Manuscript ID CE-ART-01-2014-000215.R1

Supplementary Information

Preparation, crystal structures and conformation of six complexes based on 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene

Qing-Xiang Liu*, Zhi-Xiang Zhao, Xiao-Jun Zhao, Yue Bi, Jie Yu and Xiu-Guang Wang

Tianjin Key Laboratory of Structure and Performance for Functional Molecules; Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Ministry of Education; College of Chemistry, Tianjin Normal University, Tianjin 300387, China.

* Corresponding author, E-mail: tjnulqx@163.com

Contents

1. CCDC 923228-923233 for **1-6**.
2. The structures and the crystal packings of complexes **5** and **6**.
3. Table S1 and Table S2
4. Powder X-ray diffraction of complexes **1-6**
5. Thermogravimetric analysis of complexes **1-6**

1. CCDC 923228-923233 for **1-6** contain the supplementary crystallographic data. These data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data and Figures associated with this article can be found, in the online version.

2. The structures and the crystal packings of complexes 5 and 6.

Complexes **5** and **6** contain similar 1D polymeric chains formed via ligand **L** and metal atoms (Cd(II) for **5** and Cu(II) for **6**) as shown in Fig. S1(a) and Fig. S2(a). In these complexes, the dibenzimidazolyl bidentate ligand **L** adopt trans-conformation (namely, two benzimidazole rings lie in the two sides of durene plane) as shown in Scheme 1. In each ligand of **5** and **6**, two benzimidazole rings are parallel, and the dihedral angles between the 2,3,5,6-tetramethylbenzene and two benimidazole rings are 79.4° for **5** and 79.8° for **6**. The dihedral angles between two benzimidazole rings connected to the same metal are 80.5(3)° for **5** and 84.0(9)° for **6**. In 1D polymeric chains of **5** and **6**, all interval 2,3,5,6-tetramethylbenzenes are parallel to each other, respectively, and adjacent two 2,3,5,6-tetramethylbenzenes form the dihedral angles of 21.0(4)° for **5** and 21.5(3)° for **6**. Each metal center of **5** and **6** is seven-coordinated with two nitrogen atoms from two benzimidazole rings of two ligands **L** and five oxygen atoms (four oxygen atoms being from two nitrate groups and the fifth oxygen atom being from one DMF molecule) to adopt pentagonal bipyromidal coordination polyhedron. The axial positions of pentagonal pyramid are occupied by N(1) and N(1A) with N(1)-M(1)-N(1A) bond angles of 170.6(4)° for **5** and 177.1(8)° for **6**.

In complex **5**, the bond distances of Cd(1)-N(1), Cd(1)-O(1), Cd(1)-O(2) and Cd(1)-O(4) are 2.255(2) Å, 2.486(3) Å, 2.356(3) Å and 2.309(4) Å, respectively. By comparison, the bond distance of Cd(1)-N(1) is slightly shorter than those of known Cd-N (2.275(3) Å-2.320(2) Å), and the bond distances of Cd-O are fall in the normal ranges of known values (2.193(2) Å-2.459(2) Å).[1, 2] The bond angles of N(1)-Cd(1)-O(2), N(1)-Cd(1)-O(4) and O(2)-Cd(1)-O(4) are 88.6(7)°, 90.7(0)° and 134.3(3)°, respectively, and they are fall in the normal ranges of reported values (70.5(3)°-155.5(2)° for N-Cd-O and 51.9(2)°-170.2(6)° for O-Cd-O).[1, 2]

In complex **6**, the bond distance of Cu(1)-N(1) is 1.994(3) Å, and this value is within the range of reported values (1.990(3) Å-2.237(2) Å),[3] but it is slightly longer than the bond distance of Cu-N in complex **2** (1.956(3) Å). The bond distances of Cu(1)-O(1) and Cu(1)-O(4) are 2.018(3) Å and 2.271(5) Å, respectively, and these values are slightly longer than those of known Cu-O bonds (1.930(6) Å-1.951(9) Å).[3] The bond angles of other N-Cu-O range from 89.8(4)° to 102.9(8)°, and these values are fall in the normal ranges of known N-Cu-O angle (87.7(5)°-172.7(5)°).[3]

In the crystal packings of complexes **5** and **6**, 1D polymeric chains are linked together through C-H···π contacts to form 2D supramolecular layer (Fig. S1(b) and Fig. S2(b)). Additionally, 2D supramolecular layers are extended further into 3D supramolecular frameworks through C-H···π contacts (Fig. S1(c) and Fig. S2(c)). In C-H···π contacts, the hydrogen atoms are from CH_3 of DMF for **5** and from CH_3 of tetramethylbenzene for **6**, and π systems are from benzimidazole rings for **5** and **6**. The description on C-H···π contacts has been reported,[4] and the values of C-H···π contacts for **5** and **6** are fall in the normal range as shown in Table S1.

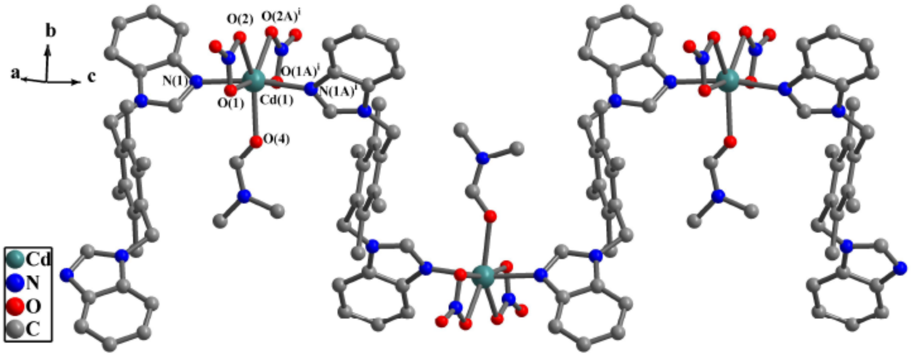
References

1 (*a*) Y. Gao, B. Twamley and J. M. Shreeve, *Inorg. Chem.*, 2006, **45**, 1150-1155; (*b*) C. Y. Su, Y. P. Cai, C. L. Chen and B. S. Kang, *Inorg. Chem.*, 2001, **40**, 2210-2211; (*c*) Y. M. Li, C. Y. Xiao, X. D. Zhang, Y. Q. Xu, H. J. Lun and J. Y. Niu, *CrystEngComm*, 2013, **15**, 7756-7762.

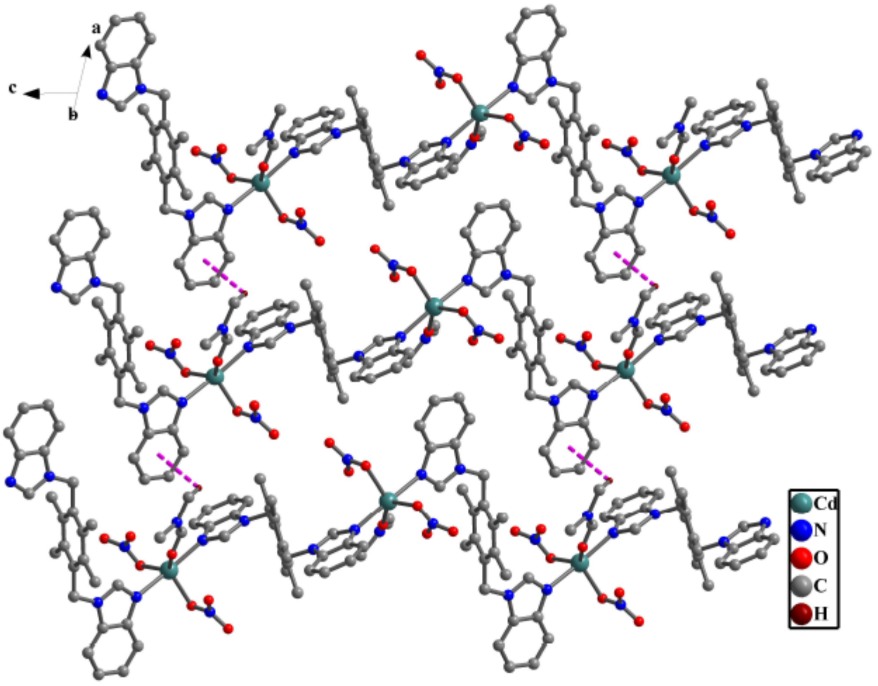
2 (*a*) B. B. Guo, L. Li, Y. Wang, Y, Y, Zhu and G. Li, *Dalton Trans.*, 2013, **42**, 14268-14280; (*b*) S. Wang, L. Zhang, G. Li, Q. Huo and Y. Liu, *CrystEngComm*, 2008, **10**, 1662-1666.

3 (*a*) S. Youngme, T. Chotkhun, N. Chaichit, G. A. van Albada and J. Reedijk, *Inorg. Chem. Comm.*, 2007, **10**, 843-848; (*b*) K. X. Huang, Z. J. Xu, Y. Z. Li and H. G. Zheng, *Cryst. Growth Des.*, 2007, **7**, 202-204; (*c*) A. K. Paul, U. Sanyal and S. Natarajan, *Cryst. Growth Des.*, 2010, **10**, 4161-4175; (*d*) D. Krishna Kumar, A. Das and P. Dastidar, *Cryst. Growth Des.*, 2007, **7**, 205-207.

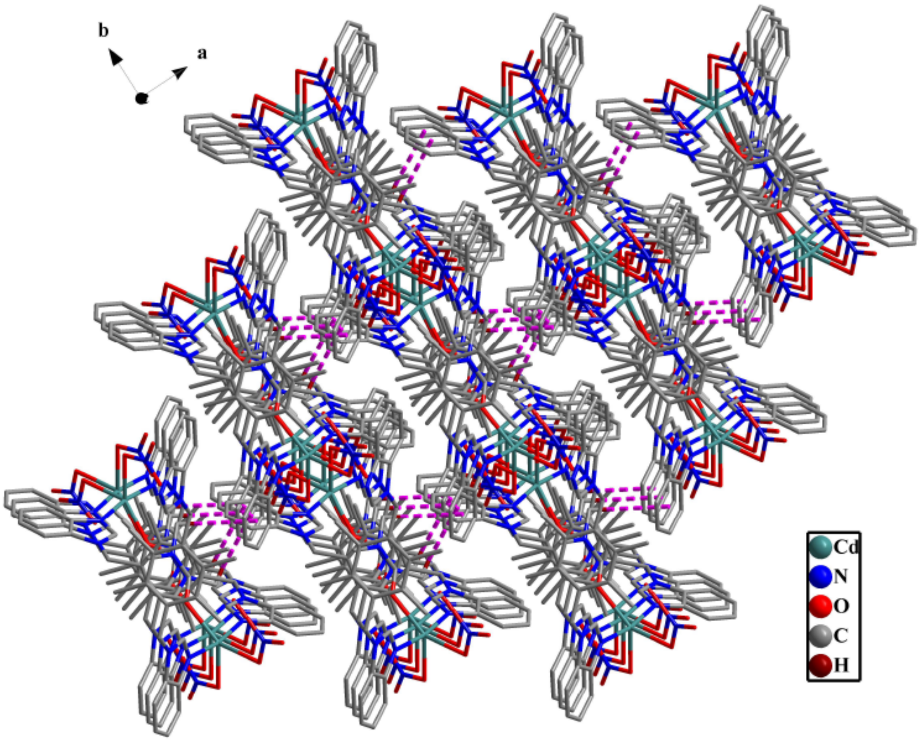
4 (*a*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, UK, 1999; (*b*) R. T. E. Tiekink and J. Zukerman-Schpector, *The Importance of Pi-Interactions in Crystal Engineering*: *Frontiers in Crystal Engineering*, First Edition. Published 2012 by John Wiley & Sons, Ltd; (*c*) A. L. Pickering, G. Seeber, D. L. Long and L. Cronin, *CrystEngComm*, 2005, **7**, 504-510; (*d*) R. P. A. Bettens, D. Dakternieks, A. Duthie, F. S. Kuan and E. R. T. Tiekink, *CrystEngComm*, 2009, **11**, 1362-1372.



(a)

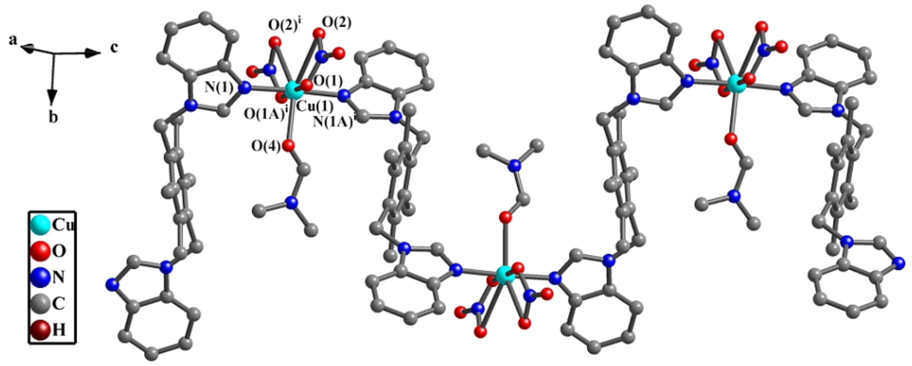


(b)

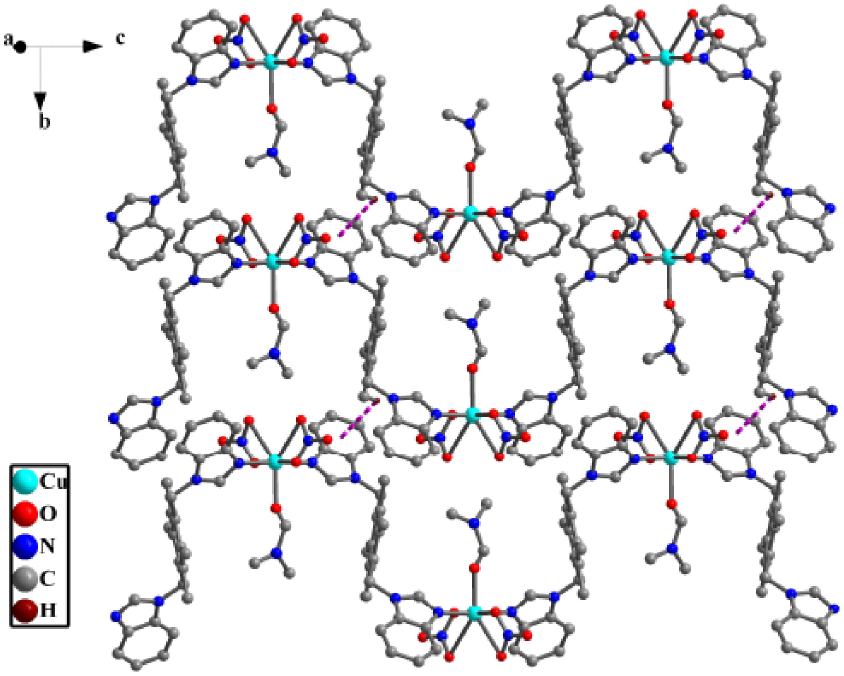


(c)

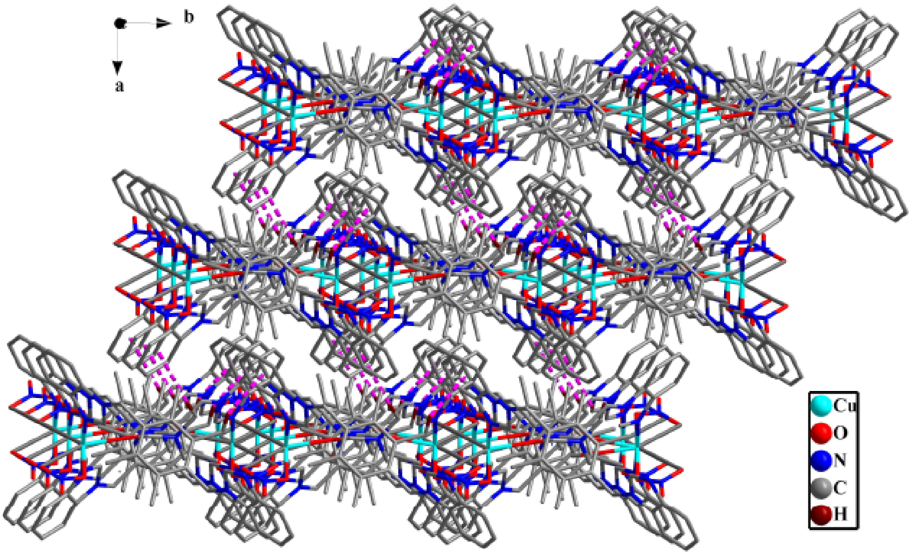
Fig. S1 (a) 1D polymeric chain of complex **5**. All hydrogen atoms were omitted for clarity. Symmetry code: i = -*x*, *y*, 0.5 - *z*. (b) 2D supramolecular layer of **5** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity. (c) 3D supramolecular network of **5** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.



(a)



(b)



(c)

Fig. S2 (a) 1D polymeric chain of complex **6**. All hydrogen atoms were omitted for clarity. Symmetry code: i = -*x*, *y*, 0.5 - *z*. (b) 2D supramolecular layer of **6** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity. (c) 3D supramolecular network of **6** via C-H···π contacts. All hydrogen atoms except those participating in the C-H···π contacts were omitted for clarity.

3. Table S1 and Table S2

Table S1 The distances (Å) and angles (˚) of C-H···π contacts for **1**, **4-6** and known complexes

Complexes	H···π	C-H···π
1	2.899	156.6
4	2.992	124.9
5	3.267	113.1
6	3.324	112.5
Values of lit.	2.4-3.6	110.0-180.0

Tables S2 Selected bond distances (Å) and angles (˚) of complexes **1-6**

Complexes	bonds		bond angles	
1	Mn(1)-N(1)	2.280(2)	N(1)-Mn(1)-N(1C)	180.0(1)
2	Cu(1)-N(1) Cu(1)-N(4) Cu(1)-O(1) Cu(1)-O(2) Cu(1)-O(6)	1.956(3) 1.957(3) 1.951(3) 2.490(9) 1.958(3)	N(1)-Cu(1)-O(1) N(1)-Cu(1)-O(6) N(4)-Cu(1)-O(6) O(1)-Cu(1)-N(4) N(1)-Cu(1)-N(4) O(1)-Cu(1)-O(6)	91.8(1) 170.8(0) 89.8(4) 150.9(7) 93.9(9) 88.8(6)
3	Co(1)-N(1) Co(1)-O(1) Co(1)-O(3)	2.083(3) 2.077(3) 2.142(3)	N(1)-Co(1)-N(1A) O(1)-Co(1)-O(1A) O(3)-Co(1)-O(3A) N(1)-Co(1)-O(3) N(1)-Co(1)-O(1) O(1)-Co(1)-O(3)	180.0(0) 180.0(0) 180.0(0) 93.2(6) 87.2(3) 88.5(9)
4	Co(1)-N(1) Co(1)-O(1) Co(1)-O(2) Co(1)-O(4)	2.101(4) 2.231(5) 2.205(4) 2.118(6)	N(1)-Co(1)-N(1A) N(1)-Co(1)-O(2) N(1)-Co(1)-O(4) O(2)-Co(1)-O(4)	174.5(2) 98.1(8) 93.1(4) 148.6(2)
5	Cd(1)-N(1) Cd(1)-O(1) Cd(1)-O(2) Cd(1)-O(4)	2.255(2) 2.486(3) 2.356(3) 2.309(4)	N(1)-Cd(1)-N(1A) N(1)-Cd(1)-O(2) N(1)-Cd(1)-O(4) O(2)-Cd(1)-O(4)	170.6(4) 88.6(7) 90.7(0) 134.3(3)
6	Cu(1)-N(1) Cu(1)-O(1) Cu(1)-O(4)	1.994(3) 2.018(3) 2.271(5)	N(1)-Cu(1)-N(1A) N(1)-Cu(1)-O(1) N(1)-Cu(1)-O(4) O(1)-Cu(1)-O(4)	177.1(8) 92.2(1) 84.0(2) 81.1(4)

4. Powder X-ray diffraction of complexes 1-6

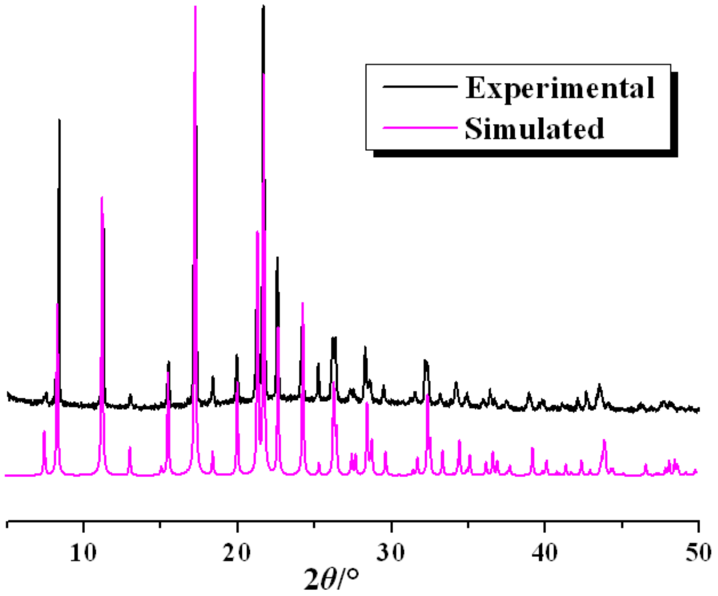


Fig. S3 The simulated (purple) and the experimental (black) PXRD patterns of **1**.

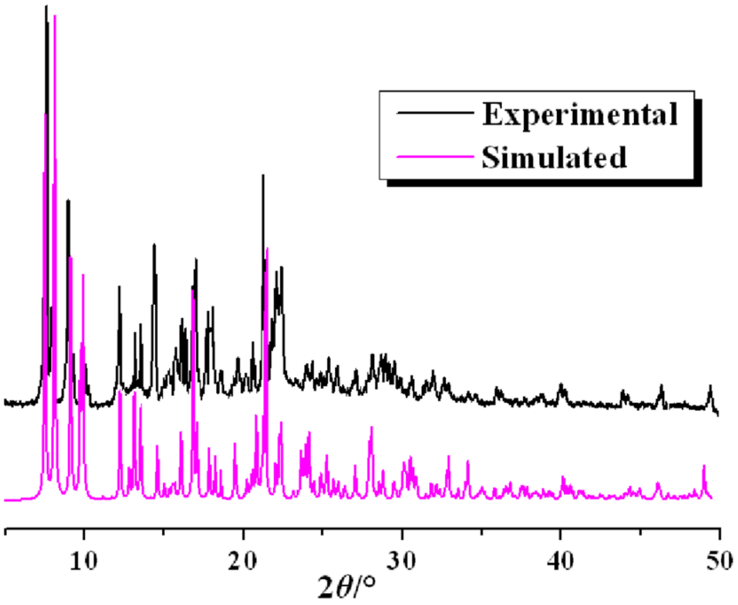


Fig. S4 The simulated (purple) and the experimental (black) PXRD patterns of **2**.

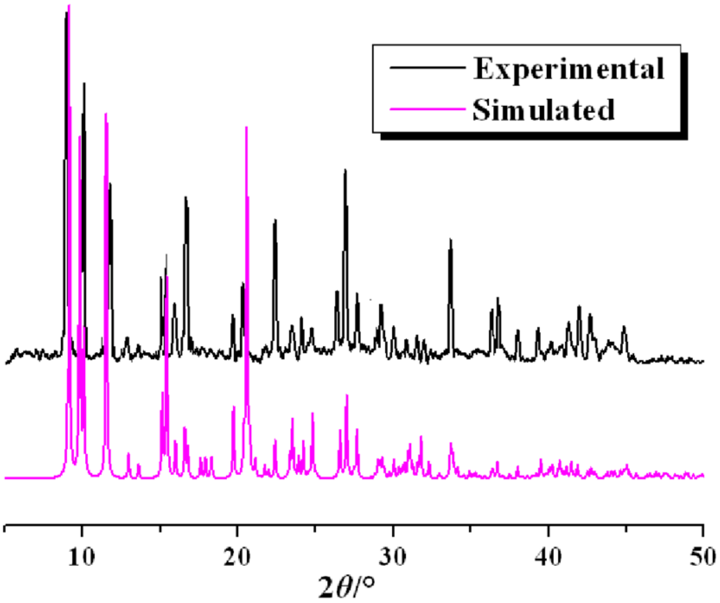


Fig. S5 The simulated (purple) and the experimental (black) PXRD patterns of **3**.

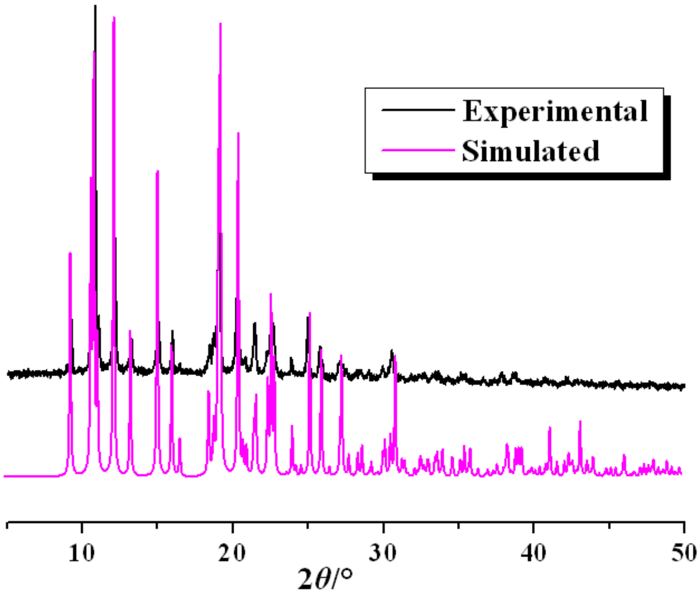


Fig. S6 The simulated (purple) and the experimental (black) PXRD patterns of **4**.

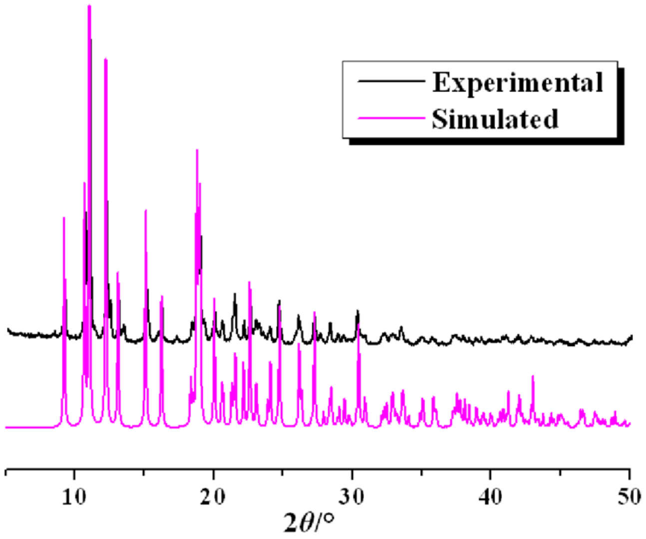


Fig. S7 The simulated (purple) and the experimental (black) PXRD patterns of **5**.

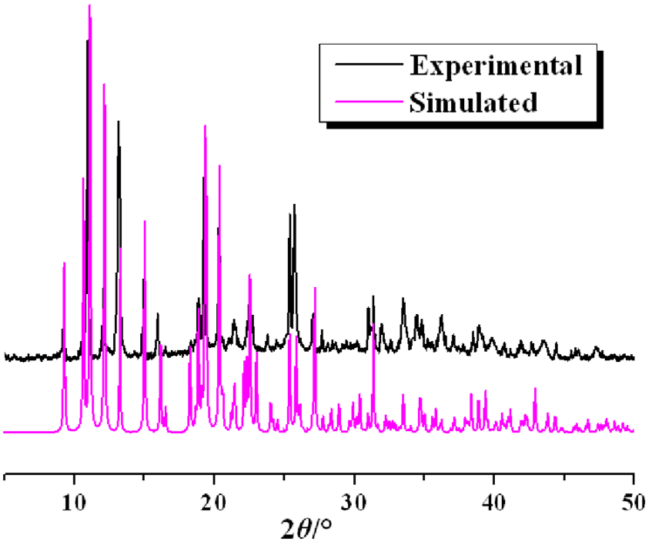


Fig. S8 The simulated (purple) and the experimental (black) PXRD patterns of **6**.

5. Thermogravimetric analysis of complexes 1-6

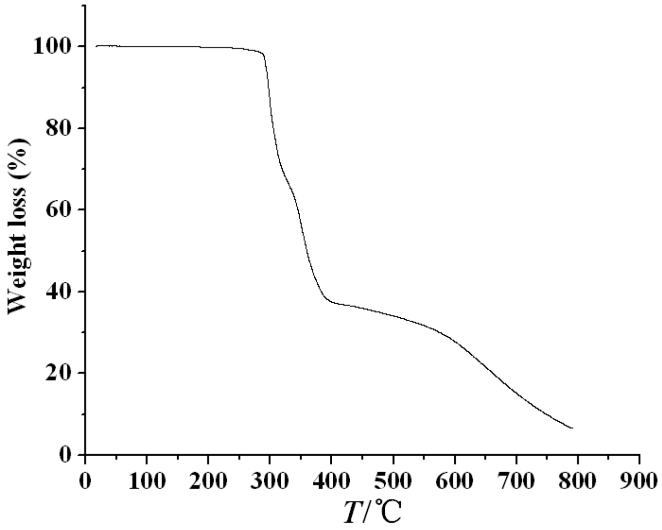


Fig. S9 TG curve from room temperature to 800 ˚C for **1.**

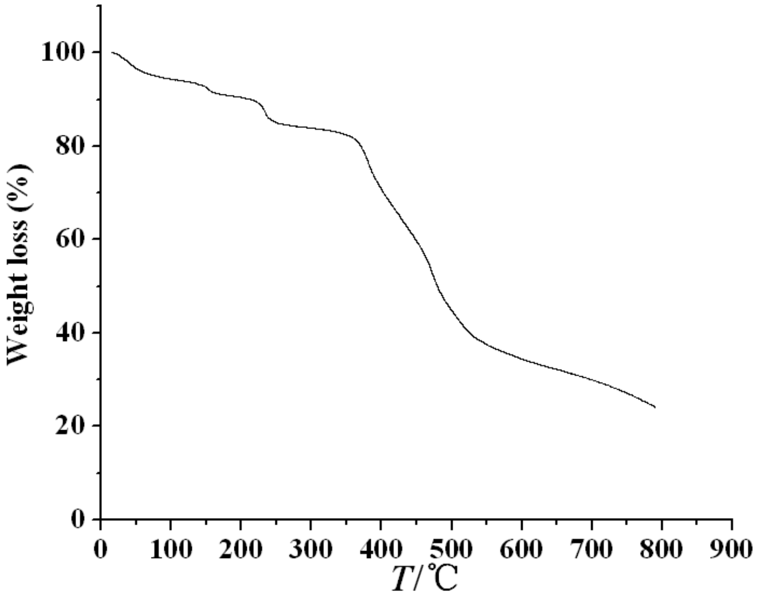


Fig. S10 TG curve from room temperature to 800 ˚C for **2.**

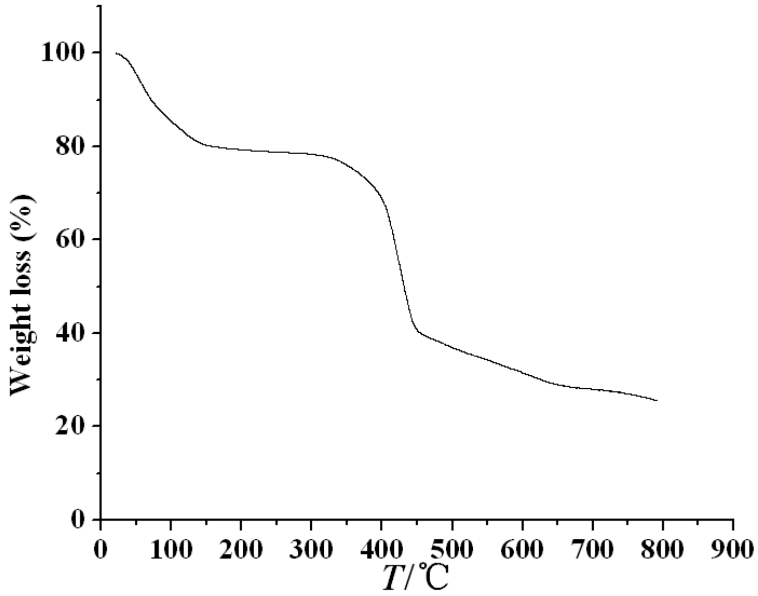


Fig. S11 TG curve from room temperature to 800 ˚C for **3.**

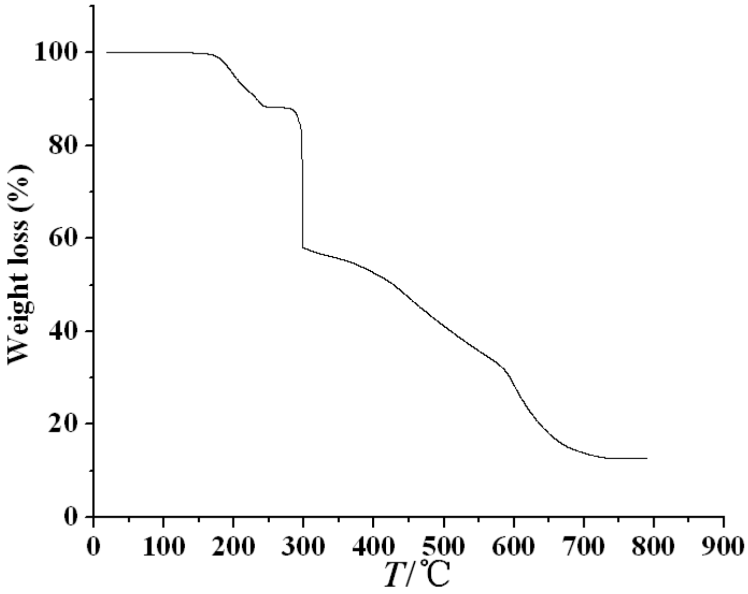


Fig. S12 TG curve from room temperature to 800 ˚C for **4.**

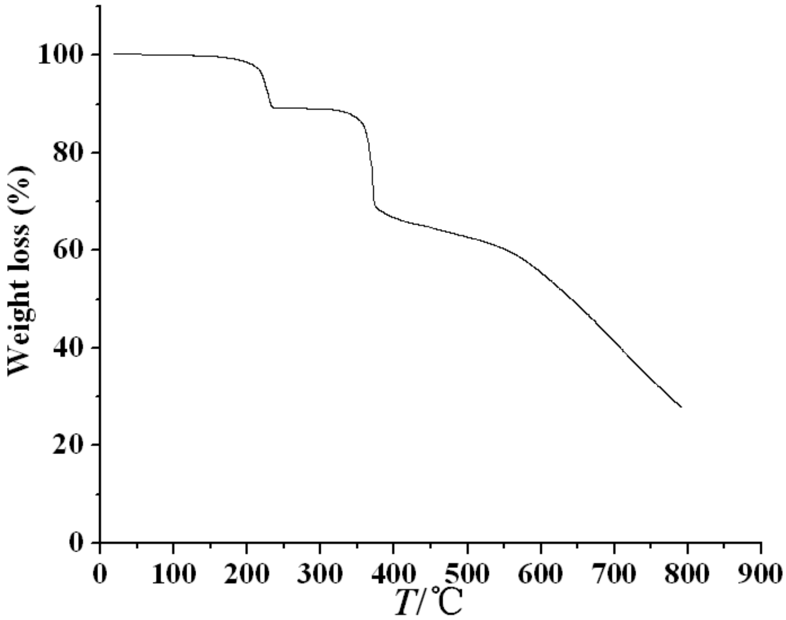


Fig. S13 TG curve from room temperature to 800 ˚C for **5.**

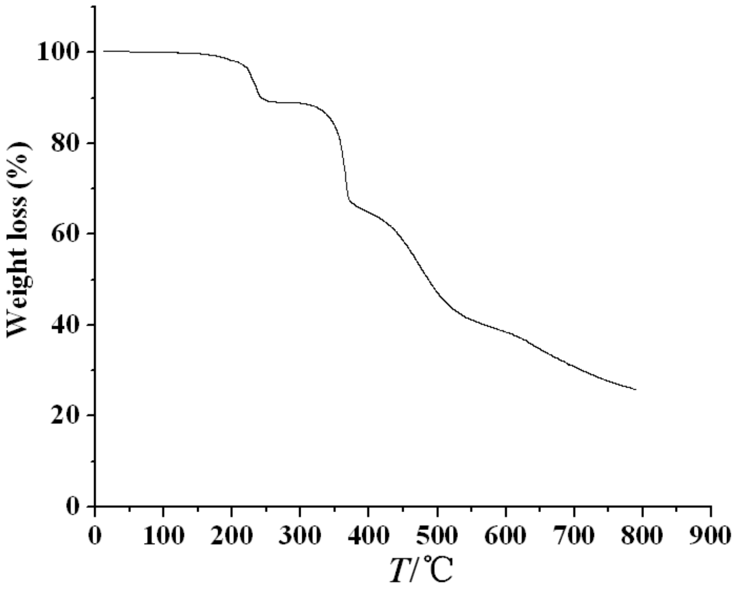


Fig. S14 TG curve from room temperature to 800 ˚C for **6.**