# Heterometallic hexanuclear $Ni_4M_2$ (M = Dy, Y) complexes: structure and single-molecule magnet for the Dy(III) derivative

Shaomin Pei,[a] Zhaobo Hu,[a] Zilu Chen,*[,a] Shui Yu,[a] Bo Li,*[,b] Yuning Liang,[a] Dongcheng Liu,[a] Di Yao[a] and Fupei Liang*[,a,c]

[a] *State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, P. R. China. E-mail: zlchen@mailbox.gxnu.edu.cn; fliangoffice@yahoo.com*

[b] *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, P. R. China. E-mail: libozzu0107@163.com*

[c] *Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin, 541004, P. R. China. E-mail: fliangoffice@yahoo.com*

## Electronic Supplementary Information

**Table S1** Selected bond lengths / Å and bond angles / ° for **1.**

| | | | | | |
|---|---|---|---|---|---|
| Dy1-O9 | 2.266(3) | O5-Dy1-O3 | 85.62(11) | O7-Ni1-O5 | 175.53(11) |
| Dy1-O5 | 2.311(3) | O10-Dy1-O3 | 155.59(10) | N1-Ni1-O5 | 88.02(13) |
| Dy1-O10 | 2.378(3) | O2-Dy1-O3 | 81.99(13) | N4A-Ni1-O5 | 84.24(13) |
| Dy1-O2 | 2.402(3) | O9-Dy1-O4 | 80.40(11) | O11A-Ni1-O5 | 79.07(11) |
| Dy1-O3 | 2.406(3) | O5-Dy1-O4 | 117.06(12) | O10-Ni1-O5 | 85.41(11) |
| Dy1-O4 | 2.410(3) | O10-Dy1-O4 | 150.64(10) | O9-Ni2-O9A | 84.90(11) |
| Dy1-O1 | 2.454(3) | O2-Dy1-O4 | 93.18(12) | O9-Ni2-N3 | 93.07(12) |
| Dy1-O11A | 2.461(3) | O3-Dy1-O4 | 53.71(11) | O9A-Ni2-N3 | 166.49(12) |
| Dy1-Ni1 | 3.0968(6) | O9-Dy1-O1 | 125.02(10) | O9-Ni2-N2 | 164.80(13) |
| Dy1-Ni2 | 3.3985(6) | O5-Dy1-O1 | 76.60(10) | O9A-Ni2-N2 | 93.18(12) |
| Ni1-O7 | 2.037(3) | O10-Dy1-O1 | 79.87(10) | N3-Ni2-N2 | 92.18(14) |
| Ni1-N1 | 2.055(3) | O2-Dy1-O1 | 53.64(10) | O9-Ni2-O11 | 93.93(11) |
| Ni1-N4A | 2.063(4) | O3-Dy1-O1 | 78.67(12) | O9A-Ni2-O11 | 83.82(10) |
| Ni1-O11A | 2.094(3) | O4-Dy1-O1 | 126.59(11) | N3-Ni2-O11 | 83.00(12) |
| Ni1-O10 | 2.100(3) | O9-Dy1-O11A | 72.17(9) | N2-Ni2-O11 | 100.86(13) |
| Ni1-O5 | 2.256(3) | O5-Dy1-O11A | 70.95(9) | O9-Ni2-O10 | 82.57(10) |
| Ni2-O9 | 2.048(3) | O10-Dy1-O11A | 71.83(9) | O9A-Ni2-O10 | 92.35(10) |
| Ni2-O9A | 2.048(3) | O2-Dy1-O11A | 153.13(10) | N3-Ni2-O10 | 100.64(12) |
| Ni2-N3 | 2.102(3) | O3-Dy1-O11A | 119.89(12) | N2-Ni2-O10 | 82.44(12) |
| Ni2-N2 | 2.102(3) | O4-Dy1-O11A | 88.98(11) | O11-Ni2-O10 | 175.05(10) |
| Ni2-O11 | 2.125(3) | O1-Dy1-O11A | 140.37(9) | Ni1-O5-Dy1 | 85.39(10) |
| Ni2-O10 | 2.128(3) | O7-Ni1-N1 | 96.31(14) | Ni1-O10-Dy1 | 87.27(9) |
| Ni2-Dy1A | 3.4352(5) | O7-Ni1-N4A | 95.76(14) | Ni1A-O11-Dy1A | 85.27(9) |
| | | N1-Ni1-N4A | 103.85(14) | Ni2-O9-Dy1 | 103.86(11) |
| O9-Dy1-O5 | 138.49(10) | O7-Ni1-O11A | 96.48(11) | Ni2A-O9-Dy1 | 105.43(11) |
| O9-Dy1-O10 | 72.77(9) | N1-Ni1-O11A | 163.92(13) | Ni2-O10-Dy1 | 97.76(10) |
| O5-Dy1-O10 | 78.18(10) | N4A-Ni1-O11A | 84.51(12) | Ni2-O11-Dy1A | 96.74(10) |
| O9-Dy1-O2 | 81.78(10) | O7-Ni1-O10 | 93.91(11) | Ni2-O9-Ni2A | 95.11(11) |
| O5-Dy1-O2 | 130.13(10) | N1-Ni1-O10 | 84.23(12) | Ni1-O10-Ni2 | 126.51(12) |
| O10-Dy1-O2 | 94.54(10) | N4A-Ni1-O10 | 166.61(13) | Ni1A-O11-Ni2 | 124.93(14) |
| O9-Dy1-O3 | 129.94(10) | O11A-Ni1-O10 | 85.21(10) | | |

Symmetry code: A) 0.5 – *x*, 0.5 – *y*, –*z*.

**Table S2** Selected bond lengths / Å and bond angles / ° for **2.**

| | | | | | |
|---|---|---|---|---|---|
| Y1-O9 | 2.2495(18) | O5-Y1-O3 | 85.71(8) | O7-Ni1-O5 | 175.27(8) |
| Y1-O5 | 2.3003(19) | O10-Y1-O3 | 155.18(7) | N1-Ni1-O5 | 88.15(9) |
| Y1-O10 | 2.3579(18) | O2-Y1-O3 | 81.29(9) | N4A-Ni1-O5 | 84.49(9) |
| Y1-O2 | 2.389(2) | O9-Y1-O4 | 80.36(7) | O11A-Ni1-O5 | 78.79(7) |
| Y1-O3 | 2.390(2) | O5-Y1-O4 | 116.33(8) | O10-Ni1-O5 | 84.83(7) |
| Y1-O4 | 2.396(2) | O10-Y1-O4 | 150.93(7) | O9A-Ni2-O9 | 84.91(7) |
| Y1-O1 | 2.446(2) | O2-Y1-O4 | 93.38(9) | O9A-Ni2-N3 | 165.99(8) |
| Y1-O11A | 2.4502(18) | O3-Y1-O4 | 53.83(8) | O9-Ni2-N3 | 93.05(9) |
| Y1-Ni1 | 3.0904(5) | O9-Y1-O1 | 125.17(7) | O9A-Ni2-N2 | 93.40(9) |
| Y1-Ni2 | 3.3841(5) | O5-Y1-O1 | 76.63(7) | O9-Ni2-N2 | 164.28(8) |
| Ni1-O7 | 2.031(2) | O10-Y1-O1 | 79.63(7) | N3-Ni2-N2 | 92.23(10) |
| Ni1-N1 | 2.055(2) | O2-Y1-O1 | 53.92(7) | O9A-Ni2-O11 | 83.46(7) |
| Ni1-N4A | 2.060(3) | O3-Y1-O1 | 78.30(8) | O9-Ni2-O11 | 94.13(7) |
| Ni1-O11A | 2.1004(18) | O4-Y1-O1 | 126.84(8) | N3-Ni2-O11 | 82.87(8) |
| Ni1-O10 | 2.1018(18) | O9-Y1-O11A | 72.23(6) | N2-Ni2-O11 | 101.21(8) |
| Ni1-O5 | 2.253(2) | O5-Y1-O11A | 71.13(7) | O9A-Ni2-O10 | 92.87(7) |
| Ni2-O9A | 2.0460(18) | O10-Y1-O11A | 72.33(6) | O9-Ni2-O10 | 82.28(7) |
| Ni2-O9 | 2.0473(18) | O2-Y1-O11A | 153.17(7) | N3-Ni2-O10 | 100.60(8) |
| Ni2-N3 | 2.102(2) | O3-Y1-O11A | 120.15(8) | N2-Ni2-O10 | 82.20(8) |
| Ni2-N2 | 2.103(2) | O4-Y1-O11A | 88.23(7) | O11-Ni2-O10 | 175.10(7) |
| Ni2-O11 | 2.1216(18) | O1-Y1-O11A | 140.66(7) | Ni1-O5-Y1 | 85.47(7) |
| Ni2-O10 | 2.1347(18) | O7-Ni1-N1 | 96.40(10) | Ni1-O10-Y1 | 87.53(6) |
| Ni2-Dy1A | 3.4265(4) | O7-Ni1-N4A | 95.66(10) | Ni1A-O11-Y1A | 85.19(6) |
| | | N1-Ni1-N4A | 103.76(10) | Ni2-O9-Y1 | 103.82(7) |
| O9-Y1-O5 | 138.84(7) | O7-Ni1-O11A | 96.51(8) | Ni2A-O9-Y1 | 105.72(8) |
| O9-Y1-O10 | 73.32(6) | N1-Ni1-O11A | 163.80(9) | Ni2-O10-Y1 | 97.62(7) |
| O5-Y1-O10 | 78.25(7) | N4A-Ni1-O11A | 84.64(9) | Ni2-O11-Y1A | 96.83(7) |
| O9-Y1-O2 | 81.63(7) | O7-Ni1-O10 | 94.29(8) | Ni2A-O9-Ni2 | 95.09(7) |
| O5-Y1-O2 | 130.41(7) | N1-Ni1-O10 | 84.34(9) | Ni1-O10-Ni2 | 126.03(8) |
| O10-Y1-O2 | 94.75(7) | N4A-Ni1-O10 | 166.36(9) | Ni1A-O11-Ni2 | 125.04(9) |
| O9-Y1-O3 | 129.54(7) | O11A-Ni1-O10 | 84.97(7) | | |

Symmetry code: A) $0.5 - x$, $0.5 - y$, $-z$.

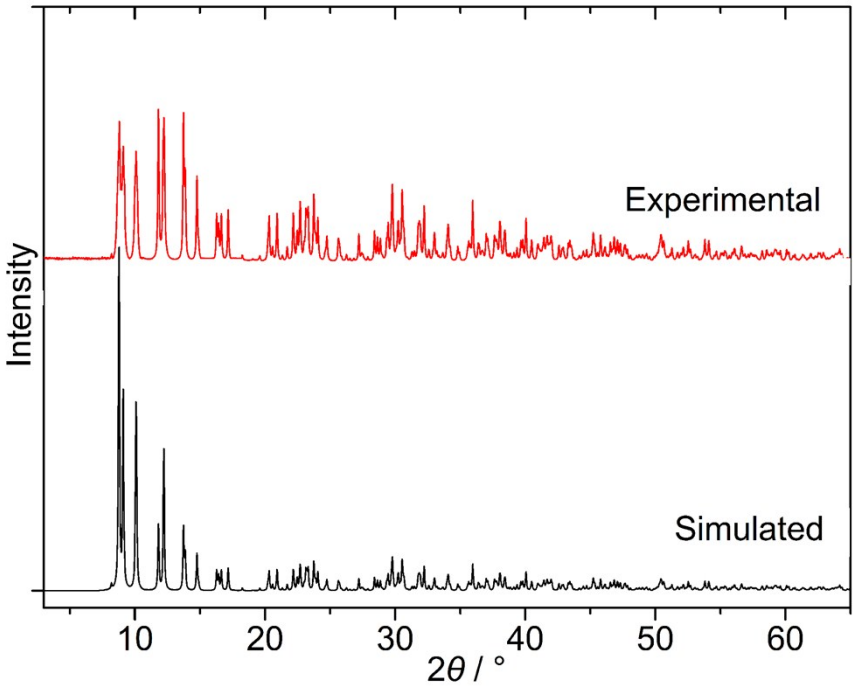


**Fig. S1** PXRD patterns of **1**.

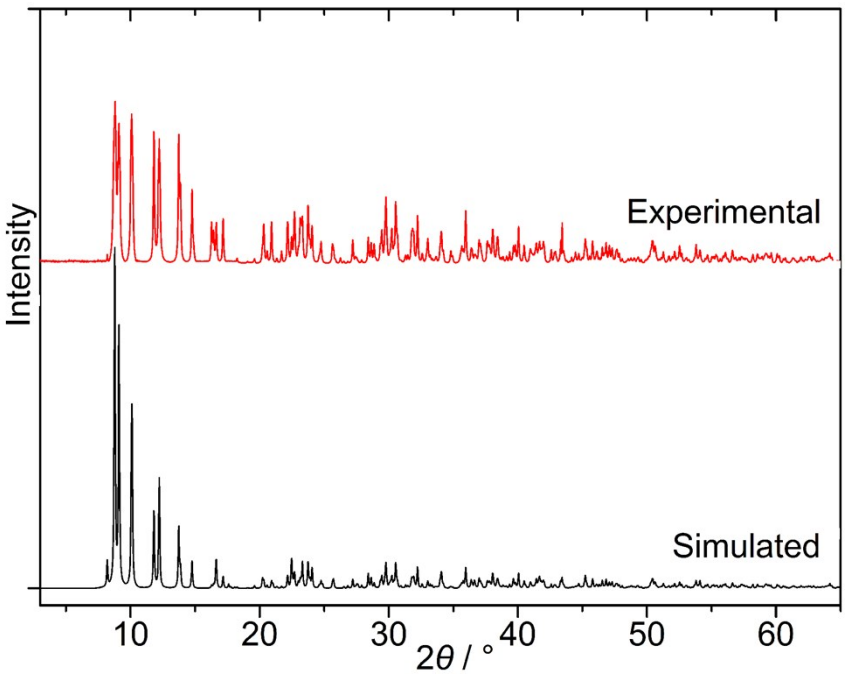


**Fig. S2** PXRD patterns of **2**.

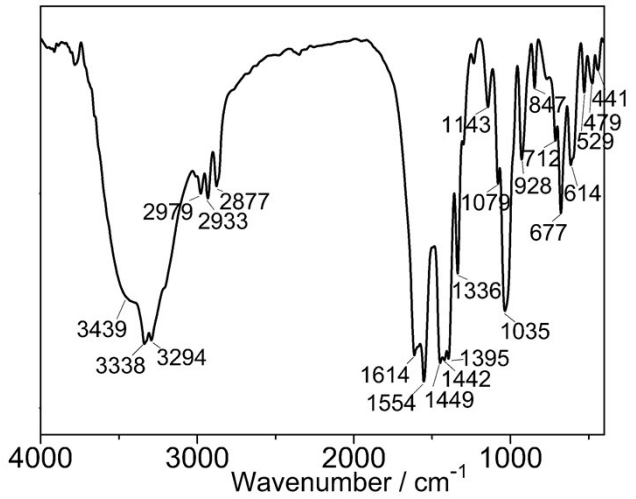


**Fig. S3** FT-IR spectrum of complex **1**.

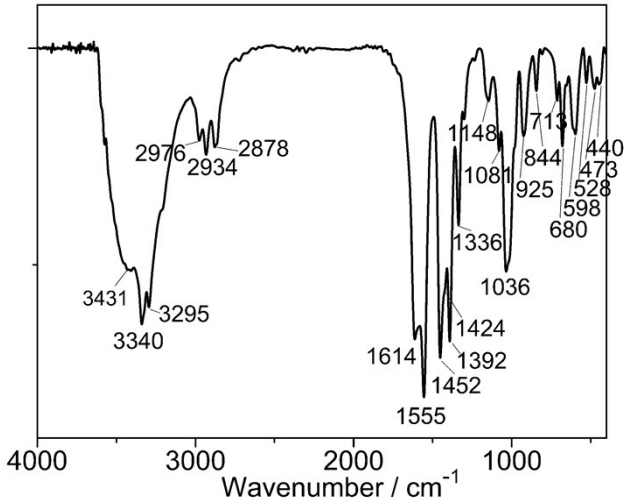


**Fig. S4** FT-IR spectrum of complex **2**.

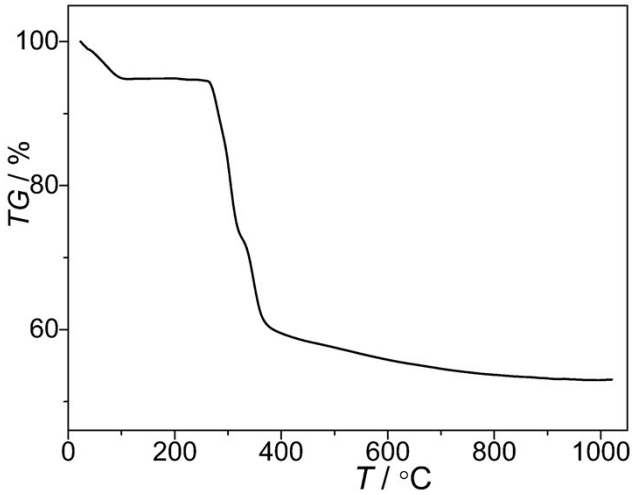


**Fig. S5** TG curve of complex **1**. It reveals a weight loss of 5.2% before 110 ºC, which corresponds to the loss of one water molecule and one mono-dentate coordinated acetate ion (5.35%). After a platform in the temperature range of 110-260 ºC, complex **1** underwent a fast weight loss before 370 ºC, and then a much slow weight loss, which is ascribed to the collapse of the skeleton of complex **1**.

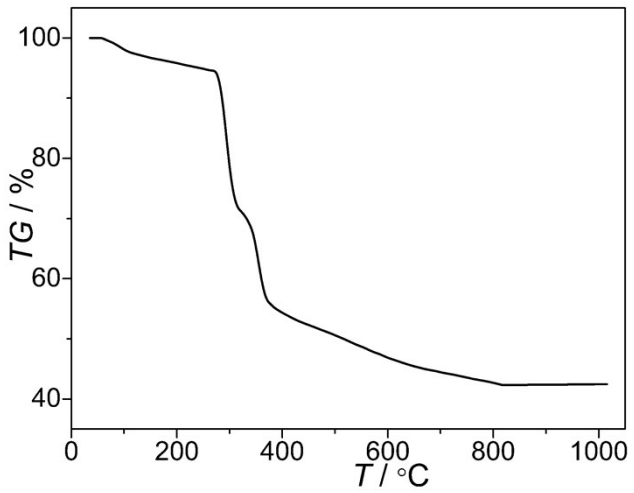


**Fig. S6** TG curve of complex **2**. It reveals a slow weight loss of 5.45% before 270 ºC, which corresponds to the loss of one water molecule and one mono-dentate coordinated acetate ion (5.26%). Then it underwent a fast weight loss before 380 ºC with a followed slow weight loss, which is ascribed to the collapse of the skeleton of complex **2**.

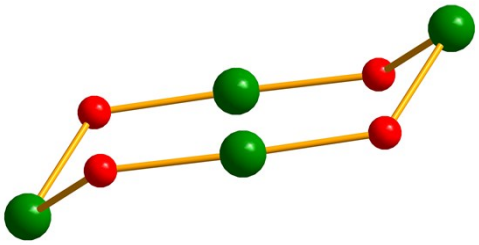

**Fig. S7** A "distortion chair" like in the $Ni_4O_4$ core.

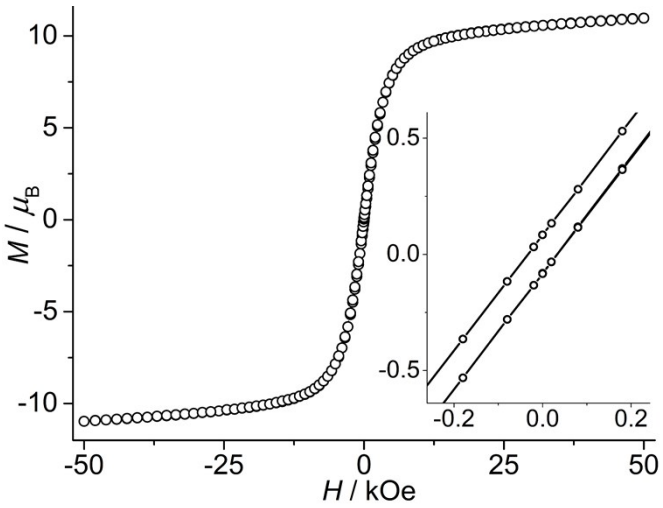


**Fig. S8** Plots of Magnetic hysteresis loops for **1.**

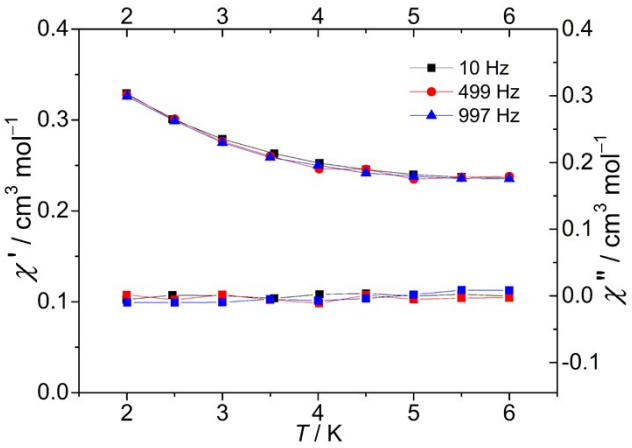


**Fig. S9** $\chi$'-$T$ and $\chi$''-$T$ plots for **2** with $H_{dc}$ = 0 Oe and $H_{ac}$ = 3 Oe.