**Supplementary Data**

# RARE-EARTH NITRATE COMPLEXES WITH DIMETHYLFORMAMIDE

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# Комплексные соединения нитратов редкоземельных элементов с диметилформамидом

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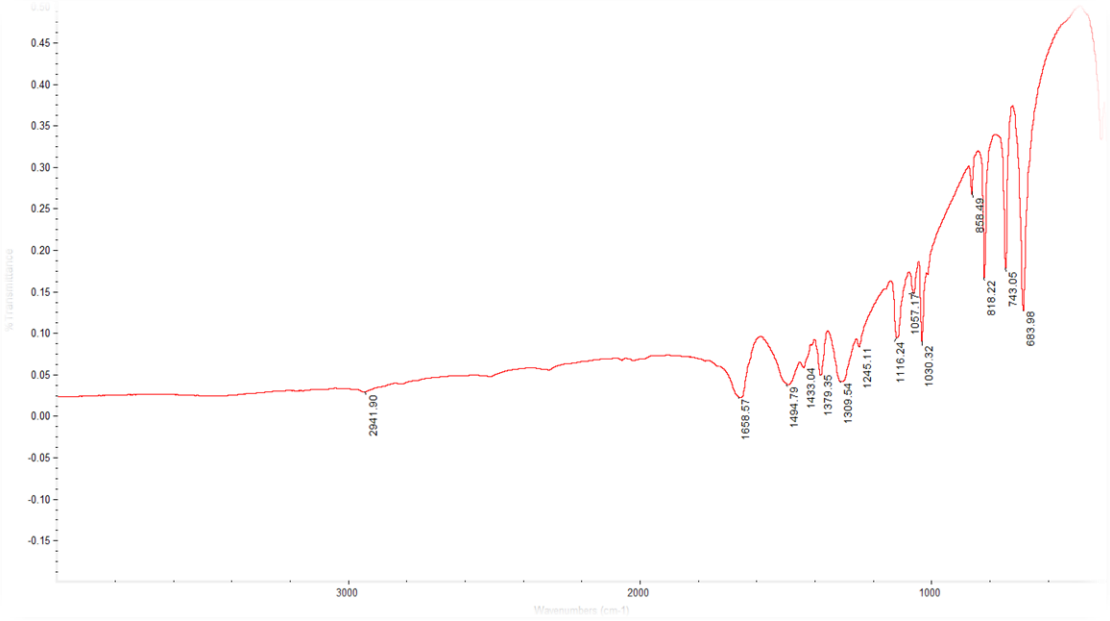


Fig. S1. IR spectrum of $[Y(DMF)_3(NO_3)_3]$.

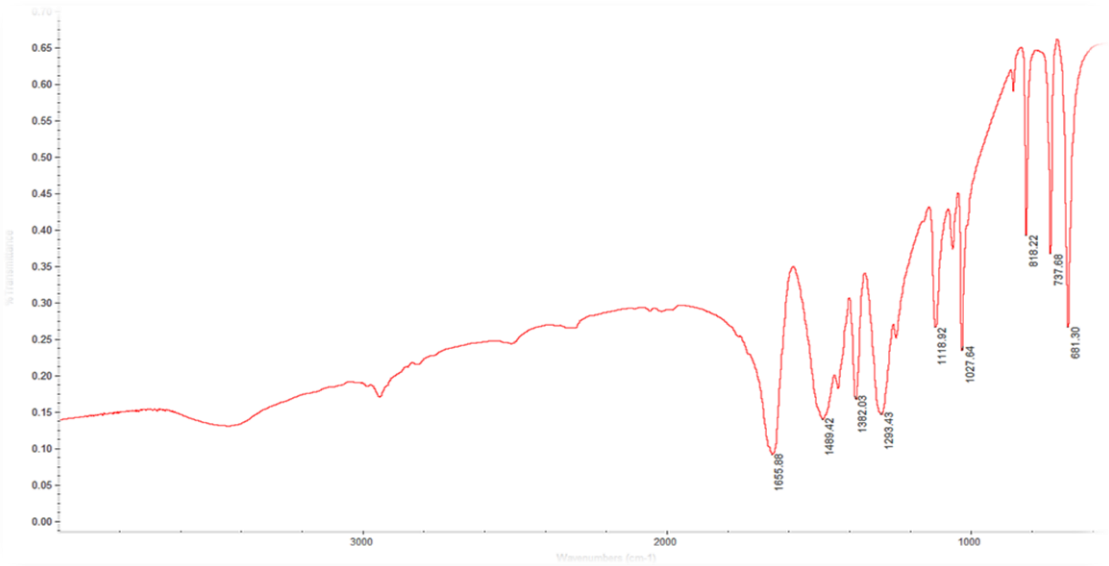


Fig. S2. IR spectrum of $[Sm(DMF)_3(NO_3)_3]$.

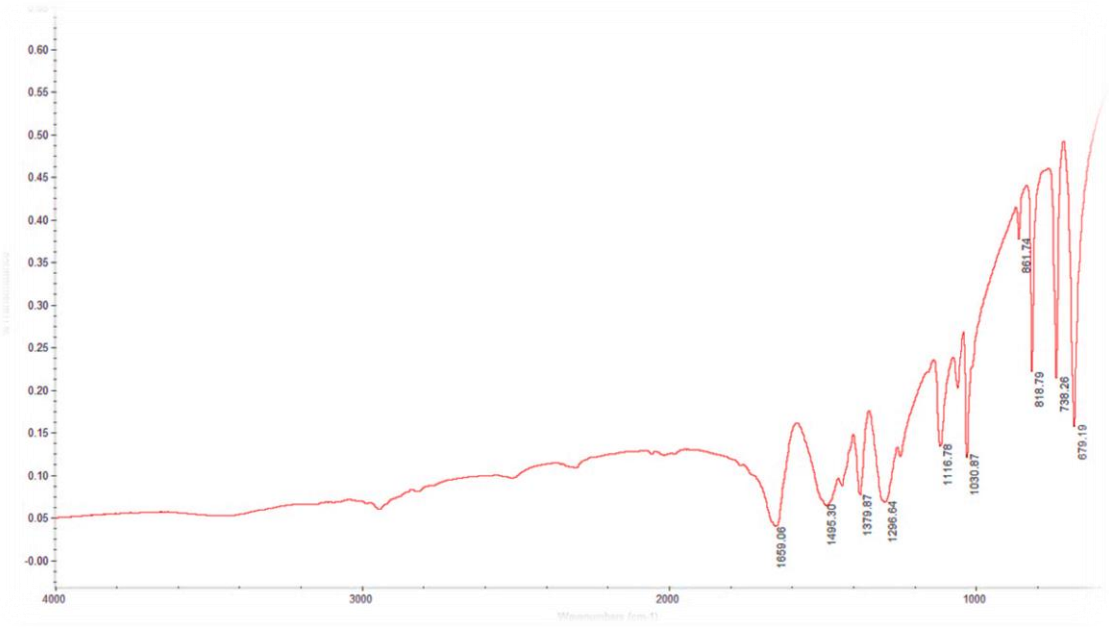


Fig. S3. IR spectrum of $[Eu(DMF)_3(NO_3)_3]$.

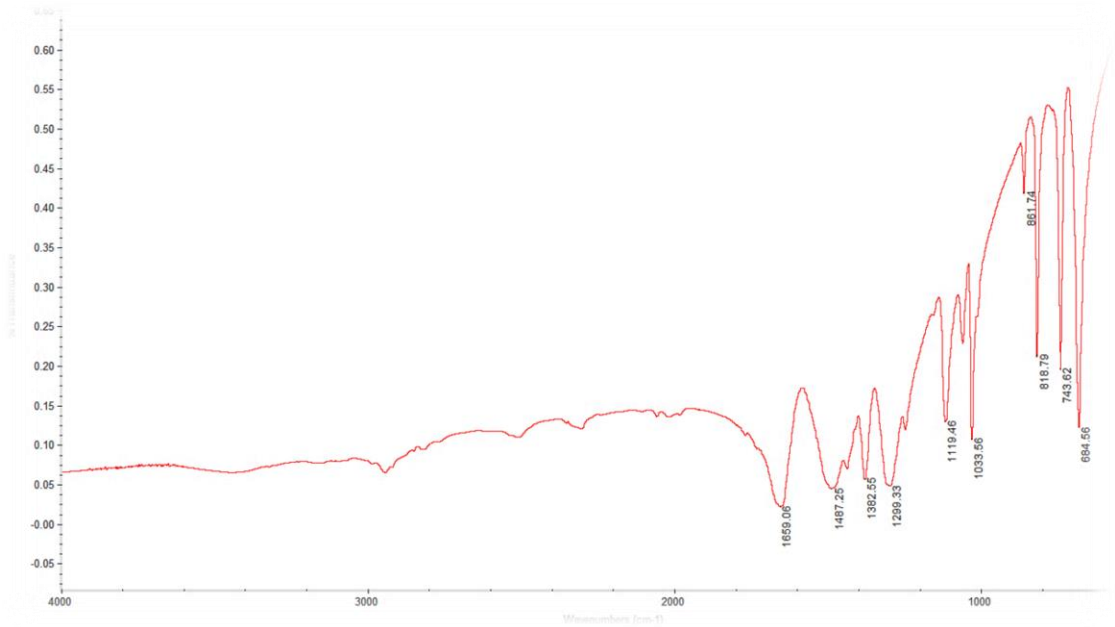


Fig. S4. IR spectrum of $[Gd(DMF)_3(NO_3)_3]$.

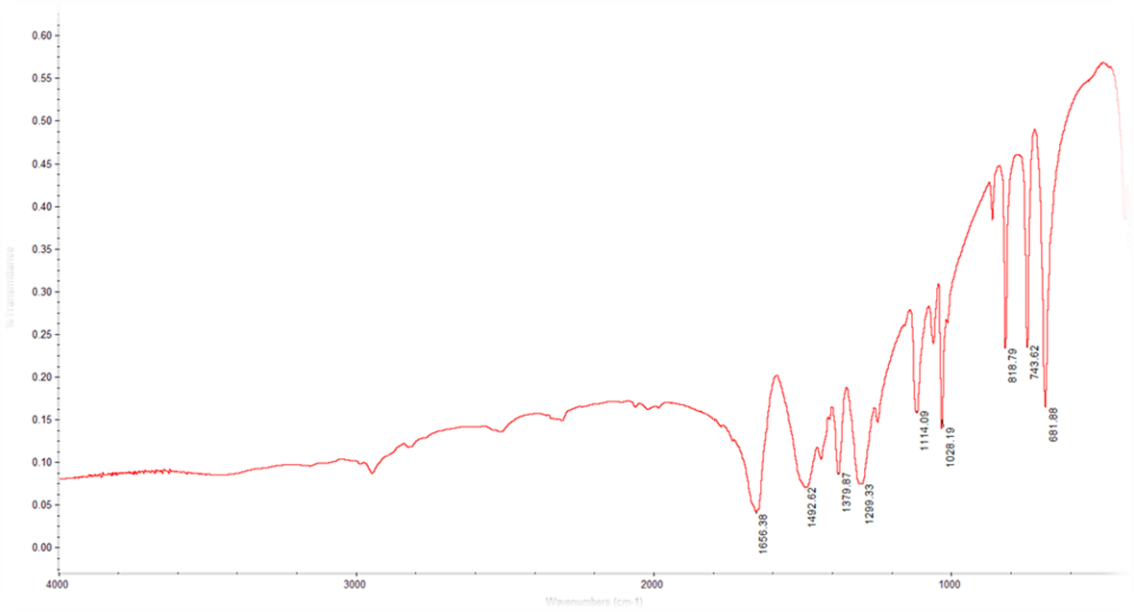


Fig. S5. IR spectrum of $[Tb(DMF)_3(NO_3)_3]$.

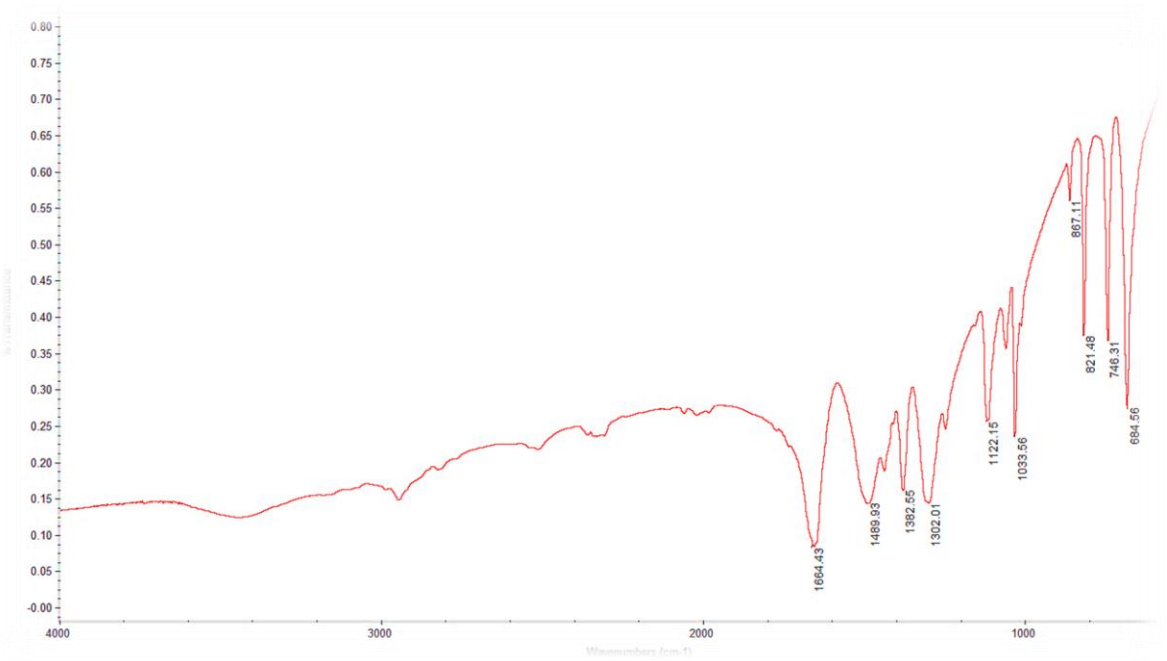


Fig. S6. IR spectrum of $[Dy(DMF)_3(NO_3)_3]$.

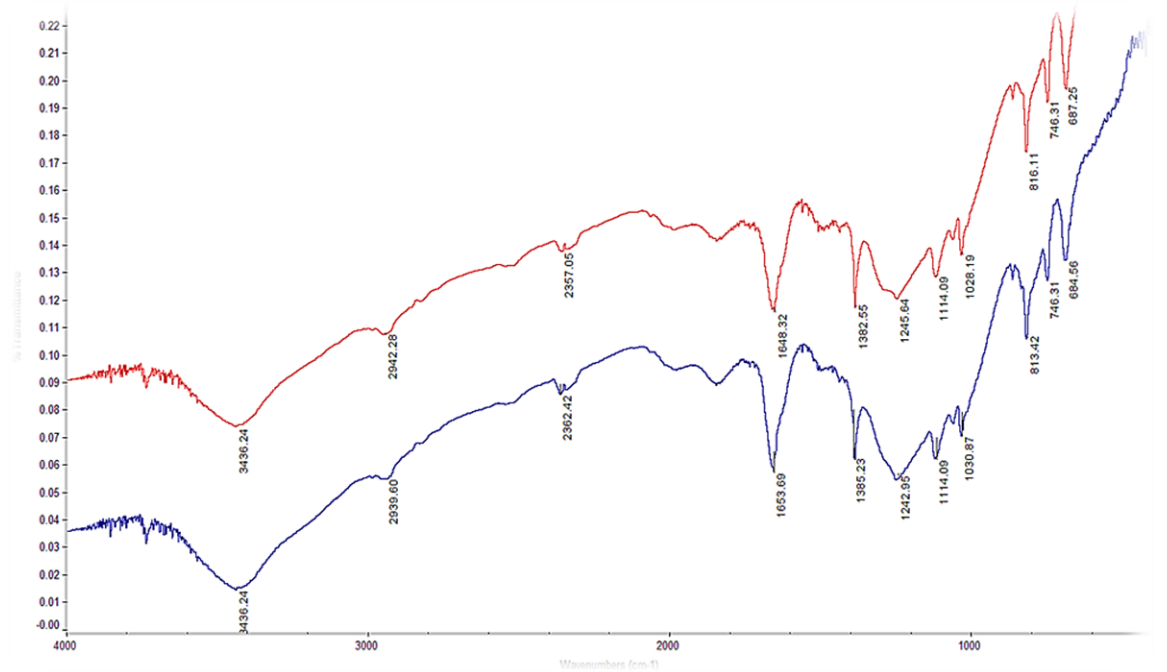


Fig. S7. IR spectra of $[Tm(DMF)_3(NO_3)_3]$ (blue curve) and $[Yb(DMF)_3(NO_3)_3]$ (red curve).

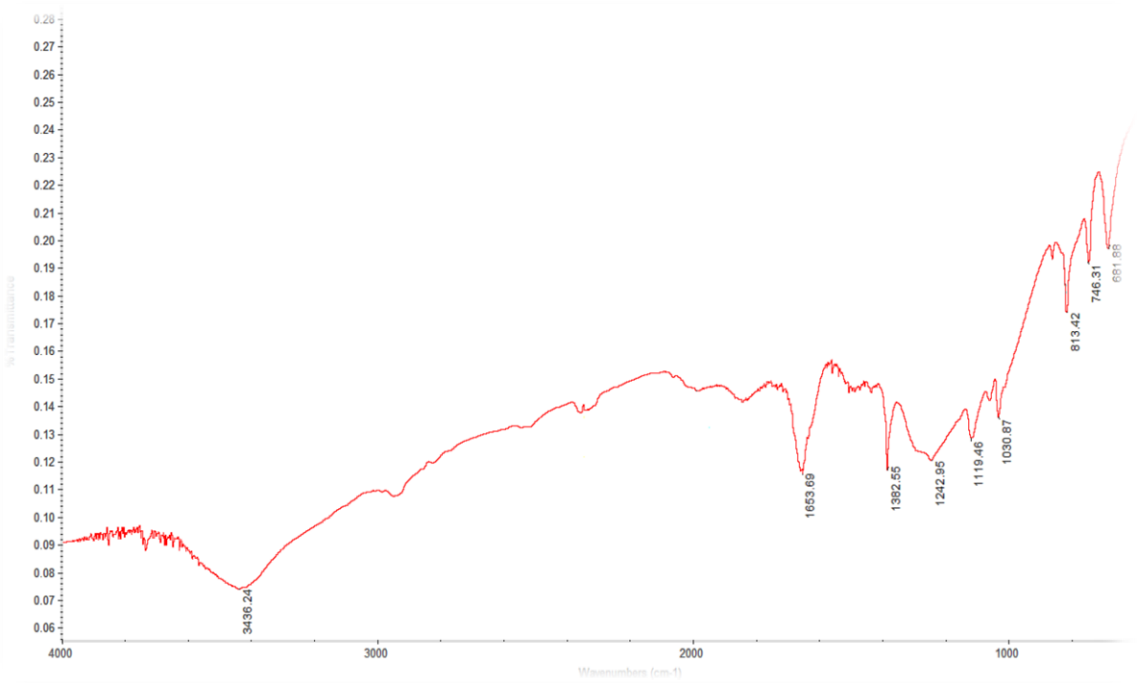


Fig. S8. IR spectrum of $[Lu(DMF)_3(NO_3)_3]$.

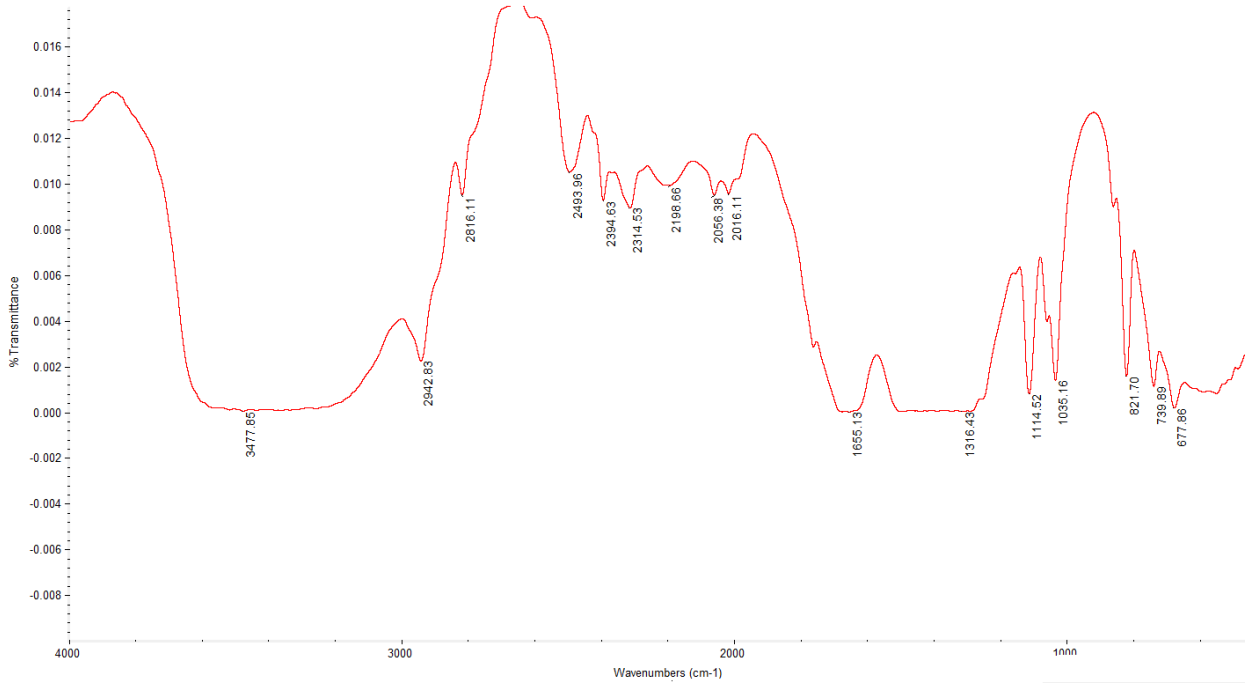


Fig. S9. IR spectrum of $[Ce(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

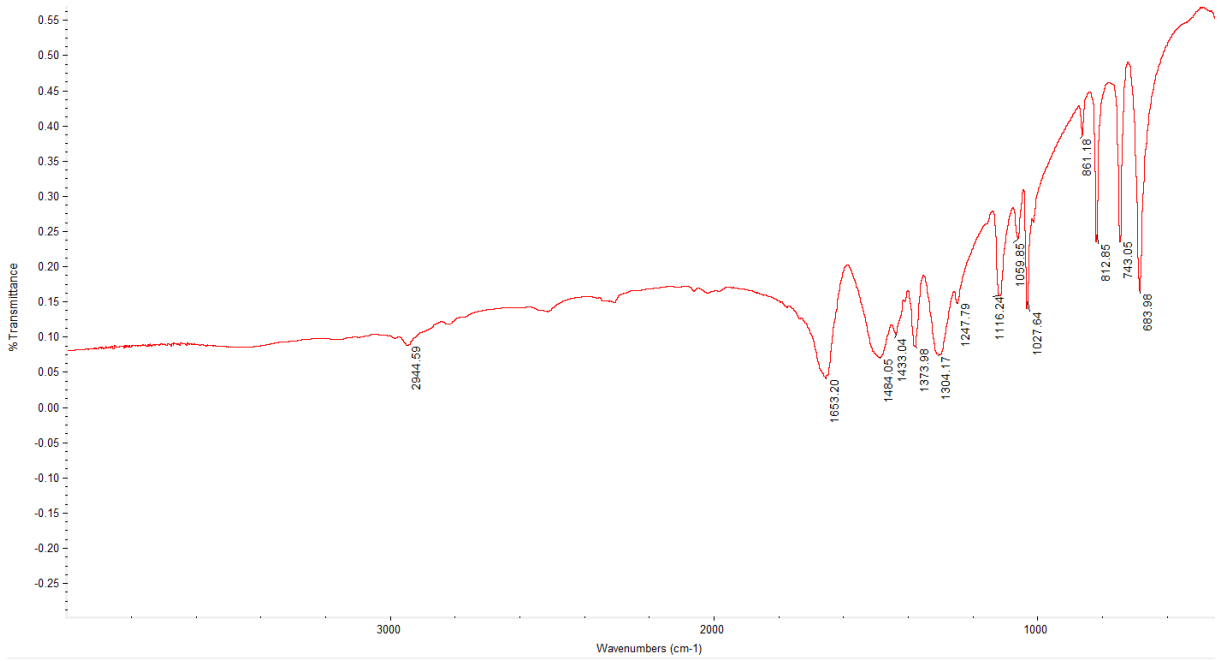


Fig. S10. IR spectrum of $[Ho(DMF)_3(NO_3)_3]$.

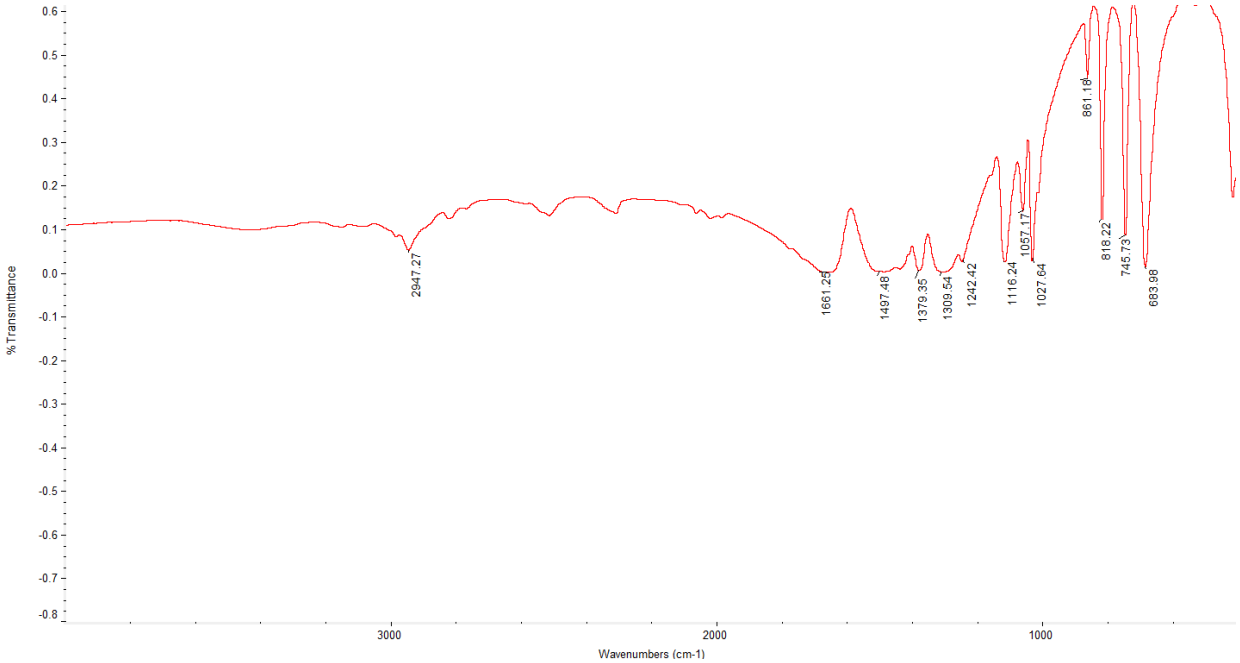


Fig. S11. IR spectrum of $[Er(DMF)_3(NO_3)_3]$.

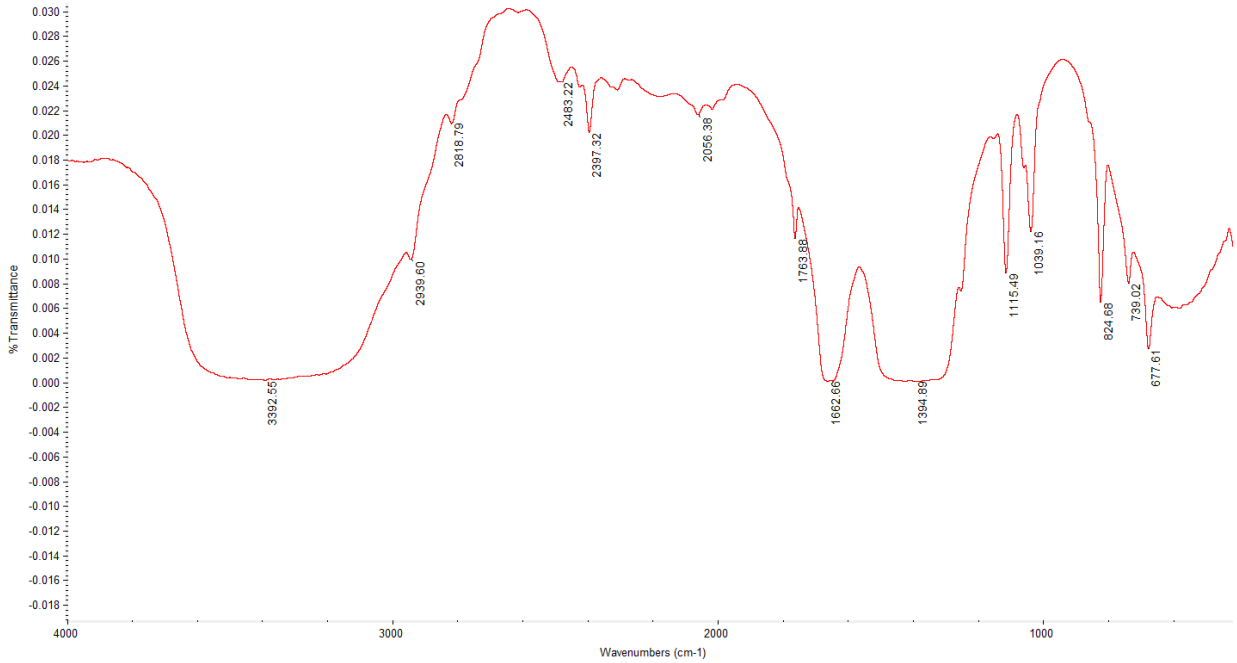


Fig. S12. IR spectrum of $[La(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

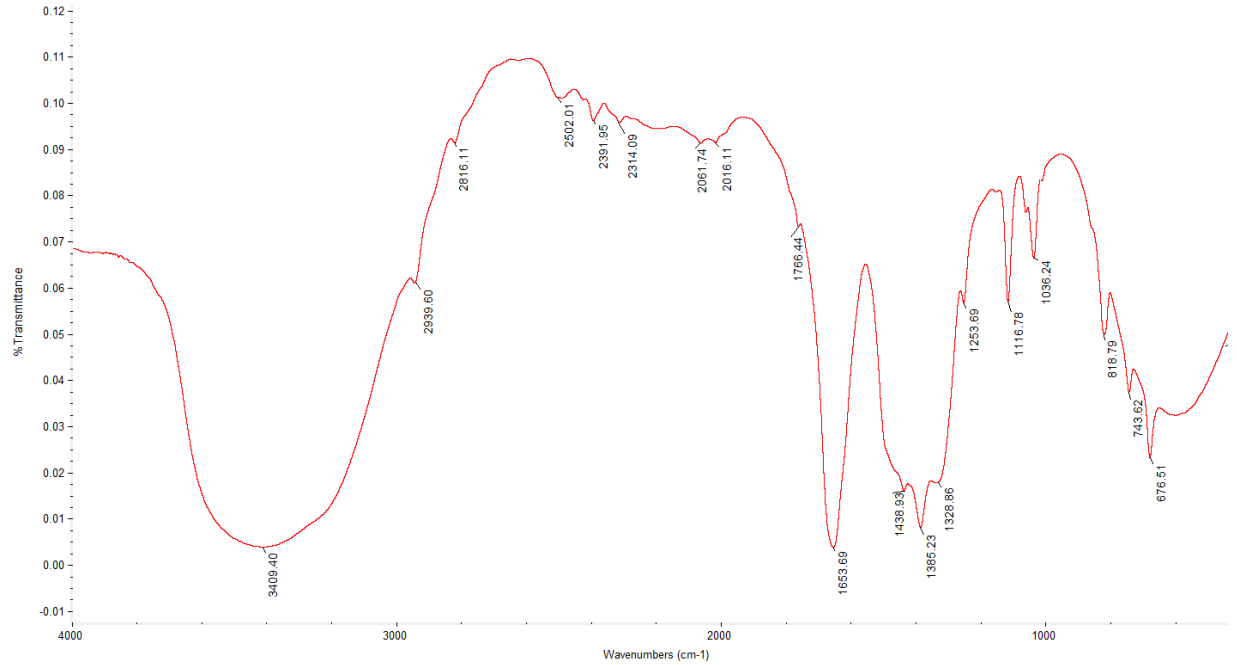


Fig. S13. IR spectrum of $[Nd(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

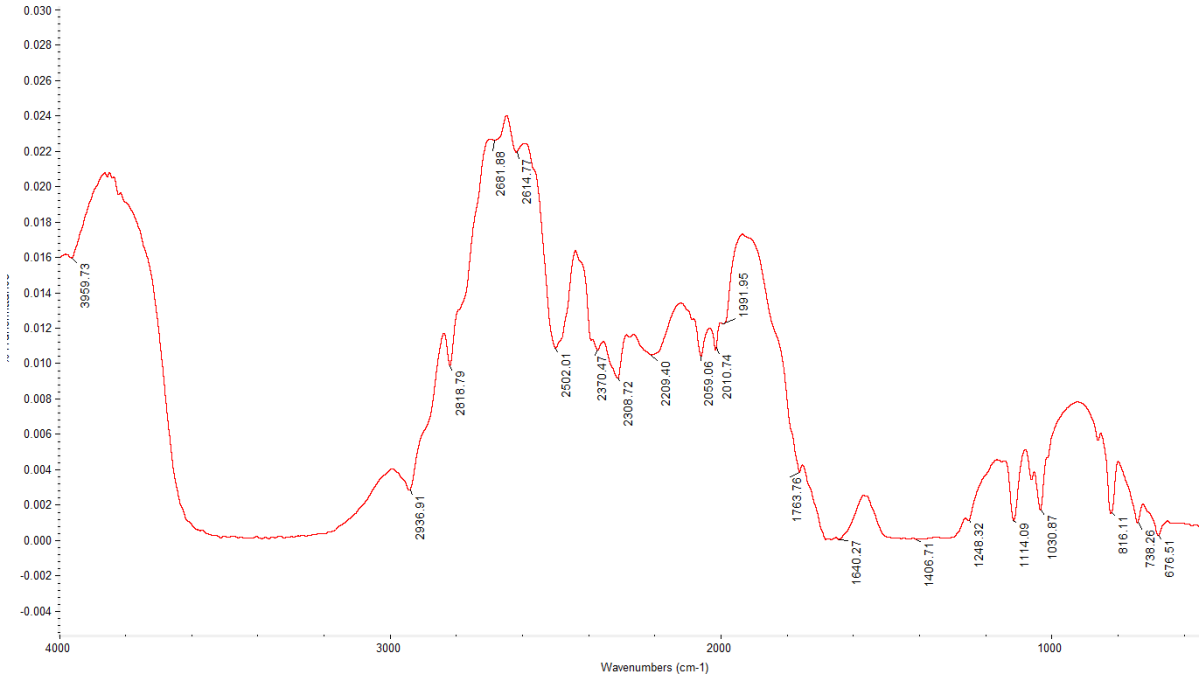


Fig. S14. IR spectrum of $[Pr(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

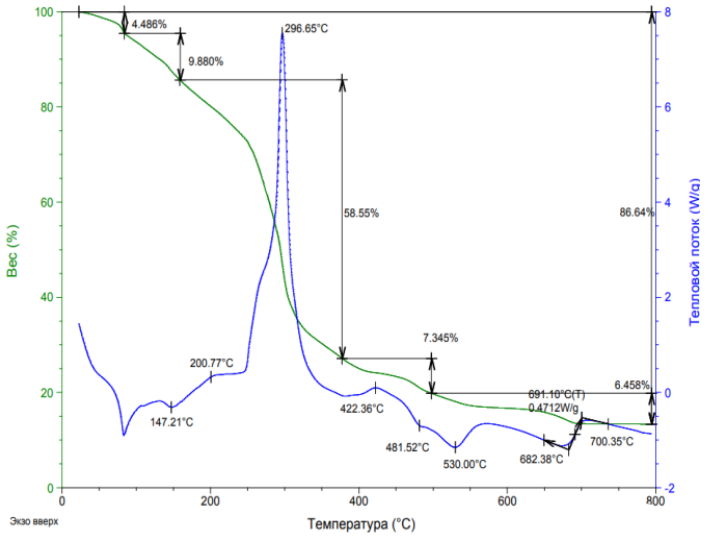


Fig. S15. Thermal curves for $[La(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

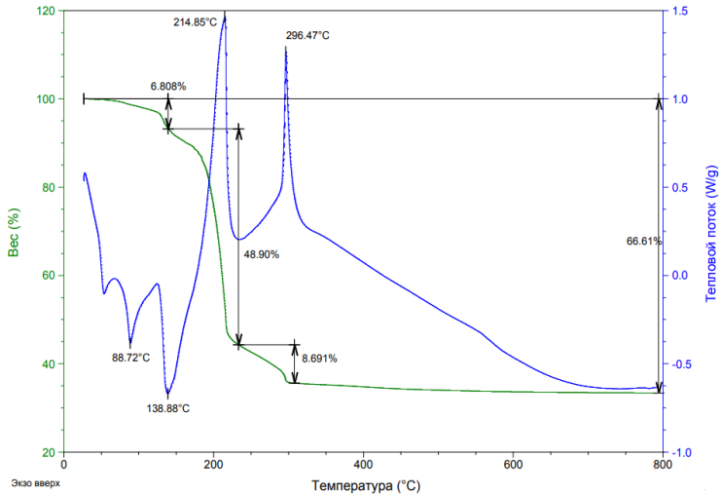


Fig. S16. Thermal curves for $[Ce(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

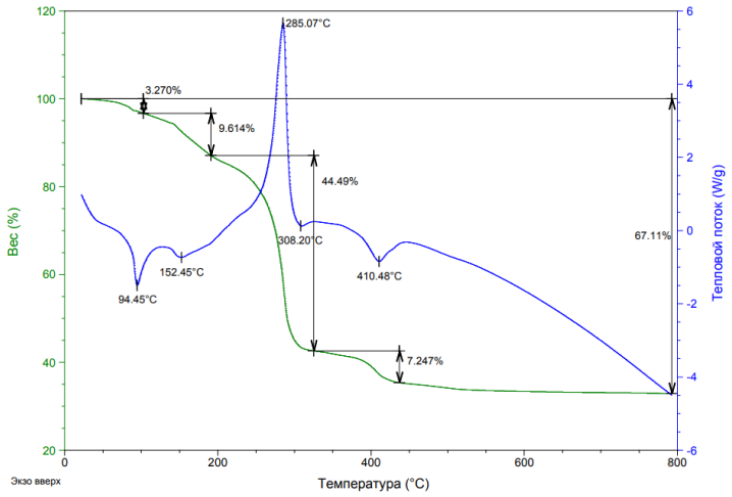


Fig. S17. Thermal curves for $[Pr(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$.

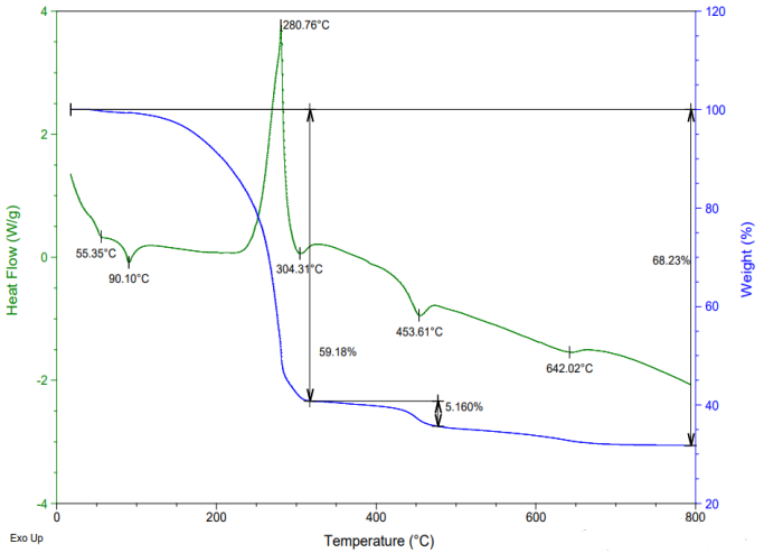


Fig. S18. Thermal curves for $[Sm(DMF)_3(NO_3)_3]$.

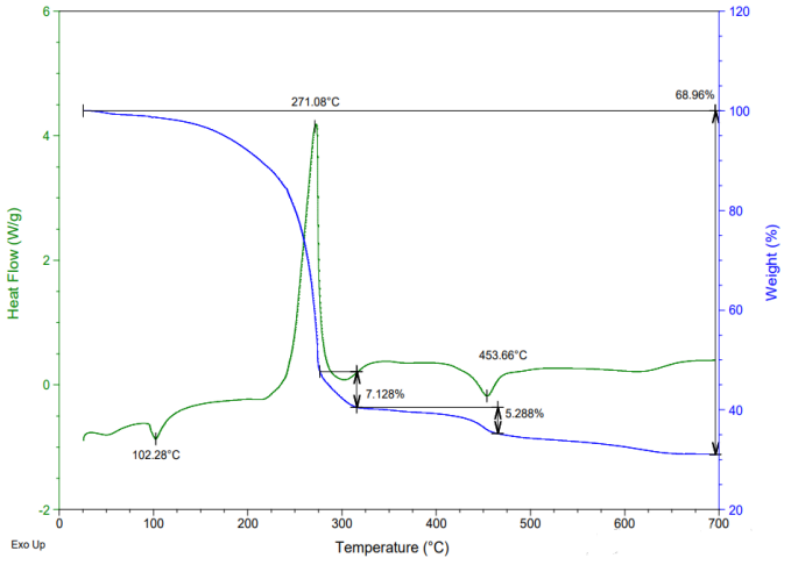


Fig. S19. Thermal curves for $[Eu(DMF)_3(NO_3)_3]$.

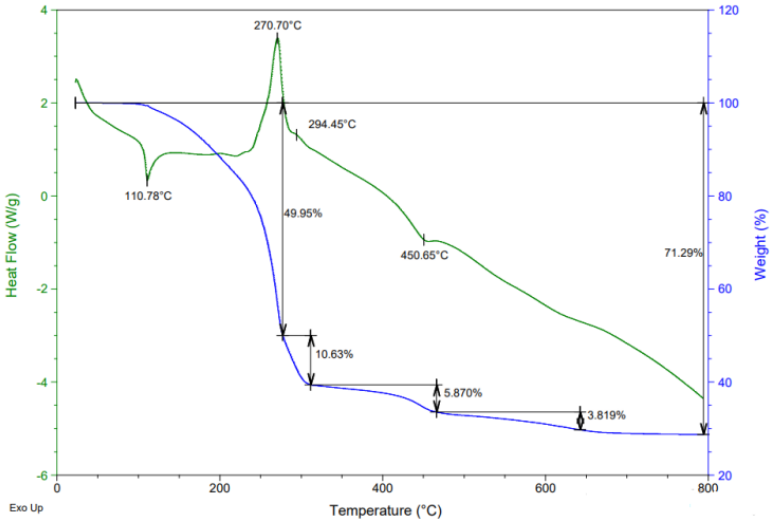


Fig. S20. Thermal curves for $[Gd(DMF)_3(NO_3)_3]$.

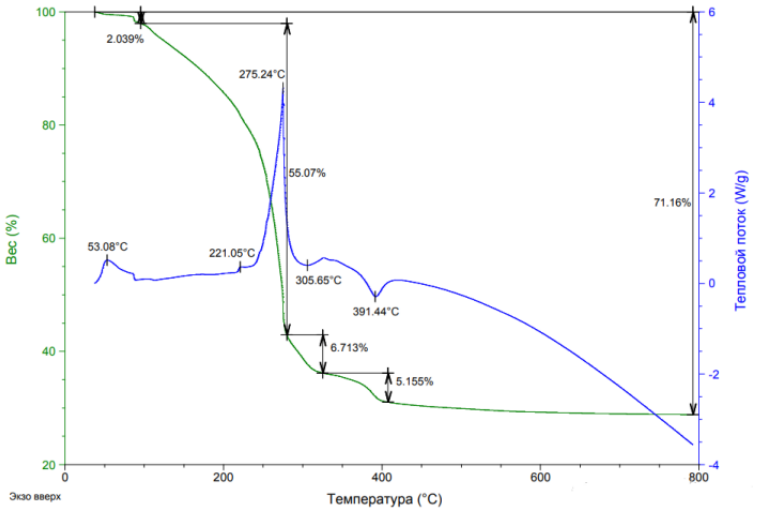


Fig. S21. Thermal curves for $[Tb(DMF)_3(NO_3)_3]$.

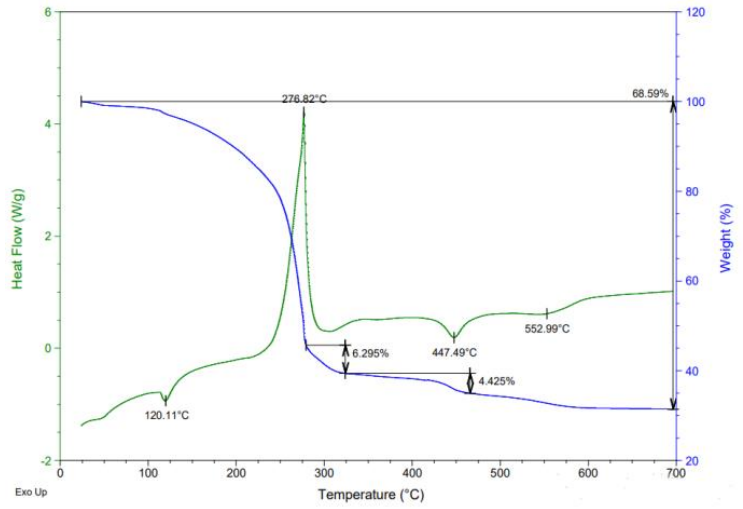


Fig. S22. Thermal curves for $[Dy(DMF)_3(NO_3)_3]$.

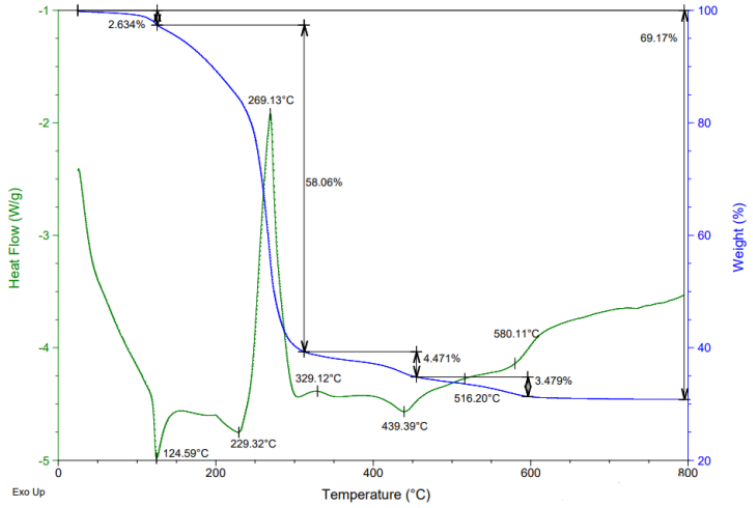


Fig. S23. Thermal curves for $[Ho(DMF)_3(NO_3)_3]$.

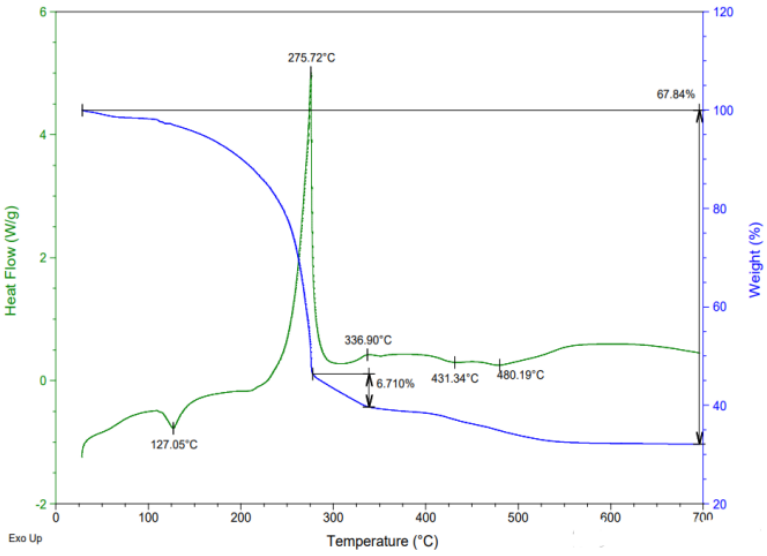


Fig. S24. Thermal curves for $[Er(DMF)_3(NO_3)_3]$.

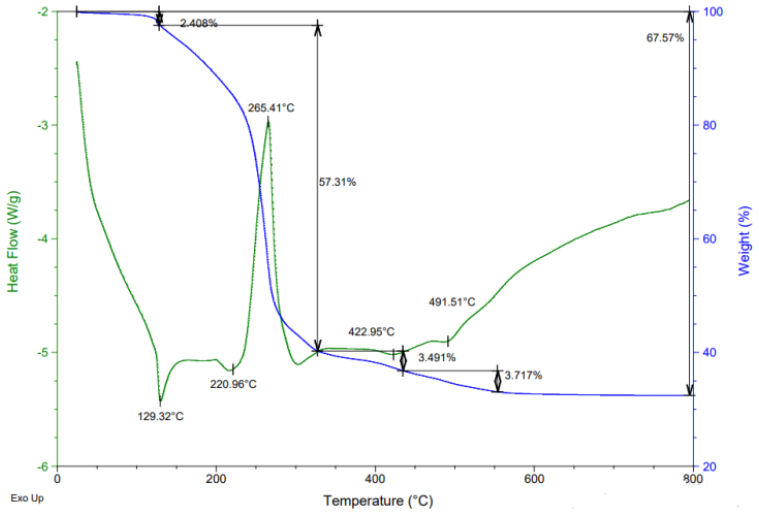


Fig. S25. Thermal curves for $[Tm(DMF)_3(NO_3)_3]$.

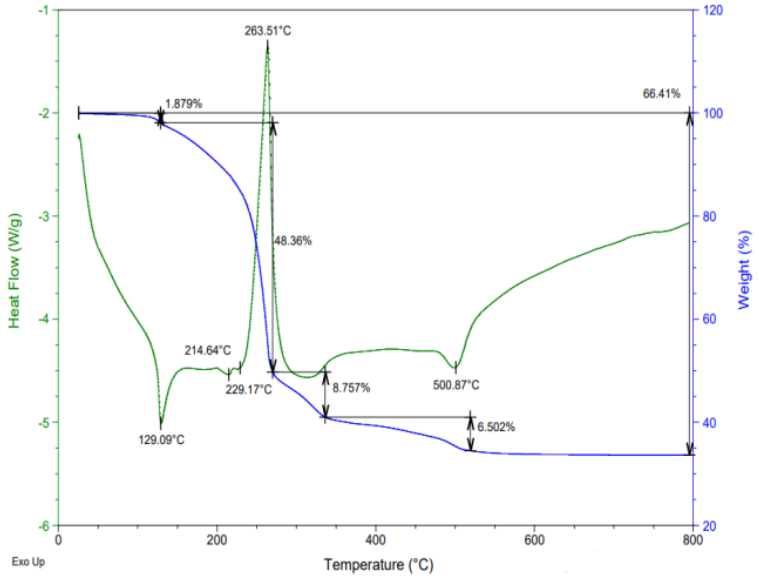


Fig. S26. Thermal curves for $[Yb(DMF)_3(NO_3)_3]$.

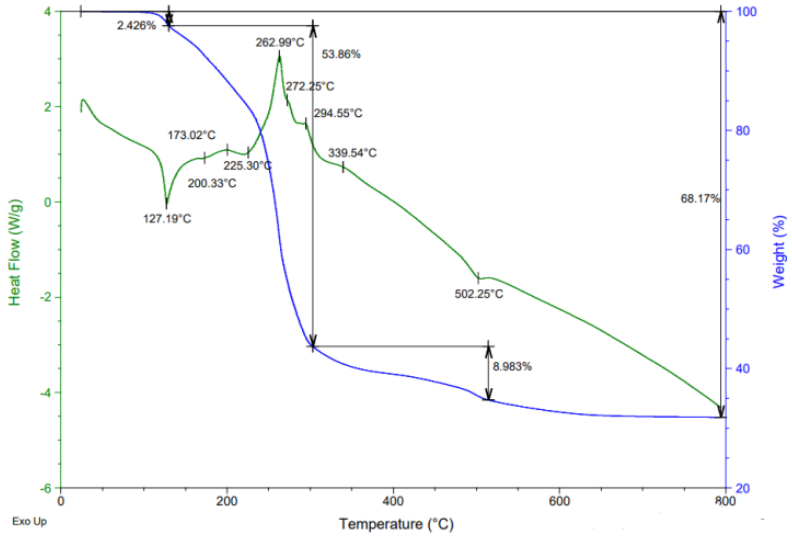


Fig. S27. Thermal curves for $[Lu(DMF)_3(NO_3)_3]$.

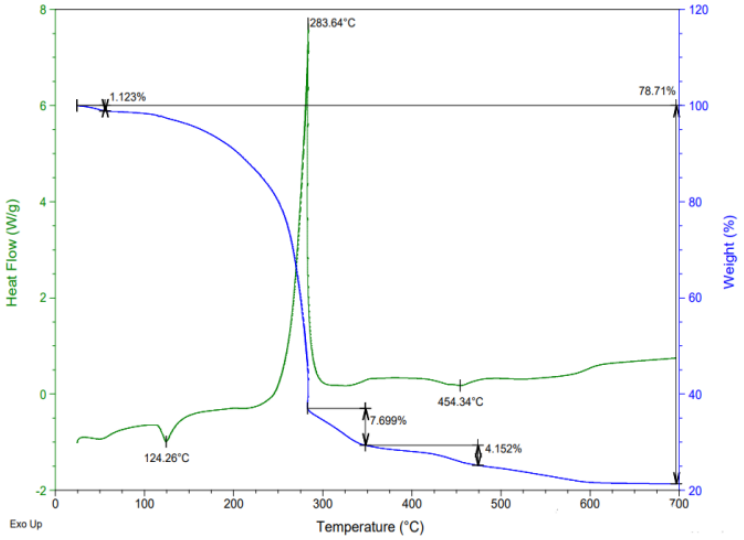


Fig. S28. Thermal curves for $[Y(DMF)_3(NO_3)_3]$.

Table S1. IR spectra ($cm^{-1}$) of the complexes

| DMF | $[M(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$ | | | | | $[M(DMF)_3(NO_3)_3]$ | | | | | | | | | | Assighment |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| 3644<br>3337 | - | 3392 | 3478 | 3341 | 3366 | - | - | - | - | - | - | - | - | - | - | ν(OH)+<br>ν(NH) |
| 1675 | 1659 | 1662 | 1655 | 1653 | 1654 | 1655 | 1659 | 1659 | 1656 | 1664 | 1657 | 1659 | 1653 | 1656 | 1653 | ν(CO) |
| 1152 | 1116 | 1115 | 1114 | 1117 | 1116 | 1118 | 1116 | 1119 | 114 | 1122 | 1114 | 1119 | 1119 | 1119 | 1120 | $\rho(NH_2)$ |
| 1064 | 1030 | 1039 | 1035 | 1034 | 1038 | 1027 | 1030 | 1033 | 1028 | 1033 | 1030 | 1036 | 1030 | 1028 | 1030 | $\nu_s(NO_2)$ |
| - | 1245 | 1243 | 1245 | 1253 | 1251 | 1291 | 1296 | 1242 | 1299 | 1248 | 1247 | 1242 | 1245 | 1247 | 1299 | $\nu_{1as}(NO_3^-)$ |
| - | 1494 | 1450 | 1450 | 1457 | 1463 | 1489 | 1495 | 1487 | 1492 | 1489 | 1487 | 1497 | 1497 | 1497 | 1489 | $\nu_{2as}(NO_3^-)$ |
| - | 818 | 824 | 821 | 818 | 818 | 818 | 818 | 818 | 818 | 821 | 816 | 818 | 813 | 816 | 814 | $\pi(NO_3)$ |
| - | 743 | 739 | 739 | 743 | 742 | 740 | 740 | 740 | 743 | 740 | 743 | 745 | 745 | 748 | 748 | ω(NH) |
| - | 683 | 677 | 677 | 679 | 679 | 679 | 678 | 678 | 681 | 679 | 683 | 683 | 686 | 689 | 684 | $\delta_{as}(NO_3)$ |

Table S2. Selected bond lengths and angles for $[Pr(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$ (**III**)

| Bond length (Å) | Bond angle (°) | Torsion angle (°) |
|---|---|---|
| Pr01 O1 2.3642(13) | C1 O1 Pr01 163.26(14) N2 | Pr01 O3 N2 O4 170.06(14) |
| Pr01 O3W 2.4439(14) | O2 Pr01 96.63(10) N2 O3 | Pr01 O3 N2 O2 -9.48(16) |
| Pr01 O1W 2.4686(14) | Pr01 97.65(10) N3 O5 Pr01 | Pr01 O2 N2 O4 –170.16(14) |
| Pr01 O2W 2.4869(14) | 96.54(10) N3 O6 Pr01 | Pr01 O2 N2 O3 9.38(15) |
| Pr01 O8 2.5757(13) | 97.72(10) N4 O8 Pr01 | Pr01 O5 N3 O7 177.85(14) |
| Pr01 O6 2.5935(13) | 97.50(10) N4 O9 Pr01 | Pr01 O5 N3 O6 –1.95(15) |
| Pr01 O9 2.6008(14) | 96.75(11) | Pr01 O6 N3 O7 –177.83(14) |
| Pr01 O5 2.6260(14) | | Pr01 O6 N3 O5 1.98(16) |
| Pr01 O3 2.6445(13) | | Pr01 O9 N4 O10 –179.35(16) |
| Pr01 O2 2.6652(14) | | Pr01 O9 N4 O8 0.88(16) |
| | | Pr01 O8 N4 O10 179.34(16) |
| | | Pr01 O8 N4 O9 –0.89(17) |
| | | Pr01 O1 C1 N1 –172.4(3) |

Table S3. Selected H-bonds in $[Pr(H_2O)_3(DMF)(NO_3)_3]\cdot H_2O$ (**III**)

| D–H–A | D–H (Å) | H–A (Å) | D–A (Å) | D–H–A [°] |
|---|---|---|---|---|
| O1W–H1B–O4W | 0.73(3) | 2.06(3) | 2.787(2) | 170(3) |
| O1W–H1C–O4W$^{i}$ | 0.76(3) | 2.06(3) | 2.818(2) | 176(3) |
| O2W–H2D–O6$^{ii}$ | 0.79(3) | 2.03(3) | 2.8240(19) | 174(2) |
| O2W–H2E–O3$^{iii}$ | 0.80(3) | 2.11(3) | 2.899(2) | 173(2) |
| O3W–H3D–O2$^{iv}$ | 0.77(3) | 2.06(3) | 2.811(2) | 164(3) |
| O3W–H3E–O4$^{iii}$ | 0.78(3) | 2.01(3) | 2.786(2) | 173(3) |
| O4W–H4A–O8$^{v}$ | 0.77(3) | 2.14(3) | 2.912(2) | 175(3) |
| O4W–H4B–O5$^{vi}$ | 0.84(3) | 2.14(3) | 2.979(2) | 176(2) |

(i) 1-x, 1-y, 1-z; (ii) 1-x, 2-y, 1-z; (iii) -1+x, y, z; (iv) 1-x, 1-y, 2-z; (v) x, -1+y, z; (vi) 2-x, 1-y, 1-z.

Table S4. Selected bond lengths and angles for $[Dy(DMF)_3(NO_3)_3]$ (**IX**)

| Bond length (Å) | Bond angle (°) | Torsion angle (°) |
|---|---|---|
| Dy1 O1 2.283(3) | C11A O1 Dy1 130.8(6) | Dy1 O4 N4 O6 177.7(4) |
| Dy1 O3 2.292(2) | C11 O1 Dy1 140.2(3) | Dy1 O4 N4 O5 –2.7(3) |
| Dy1 O2 2.305(3) | C21 O2 Dy1 137.5(3) | Dy1 O5 N4 O6 –177.6(3) |
| Dy1 O5 2.429(3) | C31 O3 Dy1 138.7(2) | Dy1 O5 N4 O4 2.8(3) |
| Dy1 O10 2.433(3) | N4 O4 Dy1 95.0(2) | Dy1 O7 N5 O9 –173.2(3) |
| Dy1 O7 2.434(3) | N4 O5 Dy1 96.4(2) | Dy1 O7 N5 O8 6.0(4) |
| Dy1 O11 2.468(3) | N5 O7 Dy1 97.2(2) | Dy1 O8 N5 O9 173.4(3) |
| Dy1 O4 2.470(3) | N5 O8 Dy1 95.3(2) | Dy1 O8 N5 O7 –5.9(4) |
| Dy1 O8 2.473(3) | N6 O10 Dy1 97.3(2) | Dy1 O11 N6 O12 –175.7(3) |
| Dy1 N4 2.870(4) | N6 O11 Dy1 95.8(2) | Dy1 O11 N6 O10 3.3(3) |
| Dy1 N5 2.875(4) | | Dy1 O10 N6 O12 175.7(3) |
| Dy1 N6 2.883(3) | | Dy1 O10 N6 O11 –3.3(3) |
| | | Dy1 O1 C11 N1 –127.3(4) |
| | | C13 N1 C11 O1 3.5(8) |
| | | C12 N1 C11 O1 –179.3(5) |
| | | Dy1 O1 C11A N1 138.7(6) |
| | | C13A N1 C11A O1 2.5(13) |
| | | C12A N1 C11A O1 172.9(9) |
| | | Dy1 O2 C21 N2 –162.7(3) |
| | | C22 N2 C21 O2 179.9(3) |
| | | C23 N2 C21 O2 1.9(5) |
| | | Dy1 O3 C31 N3 –169.2(3) |
| | | C33 N3 C31 O3 2.0(5) |
| | | C32 N3 C31 O3 –179.1(4) |

Table S5. Selected bond lengths and angles for $[Er(DMF)_3(NO_3)_3]$ (**XI**)

| Bond length (Å) | Bond angle (°) | Torsion angle (°) |
|---|---|---|
| Er1 O1 2.250(4) | C11 O1 Er1 140.4(5) | Er1 O4 N4 O6 177.3(5) |
| Er1 O3 2.267(3) | C11A O1 Er1 132.1(9) | Er1 O4 N4 O5 –1.8(5) |
| Er1 O2 2.281(4) | C21 O2 Er1 137.7(4) | Er1 O5 N4 O6 –177.3(5) |
| Er1 O5 2.381(3) | C31 O3 Er1 137.8(3) | Er1 O5 N4 O4 1.9(5) |
| Er1 O10 2.395(3) | N4 O4 Er1 93.9(4) | Er1 O8 N5 O9 173.7(5) |
| Er1 O7 2.396(5) | N4 O5 Er1 96.2(4) | Er1 O8 N5 O7 –6.3(5) |
| Er1 O11 2.427(4) | N5 O7 Er1 97.5(4) | Er1 O7 N5 O9 –173.5(5) |
| Er1 O8 2.432(5) | N5 O8 Er1 96.0(3) | Er1 O7 N5 O8 6.4(5) |
| Er1 O4 2.439(4) | N6 O10 Er1 96.8(3) | Er1 O11 N6 O12 –175.8(5) |
| Er1 N4 2.819(5) | N6 O11 Er1 95.7(3) | Er1 O11 N6 O10 3.2(5) |
| Er1 N6 2.838(4) | | Er1 O10 N6 O12 175.8(5) |
| Er1 N5 2.850(6) | | Er1 O10 N6 O11 –3.3(5) |
| | | Er1 O1 C11 N1 –127.0(7) |
| | | C13 N1 C11 O1 2.4(11) |
| | | C12 N1 C11 O1 –179.1(7) |
| | | Er1 O1 C11A N1 137.7(10) |
| | | C13A N1 C11A O1 0(2) |
| | | C12A N1 C11A O1 172.7(14) |
| | | Er1 O2 C21 N2 –162.8(4) |
| | | C23 N2 C21 O2 2.3(9) |
| | | C22 N2 C21 O2 180.0(6) |
| | | Er1 O3 C31 N3 –169.6(3) |
| | | C33 N3 C31 O3 1.6(7) |
| | | C32 N3 C31 O3 –178.8(5) |

Table S6. Selected bond lengths and angles for $[Y(DMF)_3(NO_3)_3]$ (**XV**)

| Bond length (Å) | Bond angle (°) | Torsion angle (°) |
|---|---|---|
| Y1 O1 2.264(3) | C11A O1 Y1 131.3(7) | Y1 O4 N4 O6 –177.5(4) |
| Y1 O3 2.286(2) | C11 O1 Y1 140.6(4) | Y1 O4 N4 O5 2.6(3) |
| Y1 O2 2.292(3) | C21 O2 Y1 137.9(3) | Y1 O5 N4 O6 177.4(3) |
| Y1 O5 2.404(3) | C31 O3 Y1 138.1(2) | Y1 O5 N4 O4 –2.7(3) |
| Y1 O10 2.417(3) | N4 O4 Y1 95.2(2) | Y1 O7 N5 O9 173.5(3) |
| Y1 O7 2.422(3) | N4 O5 Y1 96.2(3) | Y1 O7 N5 O8 –5.2(4) |
| Y1 O4 2.450(3) | N5 O7 Y1 97.3(2) | Y1 O8 N5 O9 –173.6(3) |
| Y1 O11 2.453(3) | N5 O8 Y1 95.3(2) | Y1 O8 N5 O7 5.1(4) |
| Y1 O8 2.463(3) | N6 O10 Y1 97.4(2) | Y1 O10 N6 O12 –176.2(3) |
| Y1 N4 2.851(4) | N6 O11 Y1 95.5(2) | Y1 O10 N6 O11 3.8(4) |
| Y1 N6 2.863(4) | | Y1 O11 N6 O12 176.3(3) |
| Y1 N5 2.869(4) | | Y1 O11 N6 O10 –3.7(3) |
| | | Y1 O1 C11 N1 127.5(5) |
| | | C13 N1 C11 O1 –1.1(9) |
| | | C12 N1 C11 O1 179.3(5) |
| | | Y1 O1 C11A N1 –138.7(7) |
| | | C13A N1 C11A O1 –1.9(16) |
| | | C12A N1 C11A O1 –171.9(11) |
| | | Y1 O2 C21 N2 161.9(3) |
| | | C23 N2 C21 O2 –1.7(6) |
| | | C22 N2 C21 O2 179.9(4) |
| | | Y1 O3 C31 N3 168.7(3) |
| | | C33 N3 C31 O3 –1.2(6) |
| | | C32 N3 C31 O3 178.9(4) |