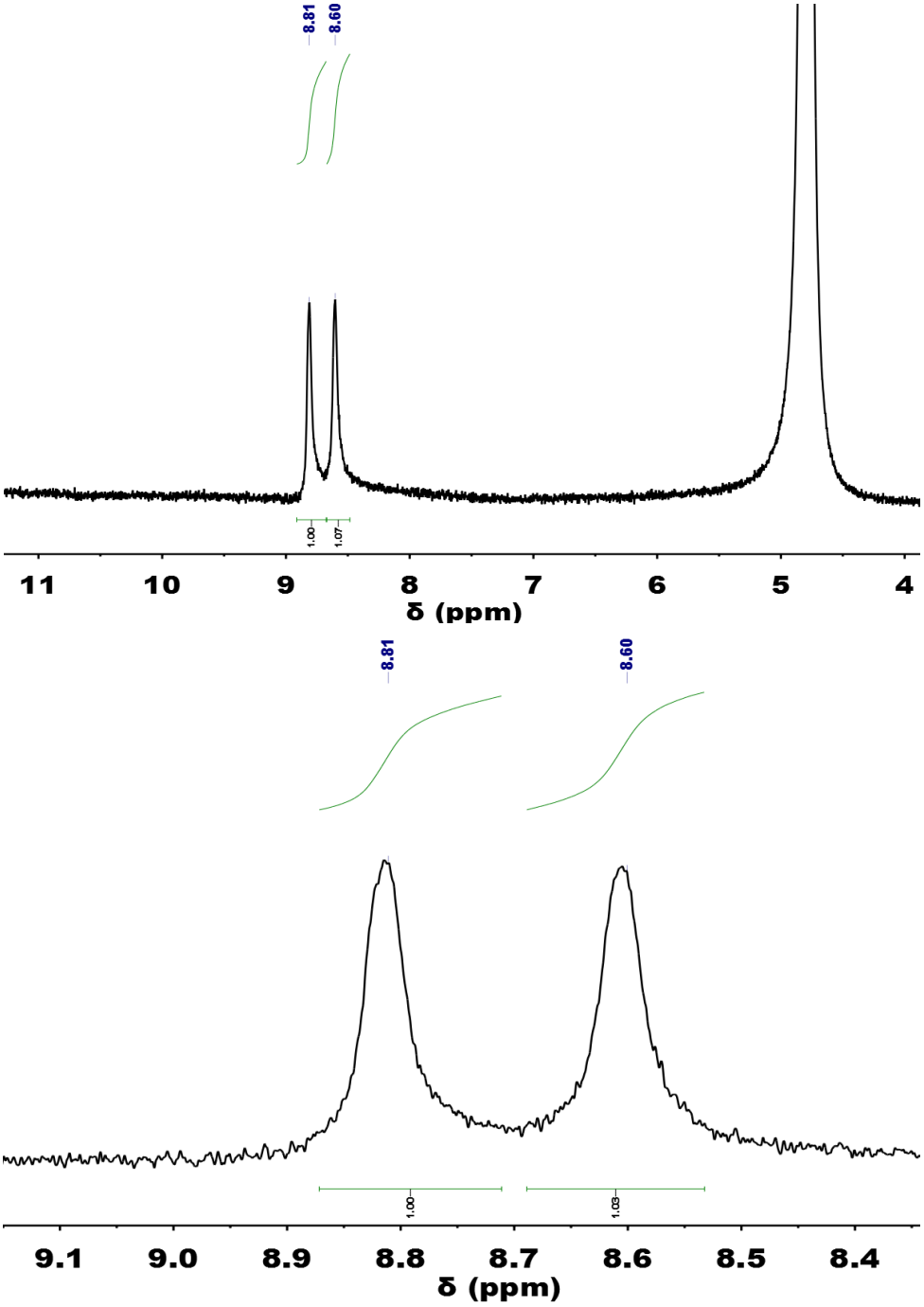


Figure S2. ^{1}H NMR spectrum of compound (**1**) after 20 days.

IR (KBr)

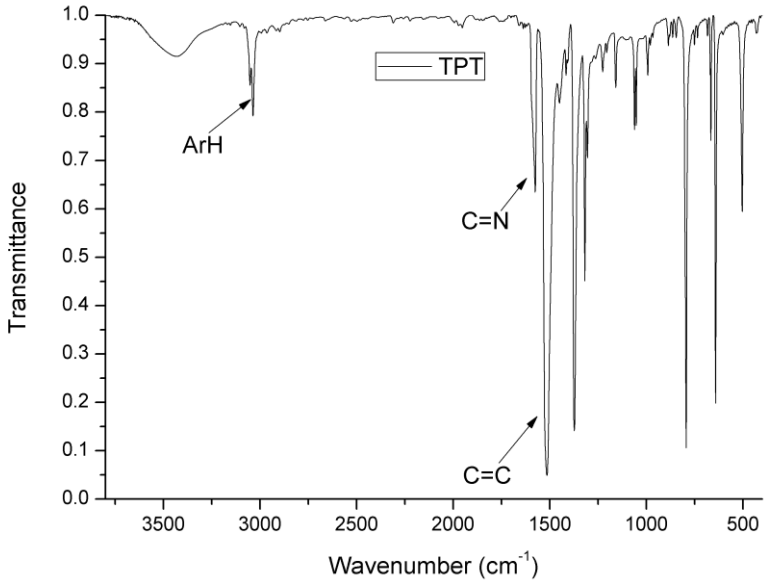


Figure S3. FT-IR spectrum of TPT [5]

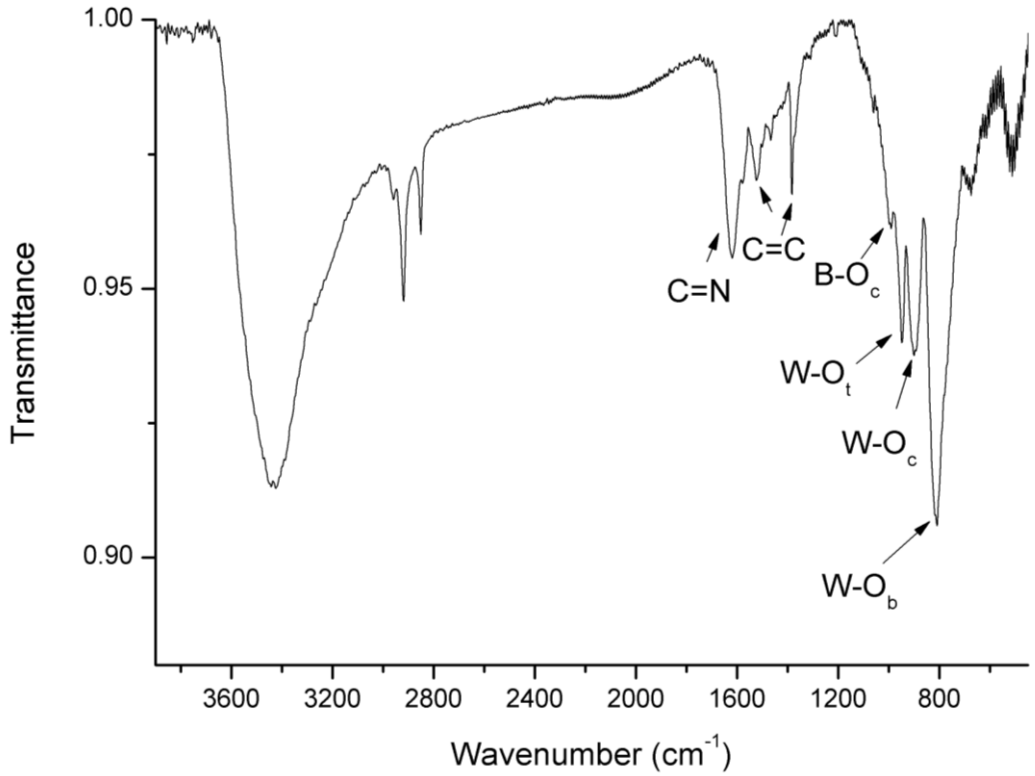


Figure S4. FT-IR spectrum of **(1)**

UV-Visible Spectroscopy

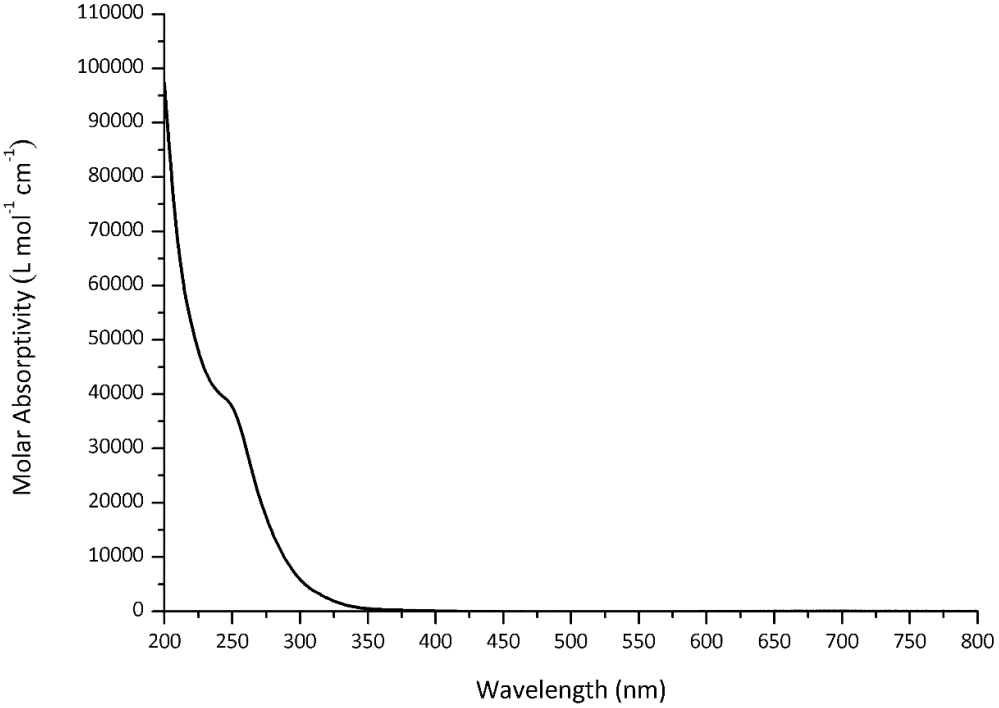


Figure S5. UV-Vis spectrum of ($Ba_3[B^{III}W^{VI}_{11}O_{39}Co^{III}(H_2O)]$). [(10 µM) in water. λ_{max} = 241 nm, ε = 4 ×10^4 L mol^{-1} cm^{-1}]

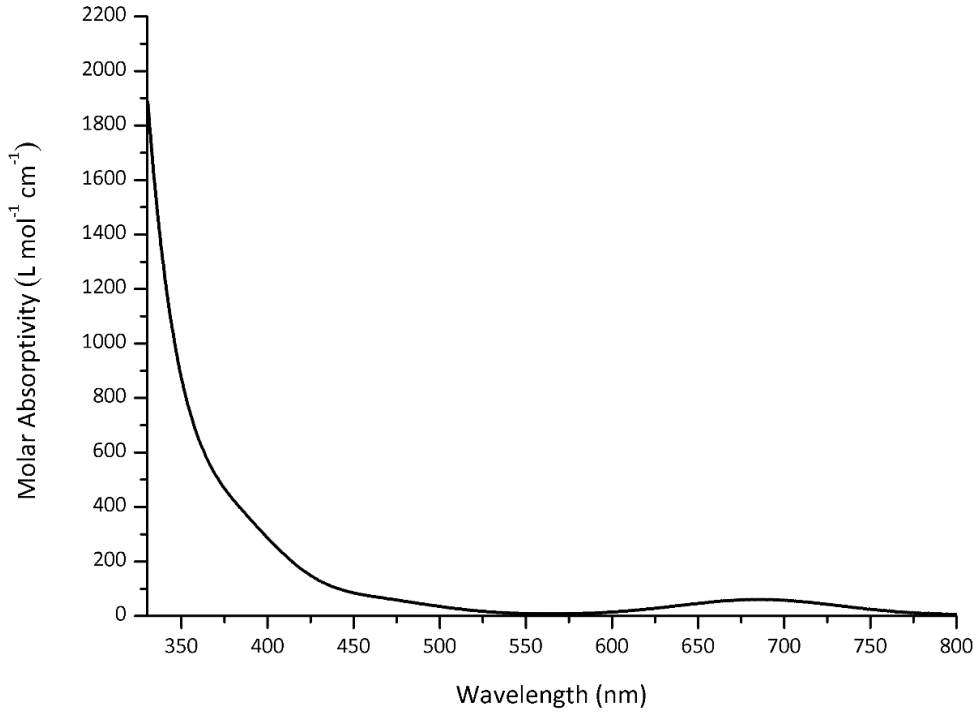


Figure S6. UV-Vis spectrum of ($Ba_3[B^{III}W^{VI}_{11}O_{39}Co^{III}(H_2O)]$), [(0.5 mM) in water. λ_{max} = 688 nm, ε = 6.14 × 10 L mol^{-1} cm^{-1}]

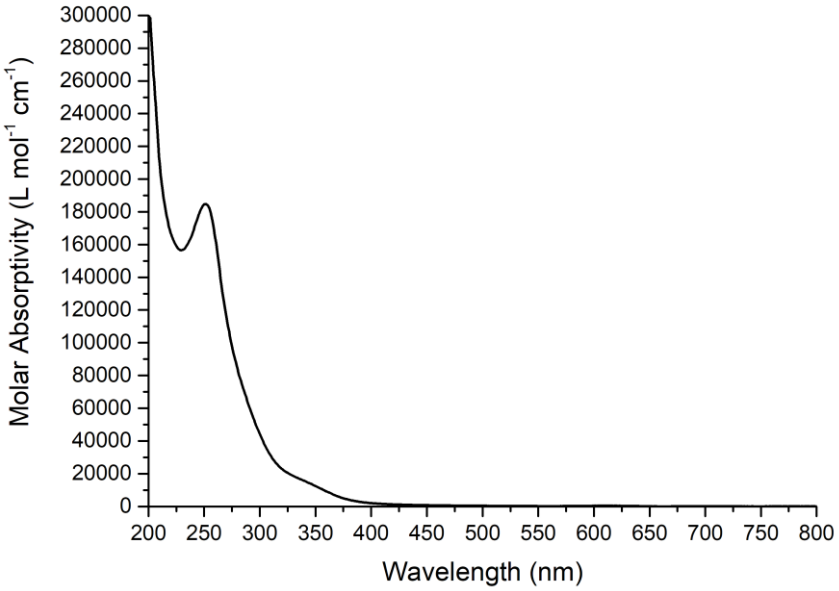


Figure S7. UV-Vis spectrum of compound **(1)** (10 µM) in water.
[λ_{max} = 251.5 nm, ε = 1.85 × 10^5 L mol^{-1} cm^{-1}]

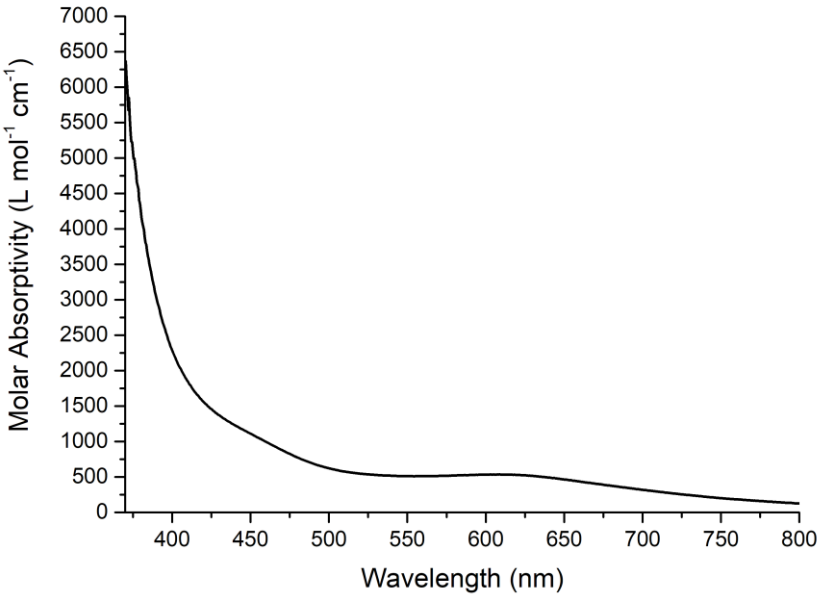


Figure S8. UV-Vis spectrum of compound **(1)**, (0.5 mM) in water.
[λ_{max} = 609 nm, ε = 5.34 × 10^2 L mol^{-1} cm^{-1}]

Thermogravimetric Analysis

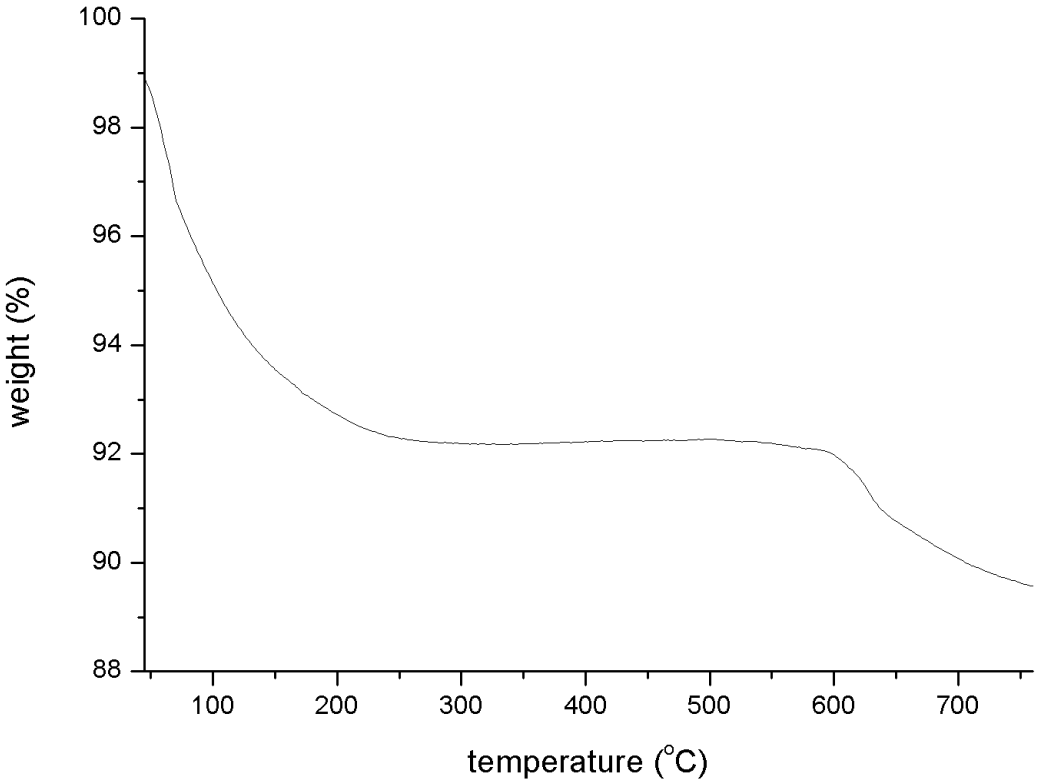


Figure S9. TGA data of compound **(1)**

Bond valence sum (BVS) calculation

The valence sum =∑ exp [(d_0 - d)/B] d_0 = 1.68 for Co, B = 0.37.

Table S1. Bond lengths and bond valence sum values for the three crystallographically independent cobalt ions in compound **(1)**.

Compound 1	**Co-O / Co-N**	**Bond length (Å)**	**Bond valence**
Co1	Co-O2	1.864	0.608
	Co-O36	1.874	0.592
	Co-O50	1.889	0.568
	Co-O15	1.943	0.491
	Co-O6	2.000	0.421
	Co-N5	1.908	0.540
BVS Sum			3.220
Co2	Co-O41	1.806	0.711
	Co-O63	1.870	0.598
	Co-O25	1.828	0.670
	Co-O44	1.788	0.746
	Co-O43	1.999	0.422
	Co-N1	1.925	0.516
BVS Sum			3.665
Co3	Co-O96	1.904	0.546
	Co-O89	1.972	0.454
	Co-O66	1.770	0.784
	Co-O60	1.880	0.582
	Co-O85	1.981	0.443
	Co-N6	1.955	0.476

BVS Sum	3.285

References

1 C. Hormillosa, S. Healy and T. Stephen, *Bond Valence Calculator version 2.00; Institute for Materials Research, McMaster University; Hamilton, Ontario*, 1993.
2 A. Tézé, M. Michelon and G. Hervé, *Inorg. Chem.*, 1997, **36**, 505–509.
3 J. Wang, F. Xu, T. Cai and Q. Shen, *Org. Lett.*, 2008, **10**, 445–448.
4 C. B. Aakeröy, S. Panikkattu, B. DeHaven and J. Desper, *CrystEngComm*, 2013, **15**, 463–470.
5 Z. Y. Fu, Y. Chen, J. Zhang, S. J. Liao, J. Mater. Chem, 2011, **21**, 7895–7897.