# Syntheses, Structures, and Characteristics of Three Metal Complexes Constructed by Using Hexavalent Carboxylic Acids

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**Table S1**. Diagnostic IR bandsfor Compounds **1–3**

| Wave Number of Characteristic Peak（$cm^{-1}$） | | | Attribution of functional groups |
|---|---|---|---|
| (1) | (2) | (3) | |
| | 3736 | | Oscillating Oscillation of O-H on Carboxyl Groups |
| 3214 | 3393,3130 | 3414 | N-H Telescopic Vibration of Nitrogen-containing Ligands |
| 1570,1483,1440 | 1609,1517 | 1552,1481 | Telescopic Vibration of Carbonyl C=O |
| | 1289,1250 | 1315,1200 | C-N Telescopic Vibration Absorption |
| 1197,1180 | 1194,1113 | 1062 | C-O stretching vibration of carboxylic acid |
| 986,818,719 | 988,811,792 | 988,855,809 | Out-of-plane bending vibration of aromatics C-H |

**Table S2**. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1–3**

| Compound (**1**) | | | |
|---|---|---|---|
| Cd(1)-O(13) | 2.2564(19) | Cd(2)#5-O(7) | 2.457(2) |
| Cd(1)-O(3)#1 | 2.261(2) | Cd(2)#6-O(2) | 2.232(2) |
| Cd(1)-O(14) | 2.297(2) | Cd(3)#3-O(1) | 2.2668(19) |
| Cd(1)-O(12) | 2.3525(19) | Cd(2)#3-O(10) | 2.255(2) |
| Cd(1)-O(11) | 2.4285(19) | Cd(1)#7-O(4) | 2.537(2) |
| Cd(1)-O(8) | 2.4450(19) | Cd(1)#7-O(3) | 2.2605(19) |
| Cd(1)-O(4)#1 | 2.537(2) | Cd(2)#5-O(8) | 2.2948(19) |
| Cd(2)-O(5) | 2.186(2) | Cd(2)-O(7)#4 | 2.457(2) |
| Cd(2)-O(2)#2 | 2.232(2) | O(13)-Cd(1)-O(3)#1 | 129.64(7) |
| Cd(2)-O(10)#3 | 2.255(2) | O(13)-Cd(1)-O(14) | 83.60(9) |
| Cd(2)-O(8)#4 | 2.2948(19) | O(3)#1-Cd(1)-O(14) | 107.86(10) |
| Cd(3)-O(1)#3 | 2.2668(19) | O(13)-Cd(1)-O(12) | 89.96(7) |
| Cd(3)-O(18) | 2.272(2) | O(3)#1-Cd(1)-O(12) | 134.80(7) |
| Cd(3)-O(11) | 2.2981(19) | O(14)-Cd(1)-O(12) | 95.91(9) |

| | | | |
|---|---|---|---|
| Cd(3)-O(17) | 2.302(2) | O(13)-Cd(1)-O(11) | 141.38(7) |
| Cd(3)-O(16) | 2.315(2) | O(3)#1-Cd(1)-O(11) | 88.94(7) |
| Cd(3)-O(15) | 2.353(2) | O(14)-Cd(1)-O(11) | 85.99(8) |
| O(11)-Cd(1)-O(8) | 99.80(7) | O(12)-Cd(1)-O(11) | 54.30(6) |
| O(3)#1-Cd(1)-O(4)#1 | 53.96(7) | O(13)-Cd(1)-O(8) | 85.29(7) |
| O(12)-Cd(1)-O(4)#1 | 170.14(7) | O(3)#1-Cd(1)-O(8) | 83.02(7) |
| O(8)-Cd(1)-O(4)#1 | 99.22(8) | O(14)-Cd(1)-O(8) | 167.88(9) |
| O(14)-Cd(1)-O(4)#1 | 83.65(9) | O(12)-Cd(1)-O(8) | 79.24(7) |
| O(11)-Cd(1)-O(4)#1 | 135.30(7) | O(13)-Cd(1)-O(4)#1 | 80.20(7) |
| O(5)-Cd(2)-O(2)#2 | 114.89(9) | O(5)-Cd(2)-O(10)#3 | 91.04(9) |
| O(2)#2-Cd(2)-O(10)#3 | 104.03(8) | O(5)-Cd(2)-O(8)#4 | 126.23(9) |
| O(2)#2-Cd(2)-O(8)#4 | 90.95(7) | O(10)#3-Cd(2)-O(8)#4 | 129.14(7) |
| O(5)-Cd(2)-O(7)#4 | 94.66(10) | O(2)#2-Cd(2)-O(7)#4 | 144.87(7) |
| O(10)#3-Cd(2)-O(7)#4 | 93.45(8) | O(8)#4-Cd(2)-O(7)#4 | 55.02(6) |
| C(1)-O(2)-Cd(2)#6 | 133.71(17) | O(1)#3-Cd(3)-O(18) | 78.63(8) |
| O(1)#3-Cd(3)-O(11) | 96.17(7) | O(18)-Cd(3)-O(11) | 93.20(9) |
| O(1)#3-Cd(3)-O(17) | 114.71(8) | O(18)-Cd(3)-O(17) | 165.17(9) |
| O(11)-Cd(3)-O(17) | 79.38(8) | O(1)#3-Cd(3)-O(16) | 98.26(9) |
| O(18)-Cd(3)-O(16) | 98.18(10) | O(11)-Cd(3)-O(16) | 163.12(9) |
| O(17)-Cd(3)-O(16) | 86.64(9) | O(1)#3-Cd(3)-O(15) | 155.62(8) |
| O(18)-Cd(3)-O(15) | 78.46(8) | O(11)-Cd(3)-O(15) | 93.30(7) |
| O(17)-Cd(3)-O(15) | 89.09(8) | O(16)-Cd(3)-O(15) | 76.93(8) |
| | | | |
| Symmetry codes: #1 -x-1,y+1/2,-z+3/2; #2 x-1,y,z; #3 -x-1,-y+1,-z+2; #4 x,-y+1/2,z+1/2; #5 x,-y+1/2,z-1/2; #6 x+1,y,z; #7 -x-1,y-1/2,-z+3/2 | | | |
| Compound (**2**) | | | |
| Cu(2)-N(5) | 1.990(5) | Cu(02)-N(8) | 1.975(5) |
| Cu(1)-N(10) | 2.021(5) | Cu(2)-O(2) | 1.939(3) |
| Cu(02)-O(3) | 2.026(4) | Cu(1)-O(5) | 1.947(4) |
| Cu(02)-N(8)#3 | 1.975(5) | Cu(02)-O(3)#3 | 2.026(4) |
| Cu(1)-O(5)#4 | 1.947(4) | Cu(1)-N(10)#4 | 2.021(5) |
| Cu(2)-O(2)#5 | 1.939(3) | Cu(2)-N(5)#5 | 1.990(5) |
| N(8)-Cu(02)-O(3)#3 | 89.5(2) | N(8)-Cu(02)-N(8)#3 | 180.0(3) |
| N(8)-Cu(02)-O(3) | 90.5(2) | N(8)#3-Cu(02)-O(3)#3 | 90.5(2) |
| O(3)#3-Cu(02)-O(3) | 180.000(1) | N(8)#3-Cu(02)-O(3) | 89.5(2) |
| O(5)-Cu(1)-N(10) | 88.93(19) | O(5)-Cu(1)-O(5)#4 | 180.0(4) |
| O(5)-Cu(1)-N(10)#4 | 91.07(19) | O(5)#4-Cu(1)-N(10) | 91.07(19) |
| N(10)-Cu(1)-N(10)#4 | 180.00(8) | O(5)#4-Cu(1)-N(10)#4 | 88.93(19) |
| O(2)-Cu(2)-N(5) | 90.21(16) | O(2)-Cu(2)-O(2)#5 | 180.00(2) |
| O(2)-Cu(2)-N(5)#5 | 89.79(16) | O(2)#5-Cu(2)-N(5) | 89.79(16) |
| N(5)-Cu(2)-N(5)#5 | 180.00(17) | O(2)#5-Cu(2)-N(5)#5 | 90.21(16) |
| | | | |
| Symmetry codes: #1 -x+2,y,-z+1/2; #2 -x+2,y,-z+3/2; #3 -x+2,-y+1,-z+1; #4 -x+2,-y,-z+1; #5 | | | |

| | | | |
|---|---|---|---|
| -x+5/2,-y+1/2,-z+1 | | | |
| Compound (**3**) | | | |
| Mn(2)-O(2) | 2.107(3) | Mn(2)-O(3) | 2.112(3) |
| Mn(2)-O(12)#1 | 2.141(3) | Mn(2)-N(7) | 2.145(3) |
| Mn(2)-O(3)#1 | 2.232(3) | O(3)-Mn(2)#1 | 2.232(3) |
| Mn(1)-OW1 | 2.178(3) | Mn(1)-OW1#3 | 2.178(3) |
| Mn(1)-OW2 | 2.219(3) | Mn(1)-OW2#3 | 2.219(3) |
| Mn(1)-O(1) | 2.220(3) | Mn(1)-O(1)#3 | 2.220(3) |
| O(12)-Mn(2)#1 | 2.141(3) | | |
| O(2)-Mn(2)-O(3) | 101.08(12) | O(2)-Mn(2)-O(12)#1 | 84.69(12) |
| O(3)-Mn(2)-O(12)#1 | 144.49(11) | O(2)-Mn(2)-N(7) | 100.20(13) |
| O(3)-Mn(2)-N(7) | 109.62(12) | O(12)#1-Mn(2)-N(7) | 103.62(12) |
| O(2)-Mn(2)-O(3)#1 | 165.34(11) | O(3)-Mn(2)-O(3)#1 | 74.51(12) |
| O(12)#1-Mn(2)-O(3)#1 | 91.07(11) | N(7)-Mn(2)-O(3)#1 | 94.43(12) |
| C(3)-O(3)-Mn(2) | 134.4(3) | C(3)-O(3)-Mn(2)#1 | 120.1(2) |
| Mn(2)-O(3)-Mn(2)#1 | 105.49(12) | C(16)-N(7)-Mn(2) | 122.2(3) |
| C(17)-N(7)-Mn(2) | 131.5(3) | C(1)-O(2)-Mn(2) | 141.3(3) |
| O(1)-Mn(1)-O(1)#3 | 180.00(17) | C(1)-O(1)-Mn(1) | 122.5(3) |
| C(15)-O(12)-Mn(2)#1 | 104.1(2) | | |
| Symmetry codes: #1 -x+1,-y,-z; #2 -x+2,-y-1,-z+1; #3 -x,-y+1,-z | | | |

**Table S3.** Complexes synthesized using $H_6L$ ligands in the literature.

| Compound | Dimensionality | Coordination number of carboxylic acid | Ref. |
|---|---|---|---|
| Compound **1** | 3D | 7 | Q. L. Zhu, T. L. Sheng, R. B. Fu, S.M. Hu, C.J. Shen, X. Ma, X. T. Wu, CrystEngComm, 2011, 13, 2096. |
| Compound **2** | 3D | 5, 8 | |
| Compound **3** | 3D | 8,8 | |
| Compound **4** | 3D | 9 | |
| Compound **1** | 3D | 16 | P. K. Goswami, M. Singh, R. Thaimattam and A. Ramanan, CrystEngComm, 2013, 15, 9787. |
| Compound **2** | 3D | 8 | |
| Compound **3a** | 1D | 4 | |
| Compound **3b** | 2D | 5 | |
| Compound **4a** | 2D | 8 | |
| Compound **4b** | 1D | 3 | |
| Compound **1** | 3D | 8 | S. Li, J. Song, J. C. Ni, Z. N. Wang, X. Gao, Z. Shi, F. Y. Bai, Y. H. Xing, RSC Adv., 2016, 6, 36000 |
| Compound **2** | 3D | 9 | |

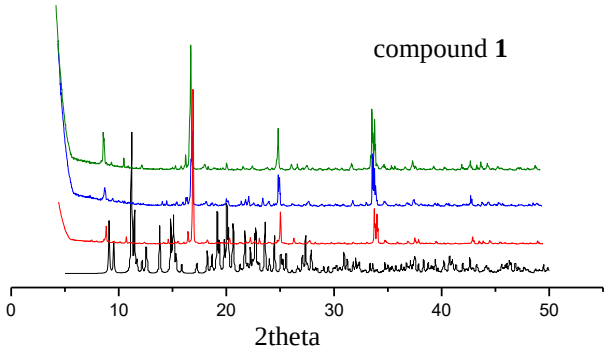


**Figure S1.** Simulated (black), experimental (red), immersed in water after 2 days (blue) and immersed in $Fe^{3+}$ (0.01M) after 2 day (green) powder X-ray diffraction patterns of compound **1**

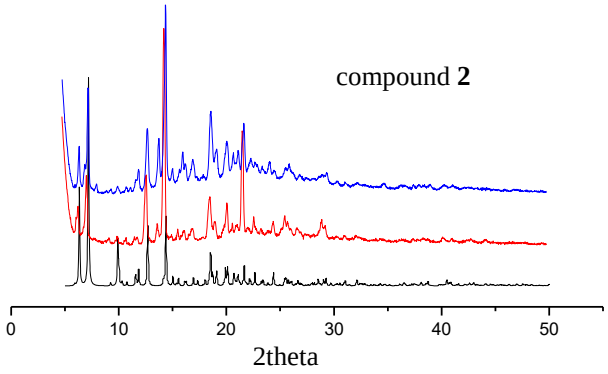


**Figure S2.** Simulated (black), experimental (red) and immersed in water after 2 days (blue) powder X-ray diffraction patterns of compound **2**

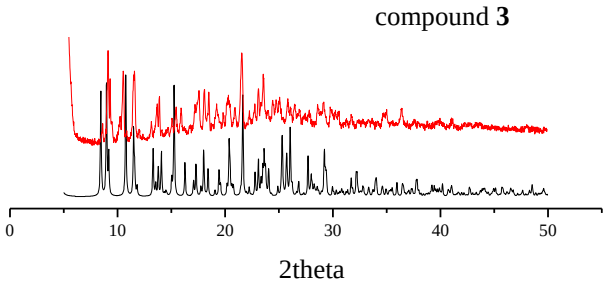


**Figure S3.** Simulated (black) and experimental (red) powder X-ray diffraction patterns of compound **3**

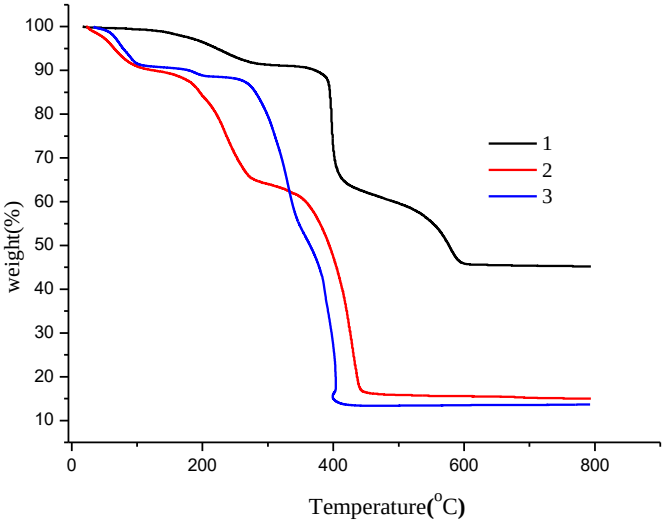


**Figure S4.** The TGA diagrams of **1**, **2** and **3**

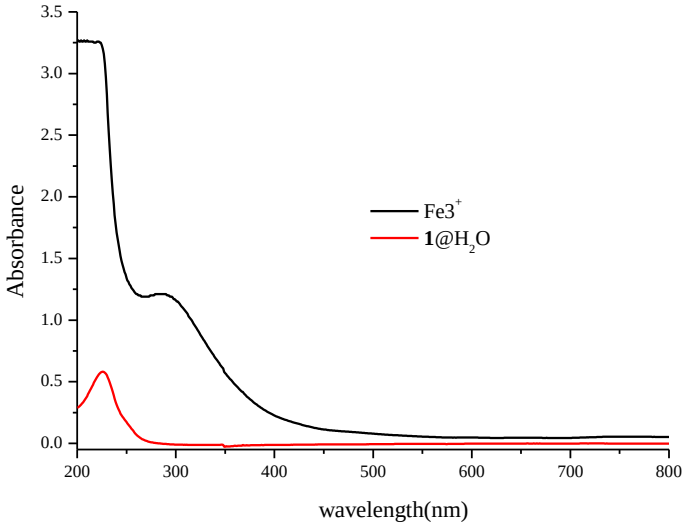


**Figure S5.** UV-Vis spectra of $Fe^{3+}$, complex **1** in aqueous solution

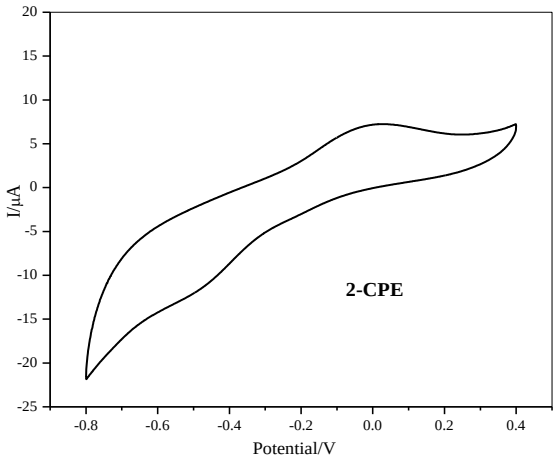


**Figure S6.** CV of **2-CPE** in 0.5 M NaOH solution at 50 mV/s