CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name

COMMUNICATION

$[Co(H_2O)_6]^{2+}$ and H_3O^+ encapsulated in a unique 3D anionic Co(II)-framework with hydrophilic hexagonal and circular channels

Jun Zhao,[a] Bo Liu,[b] Ya-Pan Wu,[a] Liang Bai,[a] Jian Zhang[a] and Dong-Sheng Li*[a]

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new metal–organic framework, $[Co(H_2O)_6\cdot(H_3O)]\cdot3[Co_2(L)(H_2O)_2]\cdot0.5H_2O$ (1) has been constructed from Co_2 clusters and a biphenyl-pentacarboxylate ligand with open hydrophilic channels, uniquely, the $[Co(H_2O)_6]^{2+}$ and H_3O^+ as guest cations coexist in the channels. Magnetic study indicates that the title compound shows significantly antiferromagnetic interaction.

In recent years, considerable attention has been paid in design and synthesis of a class of new crystalline porous materials known as metal–organic frameworks (MOFs), due to their large surface area and tuneable pore environments,[1] making them promising applications in many fields.[2] Numerous MOFs with interesting structures have been synthesized, and novel architectures have been developing continuously. Among these MOFs, the study of cationic/anionic frameworks is relatively less, while recent studies have shown that they are promising for various important applications,[3] for which their performance can be further enhanced by encapsulating functional species, such as magnetism or luminescent guest molecules, within the frameworks.[4]

To data, many cationic/anionic MOFs have been reported, meanwhile some of them show exciting functional properties.[5] Notably, most of these reported frameworks only contain one kind of counter ions to balance the charges. For example, the $Co(H_2O)_6^{2+}$ form as counterion often exists in the pores or channels of structures or serves as template in the assembly of the special network.[6] However, two or more kinds of counterions reside in one structure is rarely obtained. The study of such MOF may be able to give us more understanding of the synthesis of crystals.

In this work, we fortunately obtained a unique framework, $[Co(H_2O)_6][H_3O]\cdot3[Co_2(L)(H_2O)_2]\cdot0.5H_2O$ (**1**), which constructed from a new biphenyl-2,4,6,3',5'-pentacarboxylic acid (H_5L), containing $Co(H_2O)_6^{2+}$and H_3O^+ ions in different channels. To the best of our knowledge, this is the first example that two different countraions, namely $Co(H_2O)_6^{2+}$and H_3O^+, were obtained in Co-based MOFs.

Solvothermal reaction of $Co(ClO_4)_2\cdot6H_2O$ with H_5L in a 2:1 molar ratio in H_2O-EtOH mixed solvent at 140ºC for 3 days afforded rod-shaped crystals of $[Co(H_2O)_6\cdot(H_3O)]\cdot3[Co_2(L)(H_2O)_2]\cdot0.5H_2O$ (**1**). Single-crystal X-ray diffraction analysis (Table S1†) reveals that **1** crystallizes in the trigonal space group *P*31c, showing a 3D anionic framework encapsulating both $[Co(H_2O)_6]^{2+}$ and H_3O^+ counterions built on Co_2(II) clusters and L^{5-}. The asymmetric unit of **1** consists of two independently Co(II) ions, one L^{5-}, and

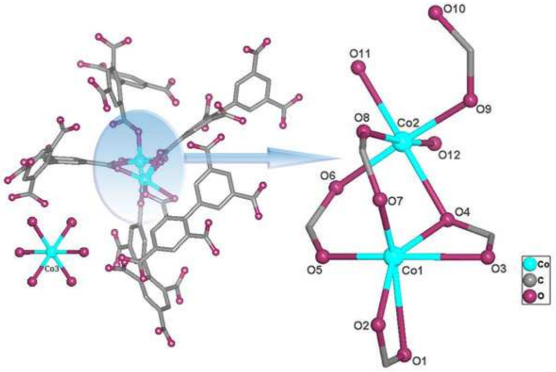

Fig. 1 Coordination environment of Co^{2+} ions in **1**.

---

[a] *College of Materials and Chemical Engineering, Hubei ProvincialCollaborative Innovation Center for New Energy Microgrid, China Three Gorges University, Yichang 443002, P.R. China. E-mail: lidongsheng1@126.com*

[b] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of theMinistry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry. College of Chemistry & Materials Science, Northwest University, Xi'an 710069, P.R. China.*

† Electronic Supplementary Information (ESI) available: Experimental details and crystallographic data, TGA, PXRD, XRPS, and addition figures. CCDC 960996. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

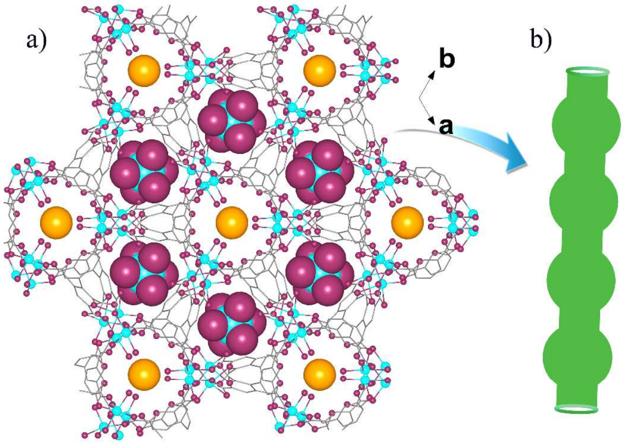

Fig. 2 (a) The 3D framework of **1** filled by H_3O^+ (yellow) and $[Co(H_2O)_6]^{2+}$ ions (purple), (b) and side-view of the 1D triangular channel.

four coordinated H_2O molecules, as well as one third $[Co(H_2O)_6]^{2+}$ which is lies on a three-fold axis, one third H_3O^+ (O15) which also lies on another three-fold axis, and one other lattice H_2O molecule (O16) on the same threefold axis with half-occupancy. As shown in Fig. 1, Co1 is coordinated by five O atoms (Co1-O: 1.991(4)-2.263 (5) Å) from four carboxylate groups of four L^{5-}, and Co2 is bound to six O atoms (Co2-O: 2.036 (4)-2.196 (4) Å) from four carboxylate groups of four L^{5-} and two aqua ligands. All the Co−O bond distances (Table S2†) are comparable to those documented values in the previous literature.[7]

The carboxylate groups of fully deprotonated μ_8-L^{5-} exhibit η^1:η^2-μ_2, η^1:η^1-μ_1, η^1:η^0-μ_1, η^1:η^1-μ_2, and η^1:η^1-μ_2 bridging fashions, at the same time, displaying three configurations of *syn-trans*, *syn-syn*, and *syn-syn-trans* (Fig. S1†). Co1 and Co2 are combined by two η^1:η^1-μ_2, two η^1:η^0-μ_1, and oneη^1:η^2-μ_2 bridging carboxylate groups, resulting into a $[Co_2(O_2C)_5(H_2O)_2]$ dimer unit with the Co···Co separations of 3.318 (9) Å, and the Co···O···Co angles is 101.2º. The Co_2 dimers are extended by carboxylate groups of μ_8-L^{5-} to form a complex 3D porous framework (Fig. 2a), and this arrangement leads to form hydrophilic hexagonal and circular channels generated along the *c*-axis. The circular channel decorated by coordination water (O11) in the in wall, sizes of *ca*. 9.9Å in diameter, and surrounded by six hexagonal channels. While the hexagonal channel surrounded by three hexagonal channels and three circular channels, showing alternating large cages with coordinated carboxylate-O (O1,O7 and O9) in the wall and small necks, the most diameters of cage and neck are ca. 12.1 and 8.0 Å, respectively (Fig. 2b).

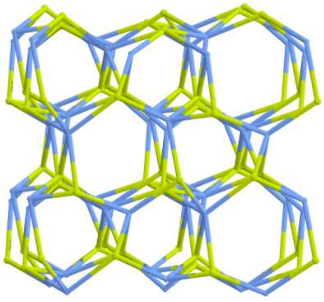

Fig. 3 Topological net of **1**.

As a matter of fact, these cavities are not empty and contain the $[Co(H_2O)_6]^{2+}$ counterions in hexagonal channels and H_3O^+ and lattice H_2O in the circular channels. The water molecules of the counterions and lattice water molecules, respectively, give rise to hydrogen bonds with coordinated carboxylate-O (O13···O1: 2.715 (1) Å, O14···O9: 2.727 (5) Å and O13···O7: 2.781 (6) Å) of the hexagonal channel in wall and the coordinated water (O15···O11: 2.806 (8) Å; O15···O16: 2.885 (3) Å) of the circular channel in wall. Thus, it is reasonable for us to conceive that $[Co(H_2O)_6]^{2+}$and H_3O^+serve as a template in the assembly of the 3D network, especially in the formation of different channels. Although, the ability of $[Co(H_2O)_6]^{2+}$ to serve as a counterion in complexes has been documented,**[6]** cases of it acting as a template in the cavity of the network remain rare. Recently, a famous example has been reported by Bu *et al*,**[8]** which is a polynuclear cobalt complex with a $[Co_{24}]$ macrocycle in the presence of $[Co(H_2O)_6]^{2+}$. To the best of our knowledge, this is the first example that the $[Co(H_2O)_6]^{2+}$ and H_3O^+ ions were captured in anionic Co(II)-MOFs, which not only acts as a counterion to balance the negative charge of complex **1**, but also may serve as a template in the assembly of 3D MOFs with different channel through hydrogen-bond interactions. Excepting the H_3O^+, lattice H_2O, and $[Co(H_2O)_6]^{2+}$ ions, the effective free volume of **1** is calculated by PLATON analysis**[9]** to be 40.3% of the crystal volume (1595.2 $Å^3$ of the unit-cell volume of 3961.4 $Å^3$). Topologically, both L^{5-} and $[Co_2(O_2C)_5(H_2O)_2]$ can be simplified as 5-connected nodes, thus the framework of **1** gives a 5-connected **acs**-$4^4 \cdot 6^6$ net (Fig. 3).

The PXRD pattern of the bulk sample of **1** matches the simulated pattern from the single-crystal structure, showing the phase purity of the as-synthesized product (Fig. S2†). The binding energy of the cobalts in **1** was measured by XPS (Fig. S3† and Fig. 4), and the two major peaks appearing at 782.1 eV and 797.6 eV are assigned to Co 2p3/2 and Co 2p1/2, respectively, of the Co(II) phase (Fig. 4). Two obvious satellite peaks were observed at 786.2 eV and 802.6 eV, and they can be ascribed to a coupling between unpaired electronsin the atom (multiplet splitting) or a multiple electron excitation (the so called ‘shake up’). The O1s XPS spectra peak with a binding energy (BE) of approximately 533 eV corresponds to oxygen species in the spinel cobalt(II) oxide phase. Thus, from BE measurements for O1s and Co2p core levels and the spectral shape of the XPS spectra, it is clear that the only presence of

Co(II) is observed in **1**, indicating the valence of the counterion [$Co(H_2O)_6$] with occupying ratio of 1/3 is +2.The valence of all cobalt centres had been calculated to be +2 by the BVS method (Table S3†), which confirmed the electronic configuration of d^7. Therefore, based on the total 1 negative charges of the anion in **1** and the H-bond configuration of O15, the encapsulated O15 molecular should be H_3O^+ with occupying ratio of 1/3.

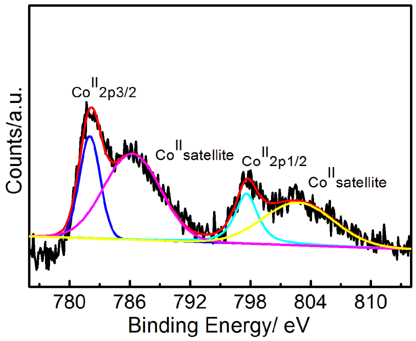

Fig. 4 X-Ray photoelectron spectrum of **1** showing the region of Co 2p3/2 and Co 2p1/2 peaks.

The TGA curve of **1** shows the first mass loss of 15.01% below 200 °C due to the release of the lattice and coordinated H_2O molecules (calcd 14.27%) (Fig. S4†). The Powder X-ray diffraction (PXRD) experiments under different temperatures were also performed to investigate the thermal stability of **1** upon the removal of all guest molecules according to the TG analysis. The PXRD patterns indicate that the framework starts to decompose at approximately 240 °C and the PXRD pattern after the removal of all guest molecules is obviously changed compared with that of the as-synthesized sample of **1** (Fig. S5†).

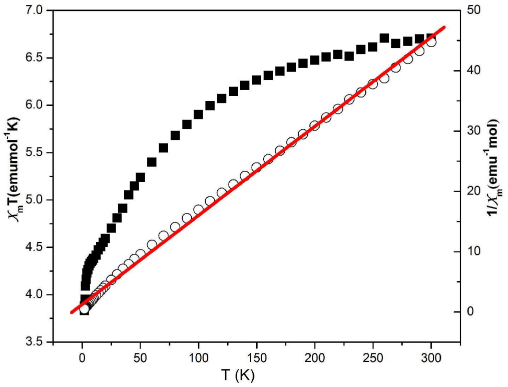

Fig. 5 Plots $\chi_M T$ and $1/\chi_M$ versus T for **1**, solid lines represent fits to the data.

The variable-temperature magnetic susceptibilities (χ_M) of **1** was examined in a 1000 Oe field in the range 1.8−300 K. As shown in Fig. 5, the value of $\chi_M T$ at 300 K is 6.71 $cm^3\ mol^{-1}\ K$, which is much higher than the calculated spin-only value for two magnetically isolated spin-only S = 3/2 Co^{2+} systems (3.75 $cm^3\ K\ mol^{-1}$), which is as expected because of the significant orbital contribution of high-spin Co^{2+} ion in an octahedral coordination environment.[10] Upon cooling, the $\chi_M T$ value declines monotonously and reaches 3.83 $cm^3\ K\ mol^{-1}$, indicating a significantly antiferromagnetic exchange between the magnetic centers in Co_2 dimer. The antiferromagnetic or ferromagnetic interaction for the Co^{2+}-carboxylate dimers is closely related to the Co−O−Co exchange angles and Co···Co distances. In the Co_2 unit of **1**, the magnetic coupling between two Co^{2+} centers is transmitted through on μ_2-Ocarboxylate and two $\mu_{1,3}$-carboxylate bridges. The big Co−Ocarboxylate−Co angle of 101.2° and the long Co···Co distance of 3.318 (5) Å are responsible for the antiferromagnetic interaction in **1**.[11]

In summary, an interesting Co-based 3D framework has been prepared, which possesses two kinds of 1D channel. In particular, **1** exhibits a rare example that the $[Co(H_2O)_6]^{2+}$ and H_3O^+ ions not only act as the counterion to balance the negative charged structure, but also may serve as a template in the assembly of framework. This work may give more insight on anionic framework.

Notes and references

1 (*a*) J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev*., 2009, **38**, 1400; (*b*) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev*., 2014, **43**, 5561.
2 (*a*) A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev*., 2009, **38**, 1284; (*b*) P.-Q. Liao, D.-D. Zhou, A.-X. Zhu, L. Jiang, R.-B. Lin, J.-P. Zhang, and X-M. Chen, *J. Am. Chem. Soc*., 2012, **134**, 17380;(*c*) P. Ramaswamy, R. Matsuda,W. Kosaka, G. Akiyama, H. J. Jeon and S. Kitagawa, *Chem. Commun.*,2014, **50**, 1144; (*d*) X. Zou, H. Ren and G. Zhu, *Chem. Commun*., 2013, **49**, 3925.(*e*) D.-S. Li, Y.-P. Wu, J. Zhao, J. Zhang and J. Y. Lu, *Coord. Chem. Rev*., 2014, **261**, 1; (*c*) J. Zhao, Y. N. Wang, W. W. Dong, Y.-P. Wu, D.-S. Li, B. Liu and Q. C. Zhang, *Chem. Commun*., 2015, **51**, 9479.
3 (*a*) H. J. Park and M. P. Suh, *Chem. Sci.*, 2013, **4**, 685; (*b*) J. An and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 5578; (*c*) J.-B. Lin and G. K. H. Shimizu, *Inorg. Chem. Front.*, 2014, **1**, 302; (*d*) C. A. Kent, D. Liu, A. Ito, T. Zhang, M. K. Brennaman, T. J. Meyer and W. Lin, *J. Mater. Chem. A*, 2013, **1**, 14982.
4 (*a*) C.-Y. Sun, X.-L. Wang, X. Zhang, C. Qin, P.Li, Z.-M. Su, D.-X. Zhu, G.-G. Shan, K.-Z. Shao, H. Wu and J. Li, *Nature Commun*., 2013, **4**, 2717; (*b*) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, and M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586;(*c*) Y.-X. Tan, Y.-P. He and J. Zhang, *Chem. Commun*., 2014, **50**, 6153.
5 (*a*) C. K. Brozekand M. Dincǎ, Chem. Soc. Rev., 2014, **43**, 5456; (*b*) B. Liu, W.-P. Wu, L. Hou and Y.-Y. Wang, *Chem. Commun*., 2014, **50**, 8731; (*c*) T. Liand N. L. Rosi, *Chem. Commun*., 2013,**49**, 11385; (*d*) J. Jia,F. Sun, T. Borjigin,H. Ren, T. Zhang, Z. Bian, L. Gao, and G. Zhu, *Chem. Commun*., 2012, **48**, 6010.
6 (*a*) C. J. Kepert, D. Hesek, P. D. Beer, and M. J. Rosseinsky, *Angew. Chem. Int. Ed*., 1998, **37**, 3158; (*b*) Y. Wang, P. Cheng, J. Chen, D.-Z. Liao, and S.-P. Yan, *Inorg. Chem*., 2007, **46**, 4530; (*c*) Y. Rodríguez-Martín, J. Sanchiz, C. Ruiz-Pérez, F. Lloret and M. Julve, *CrystEngComm*, 2002, **4**, 631; (*d*) M.-L. Cao, H.-J. Mo, and B.-H. Ye, *Cryst. Growth Des.*, 2009, **9**, 546; (*e*) H. Kumagai, C. J. Kepert, and M. Kurmoo, *Inorg. Chem*., 2002, **41**, 3410; (*f*) N. SeethaLekshmi and V. R. Pedireddi, *Inorg. Chem*., 2006, **45**, 2400; (*g*) L.-X. Shi, X. Xu and C.-D. Wu, *CrystEngComm*, 2011, **13**, 6027; (*h*) A. N.

Alsobrook, B. G. Hauser, J. T. Hupp, E. V. Alekseev, W. Depmeier, andT. E. Albrecht-Schmitt, *Cryst. Growth Des.*, 2011, **11**, 1385; (*i*) Y. Li, W.-Q. Zou, M.-F. Wu, J.-D. Lin, F.-K. Zheng, Z.-F. Liu, S.-H. Wang, G.-C. Guo and J.-S. Huang, *CrystEngComm*, 2011, **13**, 3868; (*j*) I. Park and S. S. Lee, *CrystEngComm*, 2011, **13**, 6520; (*k*) T. Arumuganathan, A. S. Rao, and S. K. Das, *Cryst. Growth Des.*, 2010, **10**, 4272; (*l*) W. L. Leong and J. J. Vittal, *Cryst. Growth Des.*, 2007, **7**, 2112; (*m*) S. Khatua, T. Harada, R. Kuroda, and M. Bhattacharjee, *Chem. Commun.*, 2007, 3927; (*n*) Z.-H. Zhou, Y.-F. Deng, and H.-L. Wan, *Cryst. Growth Des.*, 2005, **5**, 1109; (*o*) M. Jakonen,P. Hirva, T. Nivajärvi, M. Kallinen, and M. Haukka, *Eur. J. Inorg. Chem.*, 2007, 3497; (*p*) P. M. T. Piggot, L. A. Hall, A. J. P. White, D. J. Williams, andL. K. Thompson, *Inorg. Chem.*, 2004, **43**, 1167; (*q*) R. Sun, Y.-Z. Li, J. Bai, and Y. Pan, *Cryst. Growth Des.*, 2007, **7**, 890; (*r*) M.-L. Cao, J.-J. Wu, H.-J. Mo, and B.-H. Ye; *J. Am. Chem. Soc.*, 2009, **131**, 3458; (*s*) Y.-K. Lv, Z.-G. Jiang, L.-H. Gan, M.-X. Liu and Y.-L. Feng, *CrystEngComm*, 2012, **14**, 314.

7 (*a*) L. Luo, G.-C. Lv, P. Wang, Q. Liu, K. Chen and W.-Y. Sun, *CrystEngComm.*, 2013, **15**, 9537; (*b*)B. Liu, B. Liu, L. Pang, G. Yang, L. Cui, Y.-Y. Wang and Q. Shi, *CrystEngComm.*, 2013, **15**, 5205.

8 S.-D. Han, W.-C. Song, J.-P. Zhao, Q. Yang, S.-J. Liu, Y. Liand X.-H. Bu, *Chem. Commun.*, 2013, **49**, 871.

9 A.L. Spek, *Acta Cryst*. 2009, **D65**, 148.

10 (*a*) D.-S. Li, J. Zhao, Y.-P. Wu, B. Liu,L. Bai, K. Zou, and Miao Du, *Inorg. Chem.*, 2013, **52**, 8091;(*b*) J. Zhao, W.-W. Dong, Y.-P. Wu, Y.-N.Wang, C. Wang, D.-S. Li and Q.-C. Zhang, *J. Mater. Chem.A.*, 2015, **3**, 6962.

11 (*a*) Z.Su, J. Fan, M. Chen, T. Okamura, W.-Y.Sun,*Cryst. Growth Des.*, 2011, **11**, 1159; (*b*) X.-M.Zhang, X.-H.Zhang, H.-S.Wu, M.-L.Tong, S. W. Ng, *Inorg. Chem.*, 2008, **47**, 7462; (*c*) J.-Q. Liu, B. Liu, Y.-Y. Wang, P. Liu, G.-P. Yang, R.-T. Liu, Q.-Z.Shi, S. R.Batten, *Inorg. Chem.*, 2010, **49**, 10422.

Graphical abstract:

An interesting Co-based 3D framework exhibits a rare example that the $[Co(H_2O)_6]^{2+}$ and H_3O^+ ions not only act as the counterion to balance the negative charged structure, but also may serve as a template in the assembly of anionic framework with open hydrophilic channels.