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**K(I)-M(II) (M = Co, Mn) heterometallic-(perfluorinated)organic frame-
works containing rare inorganic layered K–O–M linkages: synthesis,
crystal structure, and magnetic properties**

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Abstract

Reactions of a perfluorinated ligand tetrafluorophthalic acid (1,2-H₂BDC-F₄) with KNO₃ and M(OAc)₂ (M = Co, Mn) led to the formation of two perfluorinated metal-organic frameworks [CoK₂(1,2-BDC-F₄)₂(MeOH)]_n (**1**) and [MnK₂(1,2-BDC-F₄)₂(DMF)]_n (**2**), and their structures were characterized by elemental analyses, IR spectra, and single-crystal X-ray diffraction techniques. Both complexes show similar 2-D heterometallic-organic frameworks containing unusual layered inorganic K–O–M connectivities. In the structures of **1** and **2**, *ortho* fluorine atoms of 1,2-BDC-F₄ are bound to the K^I ion, while the other F atoms participate in the linkage of adjacent coordination layers forming a 3-D supramolecular architectures via intermolecular F...F interactions. Variable-temperature magnetic susceptibility studies indicate that complex **1** displays weak antiferromagnetic effect between adjacent Co(II) ions.

Keywords: Heterometallic-organic framework; Perfluorinated phthalate ligand; Crystal structure; Layered inorganic connectivity; Magnetic property

1. Introduction

Research on the discovery and synthesis of coordination polymers (CPs) or metal-organic frameworks (MOFs) remains an active and important area in crystal engineering, coordination and material chemistry due to the compounds interesting network structures and potential applications in gas storage, separation, luminescence, catalysis, and magnetism [1]. To realize their full potential, it is necessary to construct such crystalline materials with specific structure and functionality by deliberate design with appropriate selection of organic linkers and metal-containing units. Although fluorine containing molecules are of particular interest as the strong electron-withdrawing effect of fluorine group contributes to extraordinary functional properties and numerous applications [2], fluorinated organic ligands have scarcely been explored in the aspect

of inorganic-organic hybrids, especially MOFs or CPs. In this regard, MOFs with fluorinated *N*-containing heterocycle ligands (such as pyridine-type [3] and triazole-type compounds [4]) demonstrated remarkable abilities for induced-fit enclathration of organic molecules and high hydrogen adsorption. Perfluorinated aromatic dicarboxylic acids, such as 2,3,5,6-tetrafluoroterephthalic acid (1,4-H₂BDC-F₄) [5], 2,4,5,6-tetrafluoroisophthalic acid (1,3-H₂BDC-F₄) [6], and 3,4,5,6-tetrafluorophthalic acid (1,2-H₂BDC-F₄) [7], have emerged as ideal linkers for building fluorine-functionalized MOF materials since they have shown distinctive linking modes and peculiar variations in their physical properties when compared to their non-fluorinated analogues..

We are currently engaged in the synthesis and coordination chemistry studies of perfluorinated dicarboxylic acid ligands under variable reaction conditions [7, 8]. In our previous work, a solvent-tuning strategy utilizing 1,2-H₂BDC-F₄ has been successfully employed to construct two Cd(II) CPs [8b]. Very recently, we reported a convenient template-controlled method to prepare a series of isomeric water-soluble Ag(I) complexes with 1,2-BDC-F₄, which show different 2-D layered inorganic connectivities in solid state and exceptional antibacterial activity in aqueous solution [7a]. As a continuation of our work in the field of alkali-metal-induced assemblies of coordination polymers with perhalogenated benzenedicarboxylate derivatives [7b, 9]. We herein, present two perfluorinated 2-D heterometallic-organic frameworks [CoK₂(1,2-BDC-F₄)₂(MeOH)]_n (**1**) and [MnK₂(1,2-BDC-F₄)₂(DMF)]_n (**2**) assembled from M(OAc)₂ (M = Co, Mn) and 1,2-H₂BDC-F₄ in the presence of KNO₃. Both complexes have been characterized by single-crystal X-ray diffraction analyses, infrared spectra (IR), elemental analyses, X-ray powder diffraction (XRPD), and thermogravimetric analyses (TGA). Magnetic susceptibility of **1** suggests a weak antiferromagnetic coupling interactions between adjacent Co(II) ions.

2. Experimental

2.1. Materials and general methods

All chemicals were commercially available and used as received. Elemental analyses (C, H and N) were carried out on a PE-2400II (Perkin-Elmer) analyzer. Infrared spectra were recorded on a

Nicolet ESP 460 FT-IR spectrometer with KBr pellets in the range of 4000–400 cm^{-1} . Thermogravimetric analysis (TGA) experiments were performed on a Dupont thermal analyzer from room temperature to 800 $^{\circ}\text{C}$ (heating rate of 10 $^{\circ}\text{C min}^{-1}$, nitrogen stream). The X-ray powder diffraction (XRPD) patterns were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA for a Cu-target tube ($\lambda = 1.5406 \text{ \AA}$), and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via the Internet at <http://www.iucr.org>.

Magnetic data of **1** were collected using crushed crystals of the sample on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet. The data were corrected using Pascal's constants to calculate the diamagnetic susceptibility, and an experimental correction for the sample holder was applied.

2.2. Syntheses of complexes

2.2.1. Synthesis of $[\text{CoK}_2(1,2\text{-BDC-F}_4)_2(\text{MeOH})]_n$ (1**).** Complex **1** was prepared by mixing equal molar 1,2- $\text{H}_2\text{BDC-F}_4$ (71.4 mg, 0.3 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (87.3 mg, 0.3 mmol) and KNO_3 (30.3 mg, 0.3 mmol) in the MeOH/DMF mixed solvents (*v/v*, 9mL/3mL). After *ca.* 30 min of being stirred, the purple solution was filtered and left to stand at room temperature. After seven weeks, purple block crystals of **1** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of the solvents in *ca.* 40% yield (77.3 mg, on the basis of 1,2- $\text{H}_2\text{BDC-F}_4$). Anal. Calcd. for $\text{C}_{17}\text{H}_7\text{CoF}_8\text{K}_2\text{O}_9$ (%): C, 31.69; H, 1.09. Found: C, 31.57; H, 1.08. IR (KBr, cm^{-1}): 3159 br, 2975 m, 2936 m, 1664 s, 1600 s, 1512 m, 1469 m, 1407 s, 1387 s, 1343 m, 1276 w, 1121 m, 1069 s, 953 s, 926 m, 867 m, 842 m, 815 w, 741 s, 708 m, 669 m, 616 w, 539 w, 496 w.

2.2.2. Synthesis of $[\text{MnK}_2(1,2\text{-BDC-F}_4)_2(\text{DMF})]_n$ (2**).** The procedure was the same as that for **1** except that $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was replaced with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (73.5 mg, 0.3 mmol), affording yellow block crystals of **2** in *ca.* 55% yield (111.9 mg, on the basis of 1,2- $\text{H}_2\text{BDC-F}_4$). Anal. Calcd. for $\text{C}_{19}\text{H}_7\text{F}_8\text{K}_2\text{MnNO}_9$ (%): C, 33.64; H, 1.04; N, 2.06. Found: C, 34.11; H, 1.03; N, 2.07. IR (KBr, cm^{-1}): 3540 m, 2958 m, 2923 m, 2823 m, 1631 s, 1591 s, 1513 m, 1469 s, 1426 s, 1384 s, 1343 m, 1275 m, 1130 m, 1071 s, 1017 m, 952 m, 848 m, 808 w, 772 s, 764 s, 728 m, 695 w, 616 w, 536 w, 498 w.

2.3. X-ray crystallography

Single-crystal X-ray diffraction measurements of **1** and **2** were performed on a Bruker Apex II CCD diffractometer at ambient temperature with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A semiempirical absorption correction was applied using *SADABS*, and the program *SAINTE* was used for integration of the diffraction profiles [10]. The structures were solved by direct methods using *SHELXS* program of *SHELXTL* packages and refined anisotropically for all non-H atoms by full-matrix least squares on F^2 with *SHELXL* [11]. In general, hydrogen atoms were located geometrically and allowed to ride during the subsequent refinement. O-bound H atoms were firstly located in difference Fourier maps, and then fixed geometrically with isotropic temperature factors. Further crystallographic data and structural refinement parameters are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

(Insert Table 1 & Table 2 here)

3. Results and discussion

3.1. Synthesis and general characterization

Complexes **1** and **2** were prepared in the presence of KNO₃ with metal acetate at room temperature. When using other alkali metal salts including LiOAc, NaOAc, RbOAc and CsOAc as the potential structure-directing agents, we were unable to isolate, under the same conditions, any solid products suitable for X-ray analysis. Complexes **1** and **2** are stable under ambient conditions and consistent with their polymeric nature are insoluble in water and common organic solvents. IR spectra of **1** and **2** show the antisymmetric and symmetric stretching vibrations of carboxylate in the range of 1590–1665 cm⁻¹ and 1380–1470 cm⁻¹, respectively. Additionally, the absence of strong absorption bands around 1740 and 1715 cm⁻¹ for the free 1,2-H₂BDC-F₄ molecule is characteristic of complete deprotonation of carboxyl groups in **1** and **2**. This is also confirmed by the X-ray structure analyses for **1** and **2**.

3.2. Description of crystal structures

X-Ray diffraction studies of **1** and **2** reveal that they exhibit similar 2D heterometallic-organic frameworks despite their different space groups and solvent ligands. Therefore, only the crystal

structure of **1** will be described in detail. The asymmetric unit is made up of a half Co(II) ion, one K(I) ion, one 1,2-BDC-F₄ dianion and one methanol ligand. As shown in [Figure 1a](#), each Co(II) atom adopts a six-coordinated octahedral geometry provided by six oxygen atoms from four 1,2-BDC-F₄ ligands with the Co–O bond distances in the range of 2.063(2)–2.228(2) Å. The K(I) ion is surrounded by seven oxygen atoms from five 1,2-BDC-F₄ ligands and one oxygen atom from one coordinated methanol molecule as well as one fluorine atom from one 1,2-BDC-F₄ ligand. The K–O distances are in the range of 2.696–3.102(3) Å, and the K–F distance of 3.026 Å is similar to that of 3.009 Å observed in [K₂(L)₂(tmeda)₂] (HL = *N,N*-diethyl-*N'*-2,3,5,6-tetrafluorophenylethane-1,2-diamine, and tmeda = *N,N,N',N'*-tetramethyl-1,2-ethanediamine) [12]. In **1**, the 1,2-BDC-F₄ ligand takes an unusual μ_7 -bridging mode to connect two Co^{II} ions and five K(I) ions, where one carboxylate group adopting a μ_4 - η^2 : η^3 -bridging coordination mode links one Co(II) ion and three K(I) ions while the other one taking a μ_5 - η^2 : η^3 -bridging mode bridges one Co(II) ion and four K(I) ions. The adjacent KO₈F polyhedron are linked to each other via O1 and O3 atoms of carboxylate groups in an edge-sharing mode to form a tape along the [100] direction. Such 1-D motifs are connected by O5 atoms of methanol molecules through vertex-sharing to fulfill the 2-D inorganic layer, and meanwhile the CoO₆ polyhedron are embedded (see [Figure 1b](#)). The tetrafluorine-substituted benzene rings project on both the sides of the layer. Further, such layers showing a parallel arrangement are connected by intermolecular F...F interactions (F2...F4^{*i*} distance = 3.038 Å, *i* = *x*, –*y* + 1, *z* + 1/2; F3...F3^{*ii*} distance = 2.957 Å, *ii* = –*x*, –*y* + 1, –*z*) to generate a 3-D supramolecular network (see [Figure 1c](#)). It should be pointed out that such heterometallic layered structure show extended inorganic connectivity in two directions, involving novel infinite K–O–Co linkages along zero organic connectivity (*I*²O⁰) [13]. The structure of **2** showing the atomic numbering scheme is shown in [Figure 2](#).

(Insert [Figure 1](#) here)

(Insert [Figure 2](#) here)

3.3. XRPD results

In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiments were carried out for complexes **1** and **2**. The experimental and computer-simulated patterns of **1** and **2** are shown in Figure 3. Although the experimental patterns have a few un-indexed diffraction lines and some are slightly broadened in comparison with those simulated from single-crystal X-ray diffraction, the bulk synthesized materials and the crystalline material used for single-crystal X-ray studies were the same for both complexes.

(Insert Figure 3 here)

3.4. TGA analyses

Thermogravimetric analyses (TGA) of **1** and **2** were performed by heating the crystalline samples under an atmosphere of N₂ between ambient temperature and 800 °C, and the corresponding curves are depicted in Figure 4. The TGA curves of **1** and **2** are similar, probably due to their structural similarity. Both complexes exhibit high thermal stability with the mass remaining largely unchanged until the decomposition onset temperature of approximately 260 °C. Critical weight losses in the temperature of 260–330 °C indicate the pyrolysis of organic components. Further heating to 800 °C induces a further continuous and slow weight loss.

(Insert Figure 4 here)

3.5. Magnetic studies

Variable-temperature direct current (dc) magnetic susceptibility data of **1** were measured on polycrystalline samples in the temperature range of 2–300 K with an applied magnetic field of 1000 Oe as shown in Figure 5. The $\chi_M T$ value at 300 K is 3.42 cm³mol⁻¹K, which is larger than the spin-only value (1.875 cm³mol⁻¹K, $S = 3/2$, $g = 2$) for the high-spin octahedral Co(II) ion as a consequence of unquenched orbital angular momentum [14]. Upon cooling, the $\chi_M T$ value decreases to reach a value of 1.76 cm³mol⁻¹K at 2 K. Fitting of the data above 30 K to the Curie-Weiss law gives a negative Weiss constant $\theta = -28.12$ K and a Curie constant (C) of 3.71 cm³mol⁻¹K. The negative θ value and the decrease in $\chi_M T$ above 30 K suggest the antiferromagnetic interaction between the shortest Co(II)–Co(II) distance.

(Insert Figure 5 here)

4. Conclusion

In summary, we report two 2-D K(I)-M(II) (M = Mn and Co) heterometallic-organic frameworks based on a perfluorinated phthalate ligand, giving novel K–O–M inorganic connectivities. Both complexes show strong K–F coordination, and an investigation on the crystal packing suggests that intermolecular F...F interactions may act as important driving forces for the self-assembly of these 3-D supramolecular architectures, which further enrich our knowledge of metal-fluorocarbon coordination chemistry and supramolecular fluorine chemistry. In addition, weak antiferromagnetic interaction exists between Co(II) ions.

Supplementary material

CCDC 1037711 and 1037712 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 3360-33; e-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] (a) M.P. Suh, H.J. Park, T.K. Prasad, D.-W. Lim. *Chem. Rev.*, **112**, 782 (2012); (b) J.-R. Li, J. Sculley, H.-C. Zhou. *Chem. Rev.*, **112**, 869 (2012); (c) Y. Cui, Y. Yue, G. Qian, B. Chen. *Chem. Rev.*, **112**, 1126 (2012); (d) M. O’Keeffe, O.M. Yaghi. *Chem. Rev.*, **112**, 675 (2012); (e) W. Zhang, R.-G. Xiong. *Chem. Rev.*, **112**, 1163 (2012).
- [2] C. Limban, M.C. Chifiriuc. *Int. J. Mol. Sci.*, **12**, 6432 (2011).
- [3] K. Kasai, M. Aoyagi, M. Fujita. *J. Am. Chem. Soc.*, **122**, 2140 (2000).

- [4] C. Yang, X. Wang, M.A. Omary. *J. Am. Chem. Soc.*, **129**, 15454 (2007).
- [5] (a) B. Chen, Y. Yang, F. Zapata, G. Qian, Y. Luo, J. Zhang, E.B. Lobkovsky. *Inorg. Chem.*, **45**, 8882 (2006); (b) C. Seidel, R. Ahlers, U. Ruschewitz. *Cryst. Growth Des.*, **11**, 5053 (2011); (c) C. Seidel, C. Lorbeer, J. Cybinska, A.-V. Mudring, U. Ruschewitz. *Inorg. Chem.*, **51**, 4679 (2012).
- [6] Z. Wang, V.C. Kravtsov, R.B. Walsh, M.J. Zaworotko. *Cryst. Growth Des.*, **7**, 1154 (2007).
- [7] (a) S.-C. Chen, Z.-H. Zhang, Q. Chen, L.-Q. Wang, J. Xu, M.-Y. He, M. Du, X.-P. Yang, R.A. Jones. *Chem. Commun.*, **49**, 1270 (2013); (b) S.-C. Chen, Z.-H. Zhang, K.-L. Huang, H.-K. Luo, M.-Y. He, M. Du, Q. Chen. *CrystEngComm*, **15**, 9613 (2013); (c) S.-C. Chen, F. Tian, K.-L. Huang, C.-P. Li, J. Zhong, M.-Y. He, Z.-H. Zhang, H.-N. Wang, M. Du, Q. Chen. *CrystEngComm*, **16**, 7673 (2014).
- [8] (a) S.-C. Chen, Z.-H. Zhang, Q. Chen, H.-B. Gao, Q. Liu, M.-Y. He, M. Du. *Inorg. Chem. Commun.*, **12**, 835 (2009); (b) S.-C. Chen, Z.-H. Zhang, M.-Y. He, H. Xu, Q. Chen. *Z. Anorg. Allg. Chem.*, **636**, 824 (2010).
- [9] S.-C. Chen, Z.-H. Zhang, Y.-S. Zhou, W.-Y. Zhou, Y.-Z. Li, M.-Y. He, Q. Chen, M. Du. *Cryst. Growth Des.*, **11**, 4190 (2011).
- [10] Bruker AXS, *SAINT Software Reference Manual*, Madison, WI (1998).
- [11] G.M. Sheldrick. *SHELXTL NT Version 5.1, Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
- [12] G.B. Deacon, C.M. Forsyth, P.C. Junk, J. Wang. *Chem. Eur. J.*, **15**, 3082 (2009).
- [13] A.K. Cheetham, C.N.R. Rao, R.K. Feller. *Chem. Commun.*, **46**, 4780 (2006).
- [14] (a) F.E. Mabbs, D.J. Machin. *Magnetism and Transition Metal Complexes*, Dover Publications, Inc., Mineola (2008); (b) M. Kurmoo. *Chem. Soc. Rev.*, **38**, 1353 (2009).

Table 1 Crystallographic data and structure refinement for complexes **1** and **2**

	1	2
Empirical formula	C ₁₇ H ₇ F ₈ K ₂ CoO ₉	C ₁₉ H ₇ F ₈ K ₂ MnNO ₉
Formula weight	644.36	678.40
Crystal size (mm ³)	0.24 × 0.22 × 0.22	0.20 × 0.20 × 0.18
Crystal system	monoclinic	monoclinic
Space group	<i>P2/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	7.132(1)	7.187(1)
<i>b</i> (Å)	13.664(2)	30.265(5)
<i>c</i> (Å)	11.167(1)	11.324(1)
α (deg)	90	90
β (deg)	112.426(8)	110.867(8)
γ (deg)	90	90
<i>V</i> (Å ³)	1005.9(2)	2301.6(6)
<i>Z</i>	2	4
ρ_{calcd} (g cm ⁻³)	2.127	1.958
μ (cm ⁻¹)	1.395	1.054
<i>F</i> (000)	636	1340
Range of <i>h, k, l</i>	-8/7, -16/12, -13/13	-8/8, -35/31, -13/13
Total/independent reflections	5334/1777	12371/4057
<i>R</i> _{int}	0.0436	0.0703
<i>R</i> ^a , <i>R</i> _w ^b	0.0472, 0.1263	0.0616, 0.1577
GOF ^c	1.070	1.098
Residuals (e Å ⁻³)	1.420, -0.779	0.875, -0.791

^a $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^b $R_w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$. ^c $\text{GOF} = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**

Complex 1			
Co(1)–O(1)	2.145(2)	Co(1)–O(2)	2.228(2)
Co(1)–O(3)#2	2.036(2)	K(1)–O(1)#4	2.759(2)
K(1)–O(2)#5	2.859(2)	K(1)–O(2)#6	2.892(3)
K(1)–O(3)#4	3.031(3)	K(1)–O(3)#6	3.102(3)
K(1)–O(4)	2.696(3)	K(1)–O(4)#7	2.876(3)
K(1)–O(5)	2.780(3)	K(1)–F(1)	3.026(3)
O(1)–Co(1)–O(1)#1	91.1(1)	O(1)–Co(1)–O(2)	60.0(1)
O(1)–Co(1)–O(3)#2	178.0(1)	O(1)–Co(1)–O(3)#3	90.1(1)
O(1)#1–Co(1)–O(2)	91.3(1)	O(2)–Co(1)–O(2)#1	140.1(1)
O(2)–Co(1)–O(3)#2	118.4(1)	O(2)–Co(1)–O(3)#3	90.7(1)
O(3)#2–Co(1)–O(3)#3	88.7(1)	O(1)#4–K(1)–O(2)#5	139.9(1)
O(1)#4–K(1)–O(2)#6	116.7(1)	O(1)#4–K(1)–O(3)#4	68.6(1)
O(1)#4–K(1)–O(3)#6	60.8(7)	O(1)#4–K(1)–O(4)	127.0(8)
O(1)#4–K(1)–O(4)#7	130.3(1)	O(1)#4–K(1)–O(5)	64.5(1)
O(1)#4–K(1)–F(1)	83.6(1)	O(2)#5–K(1)–O(2)#6	103.5(1)
O(2)#5–K(1)–O(3)#4	138.4(1)	O(2)#5–K(1)–O(3)#6	146.4(1)
O(2)#5–K(1)–O(4)	70.0(1)	O(2)#5–K(1)–O(4)#7	63.9(1)
O(2)#5–K(1)–O(5)	77.1(1)	O(2)#5–K(1)–F(1)	77.7(1)
O(2)#6–K(1)–O(3)#4	62.1(1)	O(2)#6–K(1)–O(3)#6	64.3(1)
O(2)#6–K(1)–O(4)	65.7(1)	O(2)#6–K(1)–O(4)#7	67.1(1)
O(2)#6–K(1)–O(5)	162.3(1)	O(2)#6–K(1)–F(1)	119.3(1)
O(3)#4–K(1)–O(3)#6	66.1(1)	O(3)#4–K(1)–O(4)	68.5(1)
O(3)#4–K(1)–O(4)#7	128.0(1)	O(3)#4–K(1)–O(5)	128.9(1)
O(3)#4–K(1)–F(1)	77.5(1)	O(3)#6–K(1)–O(4)	123.6(1)
O(3)#6–K(1)–O(4)#7	82.8(1)	O(3)#6–K(1)–O(5)	105.3(1)
O(3)#6–K(1)–F(1)	135.8(1)	O(4)–K(1)–O(4)#7	100.6(1)

O(4)–K(1)–O(5)	129.2(1)	O(4)–K(1)–F(1)	57.9(1)
O(4)#7–K(1)–O(5)	98.2(1)	O(4)#7–K(1)–F(1)	141.1(1)
O(5)–K(1)–F(1)	78.3(1)		
Complex 2			
Mn(1)–O(1)	2.303(3)	Mn(1)–O(2)	2.254(3)
Mn(1)–O(3)#8	2.229(3)	Mn(1)–O(4)#8	2.603(3)
Mn(1)–O(5)	2.155(3)	Mn(1)–O(6)	2.541(3)
Mn(1)–O(8)#9	2.123(3)	K(1)–O(1)#8	2.902(3)
K(1)–O(3)#8	3.178(4)	K(1)–O(4)#12	2.749(4)
K(1)–O(5)	2.802(3)	K(1)–O(6)#11	2.811(3)
K(1)–O(7)#10	2.801(4)	K(1)–O(8)	3.268(4)
K(1)–O(9)	2.786(4)	K(1)–F(9)#12	2.897(3)
K(2)–O(1)	2.868(3)	K(2)–O(2)#11	2.841(4)
K(2)–O(3)#11	2.949(4)	K(2)–O(4)#8	3.051(4)
K(2)–O(6)#10	2.936(3)	K(2)–O(7)#13	2.808(4)
K(2)–O(8)#10	2.958(4)	K(2)–O(9)	2.711(4)
K(2)–F(8)#13	2.859(3)		
O(1)–Mn(1)–O(2)	57.6(1)	O(1)–Mn(1)–O(3)#8	125.3(1)
O(1)–Mn(1)–O(4)#8	72.5(1)	O(1)–Mn(1)–O(5)	101.7(1)
O(1)–Mn(1)–O(6)	145.0(1)	O(1)–Mn(1)–O(8)#9	94.1(1)
O(2)–Mn(1)–O(3)#8	175.5(1)	O(2)–Mn(1)–O(4)#8	128.7(1)
O(2)–Mn(1)–O(5)	94.3(1)	O(2)–Mn(1)–O(6)	95.2(1)
O(2)–Mn(1)–O(8)#9	90.0(1)	O(3)#8–Mn(1)–O(4)#8	53.4(4)
O(3)#8–Mn(1)–O(5)	88.5(1)	O(3)#8–Mn(1)–O(6)	83.4(1)
O(3)#8–Mn(1)–O(8)#9	86.4(1)	O(4)#8–Mn(1)–O(5)	107.3(1)
O(4)#8–Mn(1)–O(6)	135.4(1)	O(4)#8–Mn(1)–O(8)#9	82.0(1)
O(5)–Mn(1)–O(6)	55.1(1)	O(5)–Mn(1)–O(8)#9	163.5(1)
O(6)–Mn(1)–O(8)#9	108.6(1)	O(1)#8–K(1)–O(3)#8	62.6(1)
O(1)#8–K(1)–O(4)#12	62.0(1)	O(1)#8–K(1)–O(5)	115.4(1)
O(1)#8–K(1)–O(6)#11	103.0(1)	O(1)#8–K(1)–O(7)#10	67.1(1)

O(1)#8-K(1)-O(8)	63.1(1)	O(1)#8-K(1)-O(9)	159.5(1)
O(1)#8-K(1)-F(9)#12	119.5(1)	O(3)#8-K(1)-O(4)#12	113.8(1)
O(3)#8-K(1)-O(5)	61.2(9)	O(3)#8-K(1)-O(6)#11	150.9(1)
O(3)#8-K(1)-O(7)#10	84.3(1)	O(3)#8-K(1)-O(8)	62.6(1)
O(3)#8-K(1)-O(9)	106.5(1)	O(3)#8-K(1)-F(9)#12	133.7(1)
O(4)#12-K(1)-O(5)	118.4(1)	O(4)#12-K(1)-O(6)#11	74.9(1)
O(4)#12-K(1)-O(7)#10	104.5(1)	O(4)#12-K(1)-O(8)	61.8(1)
O(4)#12-K(1)-O(9)	136.3(1)	O(4)#12-K(1)-F(9)#12	59.4(1)
O(5)-K(1)-O(6)#11	141.3(1)	O(5)-K(1)-O(7)#10	132.5(1)
O(5)-K(1)-O(8)	64.6(1)	O(5)-K(1)-O(9)	67.6(1)
O(5)-K(1)-F(9)#12	81.6(1)	O(6)#11-K(1)-O(7)#10	66.7(1)
O(6)#11-K(1)-O(8)	136.2(1)	O(6)#11-K(1)-O(9)	78.3(1)
O(6)#11-K(1)-F(9)#12	75.1(1)	O(7)#10-K(1)-O(8)	128.7(1)
O(7)#10-K(1)-O(9)	95.5(1)	O(7)#10-K(1)-F(9)#12	141.5(1)
O(8)-K(1)-O(9)	129.6(1)	O(8)-K(1)-F(9)#12	77.5(1)
O(9)-K(1)-F(9)#12	80.8(1)	O(1)-K(2)-O(2)#11	140.6(1)
O(1)-K(2)-O(3)#11	135.5(1)	O(1)-K(2)-O(4)#8	58.8(1)
O(1)-K(2)-O(6)#10	100.7(1)	O(1)-K(2)-O(7)#13	67.5(1)
O(1)-K(2)-O(8)#10	145.5(1)	O(1)-K(2)-O(9)	75.8(1)
O(1)-K(2)-F(8)#13	78.4(1)	O(2)#11-K(2)-O(3)#11	66.3(1)
O(2)#11-K(2)-O(4)#8	137.1(1)	O(2)#11-K(2)-O(6)#10	118.6(1)
O(2)#11-K(2)-O(7)#13	125.1(1)	O(2)#11-K(2)-O(8)#10	64.5(1)
O(2)#11-K(2)-O(9)	69.4(1)	O(2)#11-K(2)-F(8)#13	79.6(1)
O(3)#11-K(2)-O(4)#8	133.9(1)	O(3)#11-K(2)-O(6)#10	65.5(1)
O(3)#11-K(2)-O(7)#13	68.5(1)	O(3)#11-K(2)-O(8)#10	69.1(1)
O(3)#11-K(2)-O(9)	132.9(1)	O(3)#11-K(2)-F(8)#13	74.0(1)
O(4)#8-K(2)-O(6)#10	68.7(1)	O(4)#8-K(2)-O(7)#13	97.0(1)
O(4)#8-K(2)-O(8)#10	86.7(1)	O(4)#8-K(2)-O(9)	90.4(1)
O(4)#8-K(2)-F(8)#13	136.9(1)	O(6)#10-K(2)-O(7)#13	64.9(1)
O(6)#10-K(2)-O(8)#10	64.3(1)	O(6)#10-K(2)-O(9)	156.4(1)
O(6)#10-K(2)-F(8)#13	119.4(1)	O(7)#13-K(2)-O(8)#10	123.4(1)

O(7)#13–K(2)–O(9)	131.2(1)	O(7)#13–K(2)–F(8)#13	59.2(1)
O(8)#10–K(2)–O(9)	105.2(1)	O(8)#10–K(2)–F(8)#13	136.2(1)
O(9)–K(2)–F(8)#13	83.2(1)		

^aSymmetry transformations used to generate equivalent atoms. For **1**, #1: $-x, y, -z - 1/2$; #2: $x, -y, z - 1/2$; #3: $-x, -y, -z$; #4: $-x, y, -z + 1/2$; #5: $-x + 1, y, -z + 1/2$; #6: $x, -y, z + 1/2$; #7: $-x + 1, -y, -z + 1$; For **2**, #8: $x, -y + 1/2, z - 1/2$; #9: $x, -y + 1/2, z + 1/2$; #10: $x + 1, -y + 1/2, z + 1/2$; #11: $1 + x, y, z$; #12: $x, y, z - 1$; #13: $x + 1, y, z + 1$.

Caption to figures

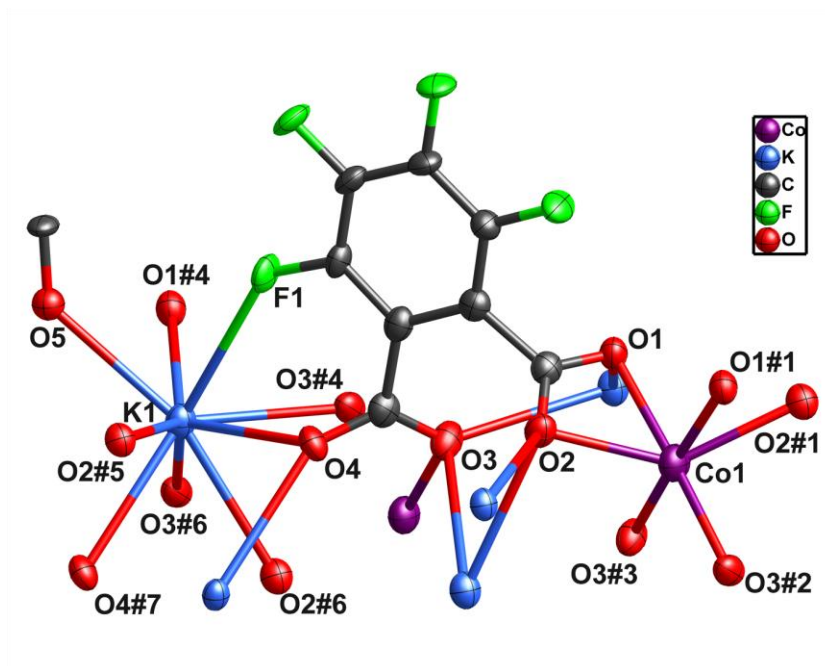
Figure 1 View of (a) the coordination environments of the Co^{II} and K^I ions in **1**. Symmetry codes: (1) $-x, y, -z - 1/2$; (2) $x, -y, z - 1/2$; (3) $-x, -y, -z$; (4) $-x, y, -z + 1/2$; (5) $-x + 1, y, -z + 1/2$; (6) $x, -y, z + 1/2$; (7) $-x + 1, -y, -z + 1$. (b) polyhedral representation of the 2-D K–O–Co inorganic connectivity of **1** (Co^{II} and K^I ions are highlighted in turquoise and pink polyhedral, respectively). (c) 3-D supramolecular framework of **1** through interlayer F...F interactions (green dashed lines). Irrelevant hydrogen atoms are omitted for clarity.

Figure 2 View of the structure of **2** showing atomic numbering scheme.

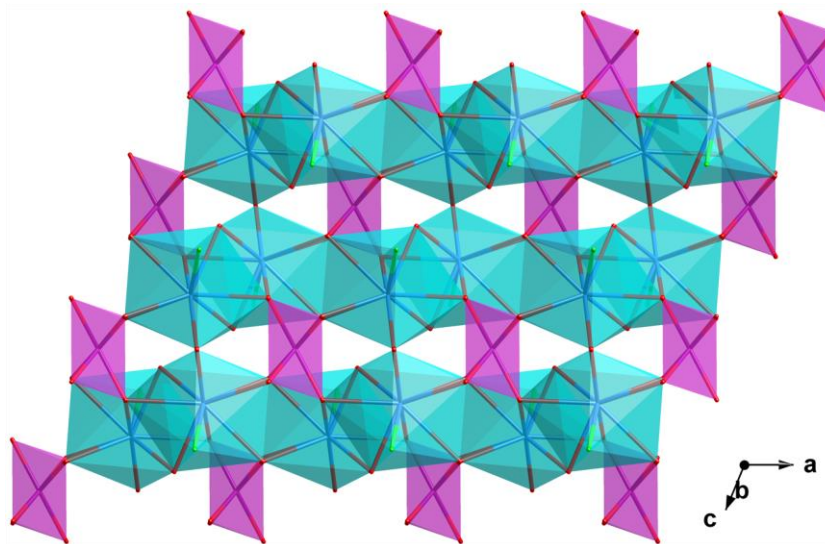
Figure 3 Experimental and simulated PXRD patterns for complexes **1** (a) and **2** (b).

Figure 4 TGA curves of complexes **1** and **2**.

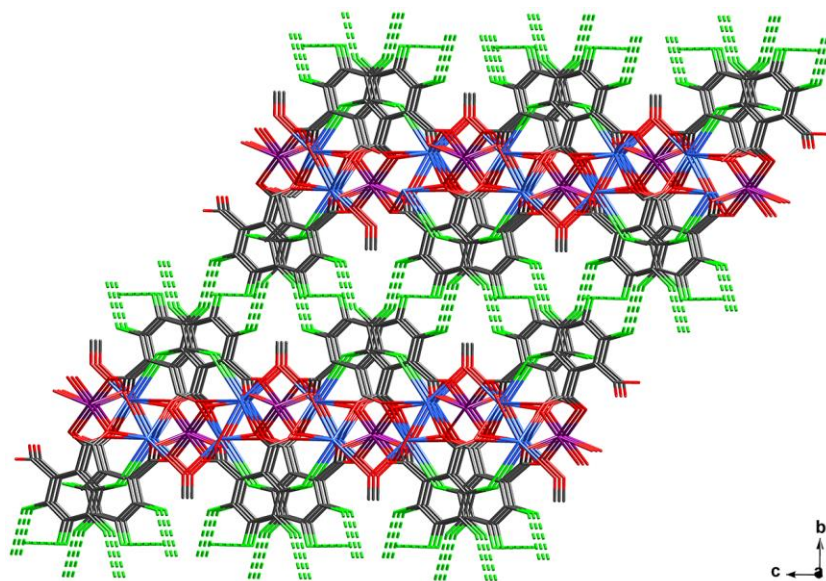
Figure 5 Temperature dependence of the $\chi_M T$ product at 1000 Oe for **1**. Inset: Plot of χ_M^{-1} vs. T (the solid red line represents a fit to the high temperature region above 30 K according to the Curie–Weiss law).



(a)



(b)



(c)

Figure 1

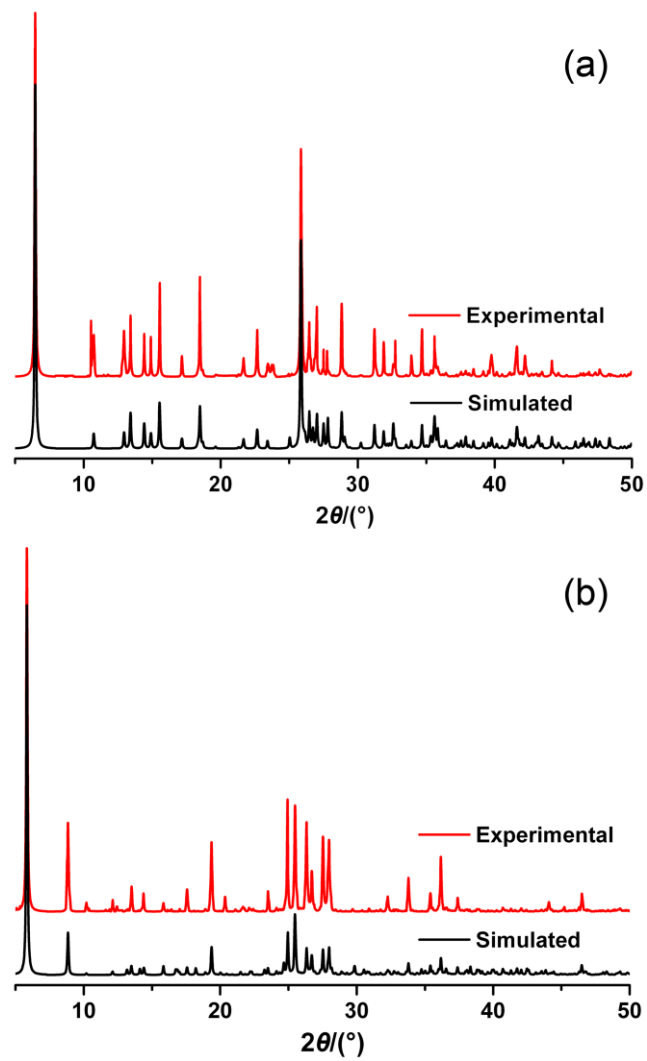


Figure 3

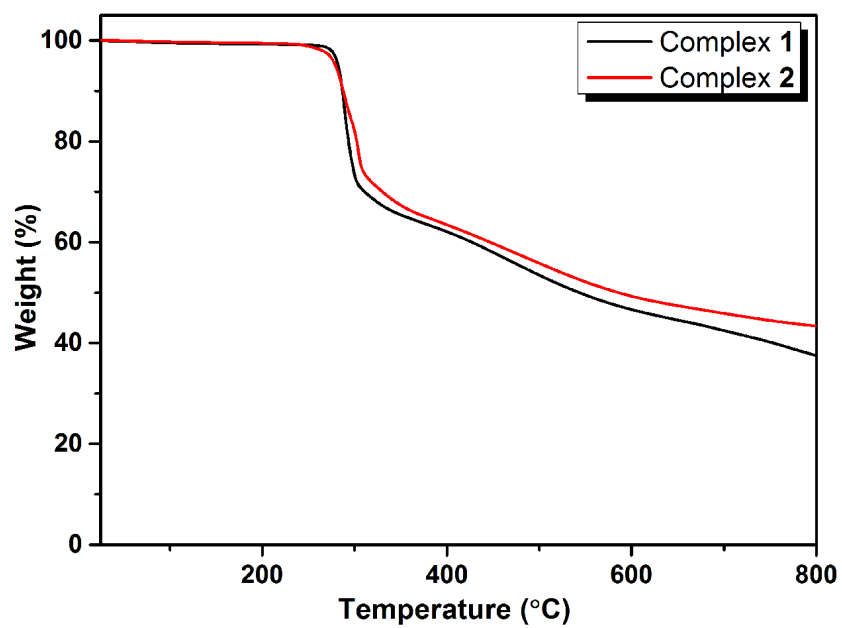


Figure 4

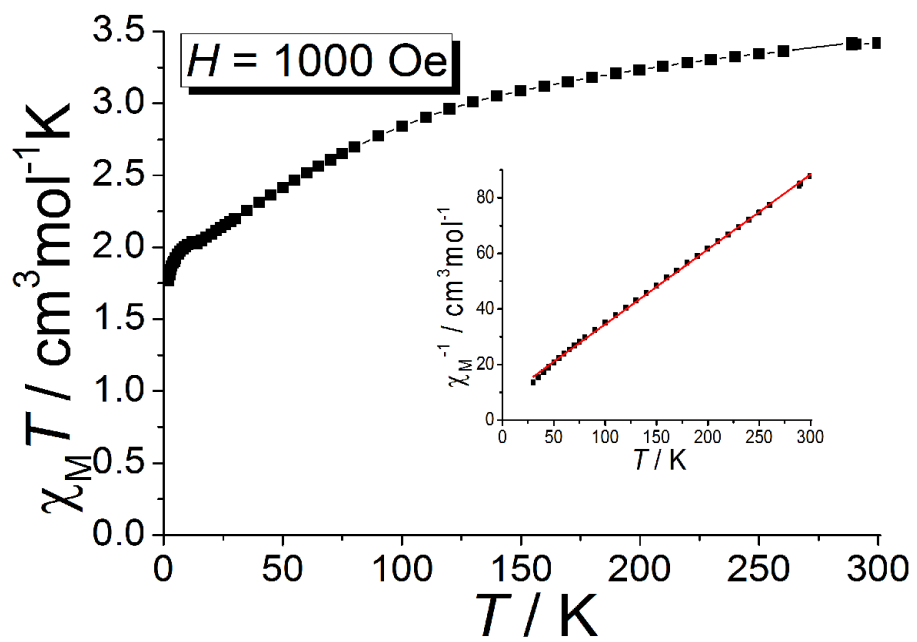


Figure 5