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# Lanthanide(III) and Group 13 Metal Ion Complexes of Tripodal Amine Phosphinate Ligands

Michael S. Kovacs, Vishakha Monga, Brian O. Patrick, and Chris Orvig*

Medicinal Inorganic Chemistry Group, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.
Email: orvig@chem.ubc.ca

**X-ray crystallographic analysis of $[Ga(H_3ppba)_2][(NO_3)_2Cl]\cdot 3CH_3OH$ (1).** Data were collected on a Rigaku/ADSC CCD diffractometer at UBC at -100(1)$^oC$. The structure was solved by direct methods[8] and was expanded using Fourier techniques.[3] All hydrogen atoms other than those involved in hydrogen-bonding were included in calculated positions but were not refined. The unit cell contains several void spaces where solvents and counterions reside. While there are areas with significant electron density, no satisfactory models for $Cl^-$, $NO_3^-$ or $CH_3OH$ were possible. As a result, the data were corrected for the electron density in these void spaces using PLATON.[5] The corrected data greatly improved the residuals (R1 = 0.12 to 0.048). No inferences should be made as to the nature of the counterions or the amount of solvent molecules in the asymmetric unit. Readers should refer to elemental analysis results for the elucidation of the exact chemical composition of this material. Complete lists of bond lengths and bond angles appear in Tables S2 and S3.

**X-ray crystallographic analysis of $[Gd(H_4ppba)_2][(NO_3)_4Cl]\cdot 3CH_3OH$ (2).** Data were collected on a Rigaku/ADSC CCD diffractometer at UBC at -100(1)$^oC$. The structure was solved by direct methods[8]and was expanded using Fourier techniques.[3] The material resides on a 3-fold inversion axis, with the Gd atom having a population of 1/6. Both N(1) and N(2) appear to be protonated, with the protons found and refined from a difference map. The anions appear to be a disordered mixture of $Cl^-$ and $NO_3^-$. Restraints were used to fix the geometries of the two disordered $NO_3^-$ fragments, and relative populations of 0.5 and 0.166667 were given to the major and minor fragments, respectively. A population of 0.166667 was also given to Cl(1). Unresolvable disordered solvent molecules reside in the large voids between the cationic Gd-complexes in the unit

cell. The data were therefore corrected using PLATON/SQUEEZE.[5] R1 was found to drop from 0.079 to 0.034. Complete lists of bond lengths and bond angles appear in Tables S4 and S5.

**References**

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**Table S1.** Selected Crystallographic Data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Formula | $C_{96}H_{114}GaN_8O_{12}P_6$ | $C_{96}H_{116}GdN_{12}O_{24}P_6Cl$ |
| FW | 1827.49 | 2200.53 |
| Crystal System | trigonal | trigonal |
| a, Å | 23.9800(7) | 14.9142(4) |
| b, Å | 23.9800(7) | 14.9142(4) |
| c, Å | 32.5706(9) | 44.202(2) |
| $\alpha$, º | 90 | 90 |
| $\beta$, º | 90 | 90 |
| $\gamma$, º | 120 | 120 |
| V, Å$^3$ | 16220.1(8) | 8514.4(5) |
| T ,K | 173 | 198 |
| Z | 6 | 3 |
| Space group | R –3c | R-3 |
| $\mu$, mm$^{-1}$ | 0.399 | 0.762 |
| # reflections | 46807 | 18646 |
| # unique | 4271 | 4368 |
| R(int) | 0.031 | 0.045 |
| $R_1$ ($I > 2\sigma(I)$) | 0.046 | 0.034 |
| $wR_2$ (all data) | 0.134 | 0.093 |

$R_1 = \Sigma| |F_o| - |F_c|| / \Sigma|F_o|$ , $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$

**Table S2.** Bond Lengths (Å) for $[Ga(H_3ppba)_2](NO_3)_2Cl\cdot 3CH_3OH$ (**1**).

| | |
|---|---|
| C(1)-N(1) | 1.479(2) |
| C(1)-C(2) | 1.520(3) |
| C(1)-H(1A) | 0.9900 |
| C(1)-H(1B) | 0.9900 |
| C(2)-N(2) | 1.511(3) |
| C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 |
| C(3)-N(2) | 1.495(2) |
| C(3)-P(1) | 1.8355(19) |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(4)-C(5) | 1.389(3) |
| C(4)-C(9) | 1.392(3) |
| C(4)-P(1) | 1.796(2) |
| C(5)-C(6) | 1.388(3) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.369(4) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.387(4) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.383(3) |
| C(8)-H(8) | 0.9500 |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.510(3) |
| C(10)-N(2) | 1.524(3) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(16) | 1.391(3) |
| C(11)-C(12) | 1.394(3) |
| C(12)-C(13) | 1.401(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.375(5) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.374(5) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.389(3) |
| C(15)-H(15) | 0.9500 |
| C(16)-H(16) | 0.9500 |
| N(1)-C(1)#1 | 1.479(2) |
| N(1)-C(1)#2 | 1.479(2) |
| N(2)-H(2N) | 0.94(3) |
| O(1)-P(1) | 1.5051(13) |
| O(1)-Ga(1) | 1.9501(13) |
| O(2)-P(1) | 1.4923(14) |
| Ga(1)-O(1)#3 | 1.9500(13) |
| Ga(1)-O(1)#1 | 1.9501(13) |
| Ga(1)-O(1)#4 | 1.9501(13) |
| Ga(1)-O(1)#2 | 1.9501(13) |
| Ga(1)-O(1)#5 | 1.9501(13) |

**Table S3.** Bond Angles (deg) for $[Ga(H_3ppba)_2](NO_3)_2Cl\cdot 3CH_3OH$ (**1**).

| | |
|---|---|
| N(1)-C(1)-C(2) | 112.39(18) |
| N(1)-C(1)-H(1A) | 109.1 |
| C(2)-C(1)-H(1A) | 109.1 |
| N(1)-C(1)-H(1B) | 109.1 |
| C(2)-C(1)-H(1B) | 109.1 |
| H(1A)-C(1)-H(1B) | 107.9 |
| N(2)-C(2)-C(1) | 112.03(17) |
| N(2)-C(2)-H(2A) | 109.2 |
| C(1)-C(2)-H(2A) | 109.2 |
| N(2)-C(2)-H(2B) | 109.2 |
| C(1)-C(2)-H(2B) | 109.2 |
| H(2A)-C(2)-H(2B) | 107.9 |
| N(2)-C(3)-P(1) | 114.14(13) |
| N(2)-C(3)-H(3A) | 108.7 |
| P(1)-C(3)-H(3A) | 108.7 |
| N(2)-C(3)-H(3B) | 108.7 |
| P(1)-C(3)-H(3B) | 108.7 |
| H(3A)-C(3)-H(3B) | 107.6 |
| C(5)-C(4)-C(9) | 119.2(2) |
| C(5)-C(4)-P(1) | 119.78(17) |
| C(9)-C(4)-P(1) | 120.86(16) |
| C(6)-C(5)-C(4) | 120.2(2) |
| C(6)-C(5)-H(5) | 119.9 |
| C(4)-C(5)-H(5) | 119.9 |
| C(7)-C(6)-C(5) | 120.2(2) |
| C(7)-C(6)-H(6) | 119.9 |
| C(5)-C(6)-H(6) | 119.9 |
| C(6)-C(7)-C(8) | 120.1(2) |
| C(6)-C(7)-H(7) | 119.9 |
| C(8)-C(7)-H(7) | 119.9 |
| C(9)-C(8)-C(7) | 120.1(3) |
| C(9)-C(8)-H(8) | 120.0 |
| C(7)-C(8)-H(8) | 120.0 |
| C(8)-C(9)-C(4) | 120.1(2) |
| C(8)-C(9)-H(9) | 119.9 |
| C(4)-C(9)-H(9) | 119.9 |
| C(11)-C(10)-N(2) | 114.52(16) |
| C(11)-C(10)-H(10A) | 108.6 |
| N(2)-C(10)-H(10A) | 108.6 |
| C(11)-C(10)-H(10B) | 108.6 |
| N(2)-C(10)-H(10B) | 108.6 |
| H(10A)-C(10)-H(10B) | 107.6 |
| C(16)-C(11)-C(12) | 118.6(2) |
| C(16)-C(11)-C(10) | 121.6(2) |
| C(12)-C(11)-C(10) | 119.7(2) |
| C(11)-C(12)-C(13) | 120.3(3) |
| C(11)-C(12)-H(12) | 119.9 |
| C(13)-C(12)-H(12) | 119.9 |
| C(14)-C(13)-C(12) | 119.7(3) |
| C(14)-C(13)-H(13) | 120.2 |
| C(12)-C(13)-H(13) | 120.2 |
| C(15)-C(14)-C(13) | 120.8(2) |

| | |
|---|---|
| C(15)-C(14)-H(14) | 119.6 |
| C(13)-C(14)-H(14) | 119.6 |
| C(14)-C(15)-C(16) | 119.8(3) |
| C(14)-C(15)-H(15) | 120.1 |
| C(16)-C(15)-H(15) | 120.1 |
| C(15)-C(16)-C(11) | 120.8(3) |
| C(15)-C(16)-H(16) | 119.6 |
| C(11)-C(16)-H(16) | 119.6 |
| C(1)#1-N(1)-C(1)#2 | 108.90(15) |
| C(1)#1-N(1)-C(1) | 108.90(15) |
| C(1)#2-N(1)-C(1) | 108.90(15) |
| C(3)-N(2)-C(2) | 111.22(15) |
| C(3)-N(2)-C(10) | 111.39(16) |
| C(2)-N(2)-C(10) | 112.16(16) |
| C(3)-N(2)-H(2N) | 105.7(17) |
| C(2)-N(2)-H(2N) | 113.9(17) |
| C(10)-N(2)-H(2N) | 101.9(17) |
| P(1)-O(1)-Ga(1) | 143.83(8) |
| O(2)-P(1)-O(1) | 120.24(8) |
| O(2)-P(1)-C(4) | 109.84(9) |
| O(1)-P(1)-C(4) | 110.32(9) |
| O(2)-P(1)-C(3) | 110.76(9) |
| O(1)-P(1)-C(3) | 104.05(8) |
| C(4)-P(1)-C(3) | 99.51(9) |
| O(1)#3-Ga(1)-O(1)#1 | 180.00(7) |
| O(1)#3-Ga(1)-O(1)#4 | 91.15(6) |
| O(1)#1-Ga(1)-O(1)#4 | 88.85(6) |
| O(1)#3-Ga(1)-O(1) | 88.85(6) |
| O(1)#1-Ga(1)-O(1) | 91.15(6) |
| O(1)#4-Ga(1)-O(1) | 180.0 |
| O(1)#3-Ga(1)-O(1)#2 | 88.85(6) |
| O(1)#1-Ga(1)-O(1)#2 | 91.15(6) |
| O(1)#4-Ga(1)-O(1)#2 | 88.85(6) |
| O(1)-Ga(1)-O(1)#2 | 91.15(6) |
| O(1)#3-Ga(1)-O(1)#5 | 91.15(6) |
| O(1)#1-Ga(1)-O(1)#5 | 88.85(6) |
| O(1)#4-Ga(1)-O(1)#5 | 91.15(6) |
| O(1)-Ga(1)-O(1)#5 | 88.85(6) |
| O(1)#2-Ga(1)-O(1)#5 | 180.0 |

**Table S4.** Bond Lengths (Å) for $[Gd(H_4ppba)_2](NO_3)_4Cl\cdot 3CH_3OH$ (**2**).

| | | | | | |
|---|---|---|---|---|---|
| Gd1 | -O2 | 2.2841(17) | C10 | -C11 | 1.379(5) |
| P1 | -O1 | 1.500(2) | C11 | -C12 | 1.392(7) |
| P1 | -O2 | 1.5104(16) | C12 | -C13 | 1.365(6) |
| P1 | -C1 | 1.797(3) | C13 | -C14 | 1.397(5) |
| P1 | -C7 | 1.845(3) | C15 | -C16 | 1.517(4) |
| O3A | -N3A | 1.214(17) | C2 | -H2 | 0.9514 |
| O3B | -N3B | 1.07(3) | C3 | -H3 | 0.9511 |
| O5A | -N3A | 1.113(14) | C4 | -H4 | 0.9502 |
| O5B | -N3B | 1.22(3) | C5 | -H5 | 0.9497 |
| N1 | -C7 | 1.498(3) | C6 | -H6 | 0.9512 |
| N1 | -C8 | 1.524(3) | C7 | -H7B | 0.9889 |
| N1 | -C15 | 1.522(3) | C7 | -H7A | 0.9893 |
| N2 | -C16 | 1.514(3) | C8 | -H8B | 0.9906 |
| N1 | -H1A | 0.98(5) | C8 | -H8A | 0.9889 |
| N2 | -H2A | 0.89(7) | C10 | -H10 | 0.9496 |
| C1 | -C2 | 1.388(4) | C11 | -H11 | 0.9497 |
| C1 | -C6 | 1.393(4) | C12 | -H12 | 0.9500 |
| C2 | -C3 | 1.387(4) | C13 | -H13 | 0.9502 |
| C3 | -C4 | 1.378(5) | C14 | -H14 | 0.9508 |
| C4 | -C5 | 1.377(6) | C15 | -H15B | 0.9907 |
| C5 | -C6 | 1.396(5) | C15 | -H15A | 0.9902 |
| C8 | -C9 | 1.502(4) | C16 | -H16A | 0.9891 |
| C9 | -C10 | 1.384(4) | C16 | -H16B | 0.9907 |
| C9 | -C14 | 1.393(5) | | | |

**Table S5.** Bond Angles (deg) for $[Gd(H_4ppba)_2](NO_3)_4Cl{\cdot}3CH_3OH$ (**2**).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O2 | -Gd1 | -O2_a | 87.52(6) | C15 | -N1 | -H1A | 104.1(19) |
| O2 | -Gd1 | -O2_b | 87.52(7) | C7 | -N1 | -H1A | 112.4(18) |
| O2 | -Gd1 | -O2_c | 180.00 | C8 | -N1 | -H1A | 109.2(16) |
| O2 | -Gd1 | -O2_d | 92.48(6) | C16 | -N2 | -H2A | 109.92(15) |
| O2 | -Gd1 | -O2_e | 92.48(7) | C16_a | -N2 | -H2A | 109.92(16) |
| O2_a | -Gd1 | -O2_b | 87.52(6) | C16_b | -N2 | -H2A | 109.92(15) |
| O2_a | -Gd1 | -O2_c | 92.48(6) | O3A | -N3A | -O5A | 122.2(14) |
| O2_a | -Gd1 | -O2_d | 180.00 | O3B | -N3B | -O5B | 118(3) |
| O2_a | -Gd1 | -O2_e | 92.48(6) | P1 | -C1 | -C6 | 121.1(2) |
| O2_b | -Gd1 | -O2_c | 92.48(7) | C2 | -C1 | -C6 | 119.3(3) |
| O2_b | -Gd1 | -O2_d | 92.48(6) | P1 | -C1 | -C2 | 119.7(2) |
| O2_b | -Gd1 | -O2_e | 180.00 | C1 | -C2 | -C3 | 120.7(3) |
| O2_c | -Gd1 | -O2_d | 87.52(6) | C2 | -C3 | -C4 | 119.5(3) |
| O2_c | -Gd1 | -O2_e | 87.52(7) | C3 | -C4 | -C5 | 120.8(3) |
| O2_d | -Gd1 | -O2_e | 87.52(6) | C4 | -C5 | -C6 | 119.9(3) |
| O1 | -P1 | -O2 | 117.45(11) | C1 | -C6 | -C5 | 119.8(3) |
| O1 | -P1 | -C1 | 112.67(11) | P1 | -C7 | -N1 | 113.9(2) |
| O1 | -P1 | -C7 | 108.17(10) | N1 | -C8 | -C9 | 115.7(2) |
| O2 | -P1 | -C1 | 107.45(11) | C8 | -C9 | -C14 | 119.1(3) |
| O2 | -P1 | -C7 | 107.94(10) | C10 | -C9 | -C14 | 118.7(3) |
| C1 | -P1 | -C7 | 101.97(12) | C8 | -C9 | -C10 | 121.9(3) |
| Gd1 | -O2 | -P1 | 143.85(10) | C9 | -C10 | -C11 | 121.0(3) |
| C7 | -N1 | -C8 | 112.1(2) | C10 | -C11 | -C12 | 119.9(4) |
| C7 | -N1 | -C15 | 111.03(19) | C11 | -C12 | -C13 | 119.8(3) |
| C8 | -N1 | -C15 | 107.59(18) | C12 | -C13 | -C14 | 120.4(3) |
| C16 | -N2 | -C16_a | 109.0(2) | C9 | -C14 | -C13 | 120.1(3) |
| C16 | -N2 | -C16_b | 109.0(2) | N1 | -C15 | -C16 | 113.4(2) |
| C16_a | -N2 | -C16_b | 109.0(2) | N2 | -C16 | -C15 | 114.7(2) |
| C3 | -C2 | -H2 | 119.61 | C11 | -C10 | -H10 | 119.54 |
| C1 | -C2 | -H2 | 119.64 | C9 | -C10 | -H10 | 119.46 |
| C4 | -C3 | -H3 | 120.30 | C10 | -C11 | -H11 | 120.05 |
| C2 | -C3 | -H3 | 120.19 | C12 | -C11 | -H11 | 120.03 |
| C5 | -C4 | -H4 | 119.71 | C11 | -C12 | -H12 | 120.07 |
| C3 | -C4 | -H4 | 119.53 | C13 | -C12 | -H12 | 120.10 |
| C4 | -C5 | -H5 | 120.05 | C12 | -C13 | -H13 | 119.81 |
| C6 | -C5 | -H5 | 120.08 | C14 | -C13 | -H13 | 119.79 |
| C1 | -C6 | -H6 | 120.13 | C13 | -C14 | -H14 | 120.02 |
| C5 | -C6 | -H6 | 120.04 | C9 | -C14 | -H14 | 119.87 |
| N1 | -C7 | -H7A | 108.84 | C16 | -C15 | -H15A | 108.81 |
| N1 | -C7 | -H7B | 108.77 | N1 | -C15 | -H15A | 108.97 |
| H7A | -C7 | -H7B | 107.55 | N1 | -C15 | -H15B | 108.94 |
| P1 | -C7 | -H7B | 108.79 | H15A | -C15 | -H15B | 107.61 |
| P1 | -C7 | -H7A | 108.77 | C16 | -C15 | -H15B | 108.92 |
| C9 | -C8 | -H8A | 108.43 | N2 | -C16 | -H16B | 108.56 |
| N1 | -C8 | -H8A | 108.32 | N2 | -C16 | -H16A | 108.64 |
| N1 | -C8 | -H8B | 108.34 | H16A | -C16 | -H16B | 107.47 |
| H8A | -C8 | -H8B | 107.47 | C15 | -C16 | -H16A | 108.61 |
| C9 | -C8 | -H8B | 108.32 | C15 | -C16 | -H16B | 108.66 |

**Table S6.** Preparative details for the synthesis of $[M(H_3ppba)_2](NO_3)_2Cl{\cdot}xCH_3OH$.

| $M^{3+}$-salt starting material | Product | Yield |
|---|---|---|
| $Al(NO_3)_3{\cdot}9H_2O$ | $[Al(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 84% |
| $Ga(NO_3)_3{\cdot}6H_2O$ | $[Ga(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ (**1**) | 84% |
| $In(NO_3)_3{\cdot}H_2O$ | $[In(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 73% |
| $Ho(NO_3)_3{\cdot}5H_2O$ | $[Ho(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 45% |
| $Er(NO_3)_3{\cdot}5H_2O$ | $[Er(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 28% |
| $Tm(NO_3)_3{\cdot}5H_2O$ | $[Tm(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 52% |
| $Yb(NO_3)_3{\cdot}5H_2O$ | $[Yb(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 46% |
| $Lu(NO_3)_3{\cdot}5H_2O$ | $[Lu(H_3ppba)_2](NO_3)_2Cl{\cdot}2CH_3OH$ | 31% |

**Table S7.** Preparative details for the synthesis of $[M(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$.

| $M^{3+}$-salt starting material | Product | Yield* |
|---|---|---|
| $La(NO_3)_3{\cdot}6H_2O$ | $[La(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |
| $Ce(NO_3)_3{\cdot}6H_2O$ | $[Ce(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |
| $Pr(NO_3)_3{\cdot}6H_2O$ | $[Pr(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |
| $Nd(NO_3)_3{\cdot}5H_2O$ | $[Nd(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |
| $Sm(NO_3)_3{\cdot}6H_2O$ | $[Sm(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |
| $Eu(NO_3)_3{\cdot}6H_2O$ | $[Eu(H_4ppba)_2](NO_3)_4Cl{\cdot}5CH_3OH$ | 8% |
| $Gd(NO_3)_3{\cdot}6H_2O$ | $[Gd(H_4ppba)_2](NO_3)_4Cl{\cdot}3CH_3OH$ (**2**) | 13% |
| $Tb(NO_3)_3{\cdot}5H_2O$ | $[Tb(H_4ppba)_2](NO_3)_4Cl{\cdot}10CH_3OH$ | 11% |
| $Dy(NO_3)_3{\cdot}5H_2O$ | $[Dy(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | |

*Yields are not reported for complexes that were not isolated in pure form (*vide infra*).

**Table S8.** Preparative details for the synthesis of $[M(H_4ppba)](NO_3)_3Cl{\cdot}xH_2O$.

| $M^{3+}$-salt starting material | Product | Yield |
|---|---|---|
| $La(NO_3)_3{\cdot}6H_2O$ | $[La(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 15% |
| $Ce(NO_3)_3{\cdot}6H_2O$ | $[Ce(H_4ppba)](NO_3)_3Cl{\cdot}5H_2O$ | 16% |
| $Pr(NO_3)_3{\cdot}6H_2O$ | $[Pr(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 18% |
| $Nd(NO_3)_3{\cdot}5H_2O$ | $[Nd(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 16% |
| $Sm(NO_3)_3{\cdot}6H_2O$ | $[Sm(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 24% |
| $Eu(NO_3)_3{\cdot}6H_2O$ | $[Eu(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 34% |
| $Gd(NO_3)_3{\cdot}6H_2O$ | $[Gd(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ (**3**) | 33% |
| $Tb(NO_3)_3{\cdot}5H_2O$ | $[Tb(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 30% |
| $Dy(NO_3)_3{\cdot}5H_2O$ | $[Dy(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 30% |
| $Ho(NO_3)_3{\cdot}5H_2O$ | $[Ho(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 22% |
| $Er(NO_3)_3{\cdot}5H_2O$ | $[Er(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 14% |

**Table S9.** Preparative details for the synthesis of $[M(H_3ppa)](NO_3)_2Cl{\cdot}xH_2O$.

| $M^{3+}$-salt starting material | Product | Yield |
|---|---|---|
| $Ga(NO_3)_3{\cdot}6H_2O$ | $[Ga(ppa)]{\cdot}3H_2O$ **(6)** | 56% |
| $In(NO_3)_3{\cdot}H_2O$ | $[In(H_3ppa)](NO_3)_2Cl{\cdot}2CH_3OH$ **(5)** | 71% |
| $La(NO_3)_3{\cdot}6H_2O$ | $[La(H_3ppa)](NO_3)_2Cl{\cdot}4H_2O$ | 50% |
| $Ce(NO_3)_3{\cdot}6H_2O$ | $[Ce(H_3ppa)](NO_3)_2Cl{\cdot}H_2O$ | 53% |
| $Pr(NO_3)_3{\cdot}6H_2O$ | $[Pr(H_3ppa)](NO_3)_2Cl{\cdot}3H_2O$ | 62% |
| $Nd(NO_3)_3{\cdot}5H_2O$ | $[Nd(H_3ppa)](NO_3)_2Cl{\cdot}3H_2O$ | 71% |
| $Sm(NO_3)_3{\cdot}6H_2O$ | $[Sm(H_3ppa)](NO_3)_2Cl{\cdot}3H_2O$ | 78% |
| $Eu(NO_3)_3{\cdot}6H_2O$ | $[Eu(H_3ppa)](NO_3)_2Cl{\cdot}3H_2O$ **(4)** | 80% |
| $Gd(NO_3)_3{\cdot}6H_2O$ | $[Gd(H_3ppa)](NO_3)_2Cl{\cdot}3H_2O$ | 50% |
| $Dy(NO_3)_3{\cdot}5H_2O$ | $[Dy(H_3ppa)](NO_3)_2Cl{\cdot}H_2O$ | 73% |
| $Er(NO_3)_3{\cdot}5H_2O$ | $[Er(H_3ppa)](NO_3)_2Cl{\cdot}2H_2O$ | 83% |
| $Yb(NO_3)_3{\cdot}5H_2O$ | $[Yb(H_3ppa)](NO_3)_2Cl{\cdot}2H_2O$ | 77% |

**Table S10.** +LSIMS data for all 2:1 $H_3$ppba complexes.

| Complex | $[M(Hppba)]^+$ *m/z* | $[MH_4(ppba)_2]^+$ *m/z* |
|---|---|---|
| $[Al(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 903 | 1782 |
| $[Ga(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 945 | 1825 |
| $[In(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 991 | 1869 |
| $[La(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1015 | 1895 |
| $[Ce(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1016 | 1896 |
| $[Pr(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1017 | 1897 |
| $[Nd(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1020 | 1899 |
| $[Sm(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1028 | 1906 |
| $[Eu(H_4ppba)_2](NO_3)_4Cl{\cdot}5CH_3OH$ | 1029 | 1908 |
| $[Gd(H_4ppba)_2](NO_3)_4Cl{\cdot}3CH_3OH$ | 1034 | 1912 |
| $[Tb(H_4ppba)_2](NO_3)_4Cl{\cdot}10CH_3OH$ | 1035 | 1913 |
| $[Dy(H_4ppba)_2](NO_3)_4Cl{\cdot}xCH_3OH$ | 1040 | 1918 |
| $[Ho(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 1041 | 1919 |
| $[Er(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 1044 | 1922 |
| $[Tm(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 1045 | 1924 |
| $[Yb(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 1050 | 1928 |
| $[Lu(H_3ppba)_2](NO_3)_2Cl{\cdot}2CH_3OH$ | 1051 | 1930 |

**Table S11.** Elemental analyses for selected 2:1 $H_3$ppba complexes.

| Complex | C | H | N |
|---|---|---|---|
| | Calcd. (found) | Calcd. (found) | Calcd. (found) |
| $[Al(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 58.28 (58.59) | 6.22 (6.35) | 6.86 (6.69) |
| $[Ga(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 57.08 (57.39) | 6.10 (6.13) | 6.72 (6.37) |
| $[In(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 55.87 (56.21) | 5.97 (5.83) | 6.58 (6.50) |
| $[Eu(H_4ppba)_2](NO_3)_4Cl{\cdot}5CH_3OH$ | 51.46 (51.45) | 5.90 (5.66) | 7.13 (7.34) |
| $[Gd(H_4ppba)_2](NO_3)_4Cl{\cdot}3CH_3OH$ | 51.77 (52.81) | 5.62 (5.68) | 7.32 (6.79) |
| $[Tb(H_4ppba)_2](NO_3)_4Cl{\cdot}10CH_3OH$ | 50.47 (50.00) | 6.23 (5.84) | 6.66 (6.61) |
| $[Ho(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 54.59 (54.75) | 5.83 (5.59) | 6.43 (6.81) |
| $[Er(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 54.53 (54.83) | 5.82 (5.57) | 6.42 (6.71) |
| $[Tm(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 54.49 (54.91) | 5.82 (5.61) | 6.42 (6.65) |
| $[Yb(H_3ppba)_2](NO_3)_2Cl{\cdot}3CH_3OH$ | 54.33 (54.75) | 5.89 (5.59) | 6.40 (6.67) |
| $[Lu(H_3ppba)_2](NO_3)_2Cl{\cdot}2CH_3OH$ | 54.59 (54.88) | 5.70 (5.68) | 6.50 (6.37) |

**Table S12.** +LSIMS data for all 1:1 $H_3$ppba complexes.

| Complex | $[M(Hppba)]^+$ *m/z* |
|---|---|
| $[La(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1015 |
| $[Ce(H_4ppba)](NO_3)_3Cl{\cdot}5H_2O$ | 1016 |
| $[Pr(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 1017 |
| $[Nd(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 1020 |
| $[Sm(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1028 |
| $[Eu(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1029 |
| $[Gd(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1034 |
| $[Tb(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1035 |
| $[Dy(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1040 |
| $[Ho(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1041 |
| $[Er(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 1044 |

**Table S13.** Elemental analyses for all 1:1 $H_3$ppba complexes.

| Complex | C | H | N |
|---|---|---|---|
| | Calcd. (found) | Calcd. (found) | Calcd. (found) |
| $[La(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 44.54 (44.83) | 4.98 (4.89) | 7.57 (7.20) |
| $[Ce(H_4ppba)](NO_3)_3Cl{\cdot}5H_2O$ | 43.30 (43.20) | 5.15 (4.90) | 7.36 (7.15) |
| $[Pr(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 43.86 (44.12) | 5.06 (4.94) | 7.46 (7.04) |
| $[Nd(H_4ppba)](NO_3)_3Cl{\cdot}4H_2O$ | 43.75 (44.04) | 5.05 (4.89) | 7.44 (7.02) |
| $[Sm(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 44.15 (43.94) | 4.94 (4.68) | 7.51 (7.25) |
| $[Eu(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 44.10 (44.58) | 4.93 (4.76) | 7.50 (7.21) |
| $[Gd(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 43.92 (43.92) | 4.91 (4.76) | 7.47 (7.31) |
| $[Tb(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 43.86 (44.19) | 4.91 (4.75) | 7.46 (7.13) |
| $[Dy(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 43.74 (43.98) | 4.89 (4.72) | 7.44 (7.05) |
| $[Ho(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 43.66 (44.98)* | 4.89 (4.69) | 7.43 (6.98) |
| $[Er(H_4ppba)](NO_3)_3Cl{\cdot}3H_2O$ | 43.59 (44.90)* | 4.88 (4.82) | 7.41 (6.91) |

* The high carbon content of these complexes is explained in the text.

**Table S14.** +LSIMS data for all 1:1 $H_3$ppa complexes.

| Complex | $[M(Hppa)]^+$ *m/z* |
|---|---|
| $[Ga(ppa)]\cdot 3H_2O$ | 675 |
| $[In(H_3ppa)](NO_3)_2Cl\cdot 2CH_3OH$ | 724 |
| $[La(H_3ppa)](NO_3)_2Cl\cdot 4H_2O$ | 745 |
| $[Ce(H_3ppa)](NO_3)_2Cl\cdot H_2O$ | 746 |
| $[Pr(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 747 |
| $[Nd(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 751 |
| $[Sm(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 758 |
| $[Eu(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 759 |
| $[Gd(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 766 |
| $[Dy(H_3ppa)](NO_3)_2Cl\cdot H_2O$ | 774 |
| $[Er(H_3ppa)](NO_3)_2Cl\cdot 2H_2O$ | 776 |
| $[Yb(H_3ppa)](NO_3)_2Cl\cdot 2H_2O$ | 780 |

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**Table S15.** Elemental analyses for all 1:1 $H_3$ppa complexes.

| Complex | C | H | N |
|---|---|---|---|
| | Calcd. (found) | Calcd. (found) | Calcd. (found) |
| $[Ga(ppa)]\cdot 3H_2O$ | 44.47 (44.89) | 5.80 (5.83) | 7.68 (7.81) |
| $[In(H_3ppa)](NO_3)_2Cl\cdot 2CH_3OH$ | 36.78 (37.17) | 5.00 (4.70) | 8.88 (8.64) |
| $[La(H_3ppa)](NO_3)_2Cl\cdot 4H_2O$ | 33.13(33.33) | 4.84 (4.64) | 8.58 (8.83) |
| $[Ce(H_3ppa)](NO_3)_2Cl\cdot H_2O$ | 35.02 (34.72) | 4.46 (4.44) | 9.07 (9.47) |
| $[Pr(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 33.68 (33.87) | 4.71 (4.44) | 8.73 (8.93) |
| $[Nd(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 33.56 (33.86) | 4.69 (4.65) | 8.70 (9.00) |
| $[Sm(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 33.35 (33.50) | 4.66 (4.49) | 8.64 (8.91) |
| $[Eu(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 33.29 (33.57) | 4.66 (4.52) | 8.63 (8.95) |
| $[Gd(H_3ppa)](NO_3)_2Cl\cdot 3H_2O$ | 33.11 (32.87) | 4.63 (4.48) | 8.58 (8.55) |
| $[Dy(H_3ppa)](NO_3)_2Cl\cdot H_2O$ | 34.19 (34.45) | 4.36 (4.52) | 8.86 (9.15) |
| $[Er(H_3ppa)](NO_3)_2Cl\cdot 2H_2O$ | 33.39 (33.51) | 4.46 (4.40) | 8.65 (8.58) |
| $[Yb(H_3ppa)](NO_3)_2Cl\cdot 2H_2O$ | 33.19 (32.98) | 4.44 (4.58) | 8.60 (8.79) |

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## Figure Captions

**Figure S1.** Selected IR spectra of $[M(H_4ppba)_2](NO_3)_4Cl$, M as indicated. The IR spectrum of **1** (M=Ga) is included for comparison.

**Figure S2.** IR spectra of $[Ln(H_4ppba)](NO_3)_3Cl$, Ln as indicated. The IR spectrum of **1** (M=Ga) is included for comparison.

**Figure S3.** IR spectra of $[Ln(H_3ppa)](NO_3)_3Cl$, $[In(H_3ppa)](NO_3)_3Cl$, $[Ga(ppa)]\cdot 3H_2O$ (**6**) and $H_3ppa\cdot HCl\cdot H_2O$.

**Figure S4.** $^1H$ NMR spectra (300 MHz) of $[La(H_3ppa)](NO_3)_3Cl$, $[In(H_3ppa)](NO_3)_3Cl$, $[Ga(ppa)]\cdot 3H_2O$ (**6**) and $H_3ppa\cdot HCl\cdot H_2O$ in $d_4$-methanol; (* = $H_2O$ and $CH_3OH$ impurities).

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**Figure S1**

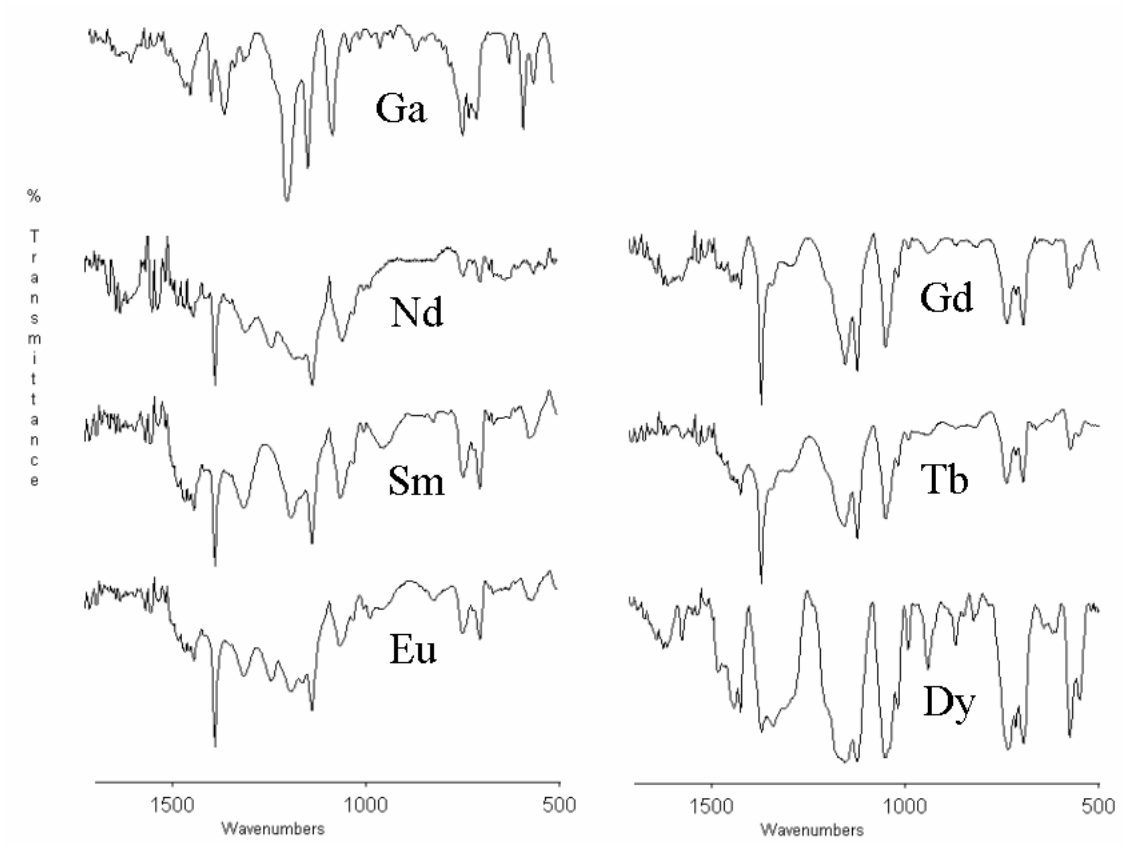

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**Figure S2**

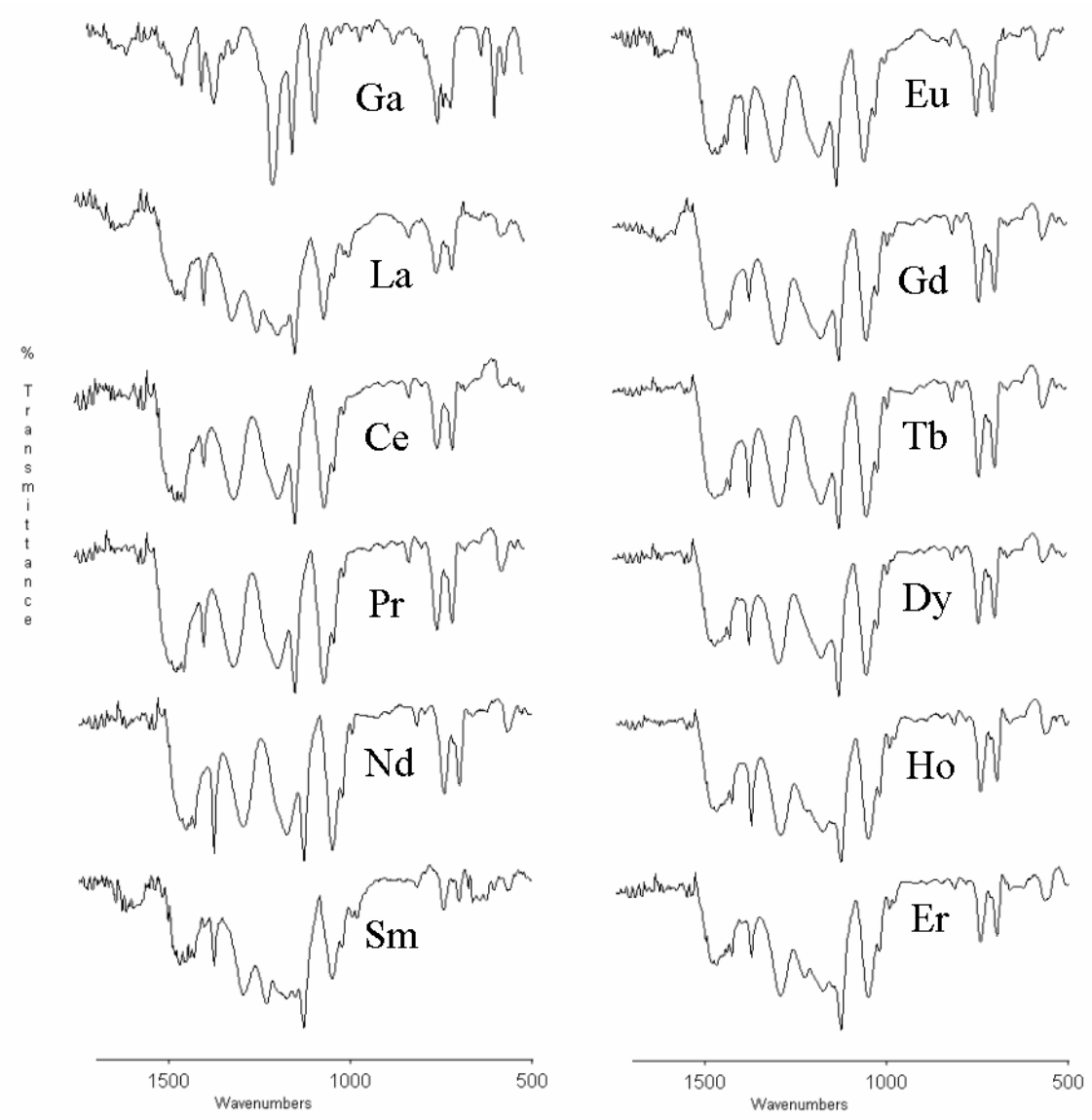

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**Figure S3**

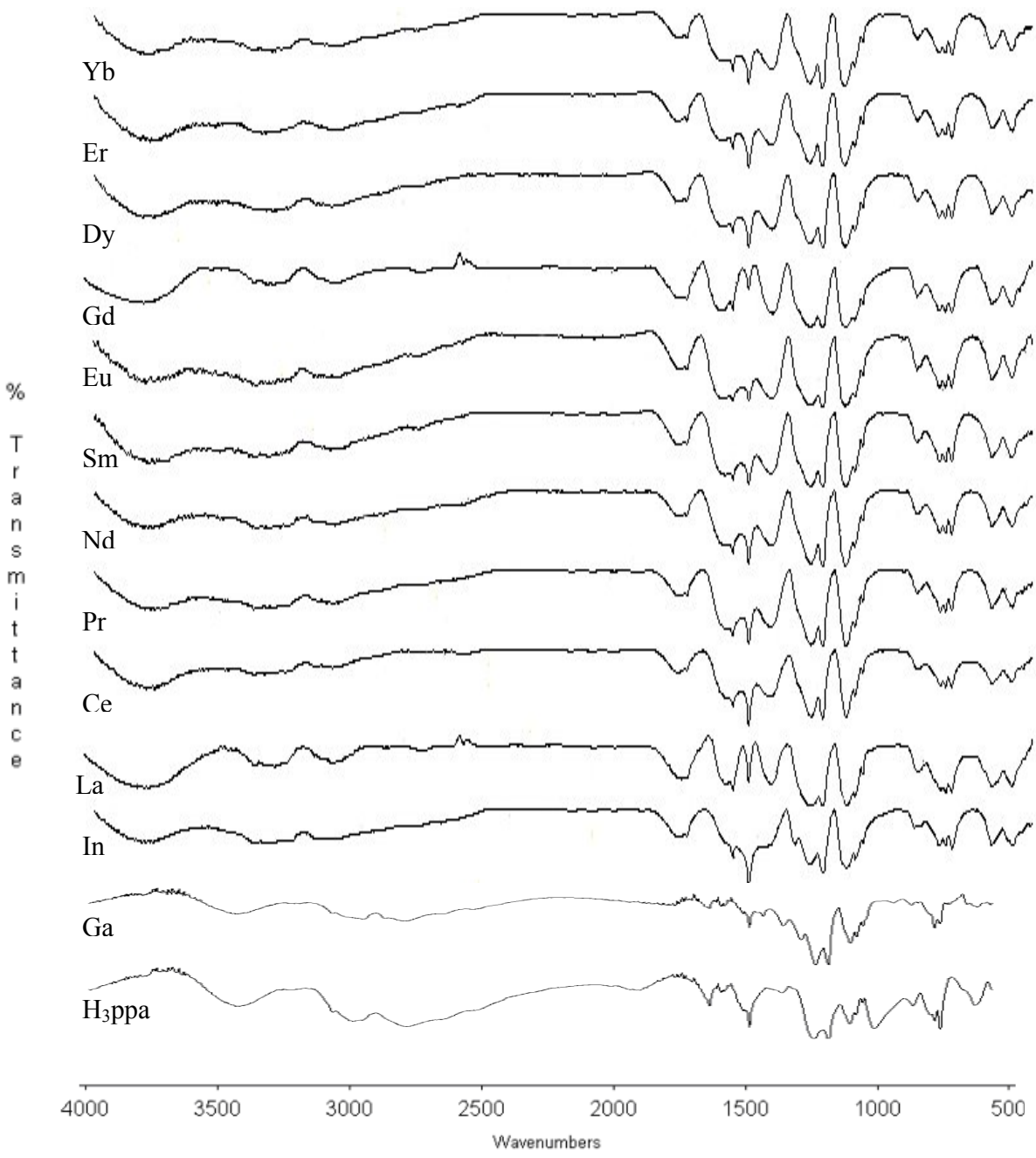

**Figure S4**