Electronic supporting material for

# The Solid-State Structures and Ligand Cavity Evaluation of Lanthanide(III) Complexes of DOTA Analogue with a (Dibenzylamino)methylphosphinate Pendant Arm

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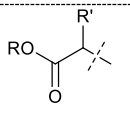
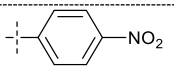
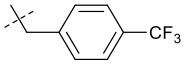
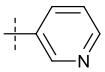
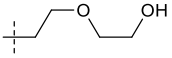
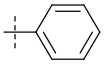
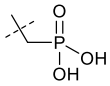
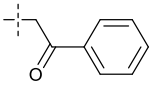
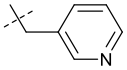
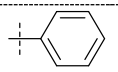
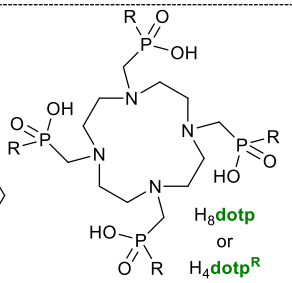
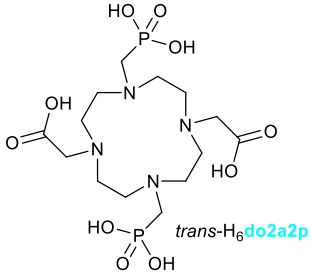
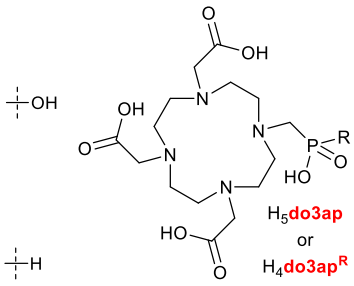
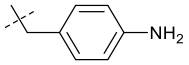
Table S1. Crystal structures from CCDC taken for comparison with present complexes.

| Ligand type | Ligand structure | Ln | Isomer | CCDC code | Reference |
|---|---|---|---|---|---|
| $H_4$**dota** | | La | 2x TSA [a] | nonjuv | 1 |
| $H_4$**dota** | | Ce | TSA | luqbii | 2 |
| $H_4$**dota** | | Gd | TSA′ | ogizou | 3 |
| $H_4$**dota** | | Tm | TSA′ | luqcef | 2 |
| $H_4$**dota** | | Sc | 2x TSA′ [a] | jogzem | 4 |
| $H_4$**dota** | | Pr | SA | luqboo | 2 |
| $H_4$**dota** | | Nd | SA | luqbuu | 2 |
| $H_4$**dota** | | Sm | SA | ogizag | 3 |
| $H_4$**dota** | | Eu | SA | cexkul | 5 |
| $H_4$**dota** | | Eu | SA | cexkul01 | 6 |
| $H_4$**dota** | $H_4$**dota** | Eu | SA | coknas | 7 |
| $H_4$**dota** | | Eu | SA | ogizek | 3 |
| $H_4$**dota** | | Gd | SA | jopjih | 8 |
| $H_4$**dota** | | Gd | SA | jopjih01 | 9 |
| $H_4$**dota** | | Gd | SA | cokmul | 7 |
| $H_4$**dota** | | Gd | SA | ogizio | 3 |
| $H_4$**dota** | | Dy | SA | luqcab | 2 |
| $H_4$**dota** | | Dy | SA | unefid | 10 |
| $H_4$**dota** | | Ho | SA | godkoz | 6 |
| $H_4$**dota** | | Lu | SA | nojyiu | 11 |
| $H_4$**dota** | | Y | SA | latkog | 9 |
| $H_4$**dota** | | Y | SA | latkog01 | 12 |
| $H_4$**dota** | | Sc | 3x SA′ [b] | luqcij | 2 |
| **dotam** | | Pr | TSA | kejbeh | 13 |
| **dotam** | | Nd | SA | veckew | 22 |
| **dotam** | | Eu | TSA | zacxac [c] | 17 |
| **dotam** | | Eu | SA | veckia | 22 |
| **dotam** | | Eu | SA | veckia01 | 22 |
| **dotam** | | Eu | SA | veckia02 | 22 |
| **dotam** | | Gd | SA | ehovay | 30 |
| **dotam** | | Gd | SA | kehzut | 13 |
| **dotam** | | Gd | 2x SA [a] | kejbad | 13 |
| **dotam** | | Gd | SA | sircay | 33 |
| **dotam** | | Gd | SA | sircec | 33 |
| **dotam** | | Gd | SA | sirdon | 33 |
| **dotam** | | Tb | SA | bosjea | 36 |
| **dotam** | | Tb | SA | tusput | 37 |
| **dotam** | | Yb | SA | xohvev | 40 |
| **dotam$^R$** | | Ce | 2x SA [a] | ufiruw | 19 |
| **dotam$^R$** | | Pr | 2x SA [a] | ufisad | 19 |
| **dotam$^R$** | | Pr | SA | eqozal | 20 |
| **dotam$^R$** | | Nd | SA | eqozep | 20 |
| **dotam$^R$** | | Sm | SA | eqozit | 20 |
| **dotam$^R$** | | Eu | SA | tuqtoo | 24 |
| **dotam$^R$** | | Eu | SA | tuqtoo01 | 25 |
| **dotam$^R$** | | Eu | SA | tuqtii | 24 |
| **dotam$^R$** | | Eu | SA | tuqtii01 | 25 |
| **dotam$^R$** | | Eu | SA | eqozoz | 20 |
| **dotam$^R$** | | Gd | 2x SA [a] | ufirac | 19 |
| **dotam$^R$** | | Gd | 2x SA [a] | ufiseh | 19 |
| **dotam$^R$** | | Gd | SA | eqozuf | 20 |
| **dotam$^R$** | | Gd | SA | sircig | 33 |
| **dotam$^R$** | | Gd | SA | sircom | 33 |
| **dotam$^R$** | | Gd | SA | sircus | 33 |
| **dotam$^R$** | | Tb | SA | ufireg | 19 |
| **dotam$^R$** | | Dy | SA | equbat | 20 |
| **dotam$^R$** | | Dy | SA | tuqtuu | 24 |
| **dotam$^R$** | | Dy | SA | tuqtuu01 | 25 |
| **dotam$^R$** | | Er | 2x SA [a] | ufisil | 19 |
| **dotam$^R$** | | Er | SA | ufirik | 19 |
| **dotam$^R$** | | Yb | SA | fibtit | 41 |

| | | | | | |
|---|---|---|---|---|---|
| **dotam$^{R}$** | | Yb | 3x SA [b] | sirdaz | 33 |
| **dotam$^{R}$** | | Yb | 2x SA [a] | sirded | 33 |
| **dotam$^{R}$** | | Yb | SA | sirdih | 33 |
| **dotam$^{R}$** | | Lu | SA | ufiroq | 19 |
| **dotam$^{R}$** | | Eu | SA | zacxac [c] | 17 |
| **dotam$^{R}$** | | Nd | SA | banxiz | 21 |
| **dotam$^{R}$** | | Gd | SA | ekezaw | 31 |
| **dotam$^{R}$** |  | Tb | SA | banxof | 21 |
| **dotam$^{R}$** | | Dy | SA | banxev | 21 |
| **dotam$^{R}$** | | Yb | SA | banxul | 21 |
| **dotam$^{R}$ (Et, H)** |  (R, R') R = Me, Et, Bn R' = H, Me | Eu | SA | xiwpic | 23 |
| **dotam$^{R}$ (Et, Me)** | | Eu | SA | fibfeb | 27 |
| **dotam$^{R}$ (Me, H)** | | Eu | SA | mubgar | 26 |
| **dotam$^{R}$ (H, H)** | | Eu | SA | zewsay | 28 |
| **dotam$^{R}$ (Bn, Me)** | | Tb | SA | ruznuv | 34 |
| **dotam$^{R}$** |  | Eu | TSA | abofom | 14 |
| **dotam$^{R}$** | | Lu | 2x SA [a] | abofus | 14 |
| **dotam$^{R}$** |  | Eu | 2x TSA [a] | pekdob | 16 |
| **dotam$^{R}$** |  | Eu | TSA | walvel | 15 |
| **dotam$^{R}$** |  | La | SA | kawmay | 18 |
| **dotam$^{R}$** |  | Eu | SA | abofig | 14 |
| **dotam$^{R}$** |  | Gd | SA | gegcie | 29 |
| **dotam$^{R}$** | | Dy | SA | goybol | 38 |
| **dotam$^{R}$** |  | Gd | SA | pehfug | 32 |
| **dotam$^{R}$** | | Gd | SA | pehgan | 32 |
| **dotam$^{R}$** |  | Tb | SA | efumat | 35 |
| **dotam$^{R}$** |  | Tm | SA | tavsiv | 39 |
| **dotam$^{R}$** |  | Lu | SA | iwuqex | 42 |
| **H$_8$dotp** | | Eu | 2x TSA′ [a] | axamap | 45 |
| **H$_8$dotp** |  | Eu | 2x TSA′ [a] | axamet | 45 |
| **H$_8$dotp** | | Gd | 2x TSA′ [a] | eqiyim | 46 |
| **H$_4$dotp$^{R}$** |  | La | 2x TSA [a] | ciqyoq | 43 |
| **H$_4$dotp$^{R}$** |  H$_8$dotp or H$_4$dotp$^{R}$ | Ce | 2x TSA [a] | ciqyuw | 43 |
| **H$_4$dotp$^{R}$** | | Eu | TSA′ | ruhmem | 44 |
| **H$_4$dotp$^{R}$** | | La | TSA | ruhmiq | 44 |
| **H$_4$dotp$^{R}$** | | Dy | TSA′ | yeqded | 48 |
| **H$_4$dotp$^{R}$** | | Dy | TSA′ | yeqded01 | 48 |
| **H$_4$dotp$^{R}$** | | Yb | 2x TSA′ [a] | ruhmow | 44 |
| **H$_4$dotp$^{R}$** | | Y | TSA′ | lijfal | 49 |
| **H$_4$dotp$^{R}$** |  | Gd | 2x TSA′ [a] | sonduv | 47 |
| **H$_4$dotp$^{R}$** | | Gd | TSA′ | sonfad | 47 |
| *trans*-H$_6$do2a2p |  *trans*-H$_6$do2a2p | Ce | TSA | babfob | 50 |
| *trans*-H$_6$do2a2p | | Nd | TSA | babcog | 50 |
| *trans*-H$_6$do2a2p | | Sm | 2x TSA [a] | babhap | 50 |
| *trans*-H$_6$do2a2p | | Sm | TSA′ | babgui | 50 |
| *trans*-H$_6$do2a2p | | Eu | 2x TSA′ [a] | babgiw | 50 |
| *trans*-H$_6$do2a2p | | Tb | TSA′ | babhet | 50 |
| *trans*-H$_6$do2a2p | | Dy | TSA′ | babgao | 50 |
| *trans*-H$_6$do2a2p | | Er | TSA′ | babges | 50 |
| *trans*-H$_6$do2a2p | | Yb | TSA′ | babhix | 50 |

| | | | | | |
|---|---|---|---|---|---|
| $H_5$**do3ap** |  | Nd | 2x TSA [a] | lanqat | 51 |
| $H_5$**do3ap** | | Tb | TSA | larlia | 53 |
| $H_5$**do3ap** | | Dy | TSA′ | larkof | 53 |
| $H_5$**do3ap** | | Er | TSA′ | larkul | 53 |
| $H_5$**do3ap** | | Lu | TSA′ | larlas | 53 |
| $H_5$**do3ap** | | Lu | TSA′ | larlew | 53 |
| $H_5$**do3ap** | | Y | TSA′ | larlog | 53 |
| $H_4$**do3ap**$^{R}$ | | Eu | TSA | ofayec | 53 |
| $H_4$**do3ap**$^{R}$ |  | Y | TSA + SA + TSA′ | kejroh [d] | 54 |

[a]Two complex molecules present in the structurally independent part. [b]Three complex molecules present in the structurally independent part. [c]Disorder in macrocyclic part was found but positions of the corresponding carbon atoms only were refined. [d]Two complex molecules were present in the structurally independent part, one of them with disordered macrocyclic part. Positions of corresponding carbon and nitrogen atoms were refined.

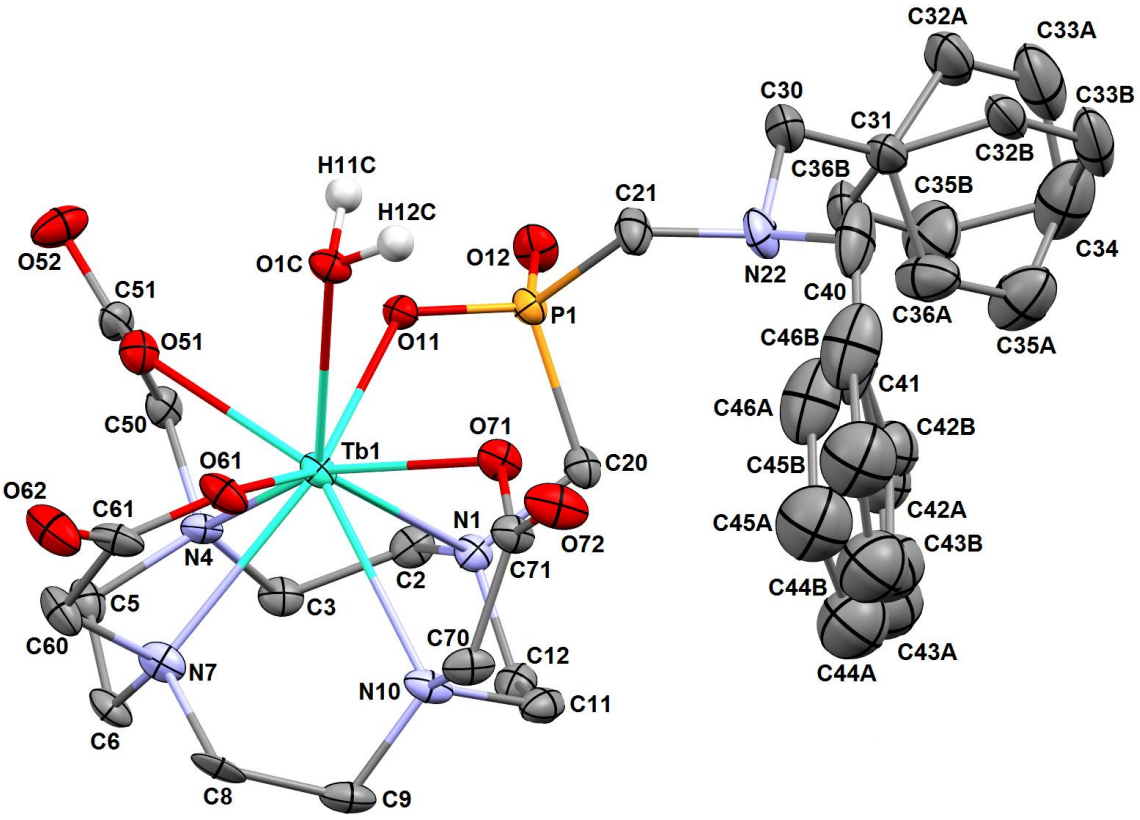



Figure S1. Molecular structure of the $[Tb(H_2O)(\textbf{do3ap}^{DBAm})]^-$ anion found in the crystal structure of $(NH_4)[Tb(H_2O)(\textbf{do3ap}^{DBAm})]\cdot 3H_2O$. Disordered phenyl rings are shown. All carbon-bound hydrogen atoms are omitted for clarity.

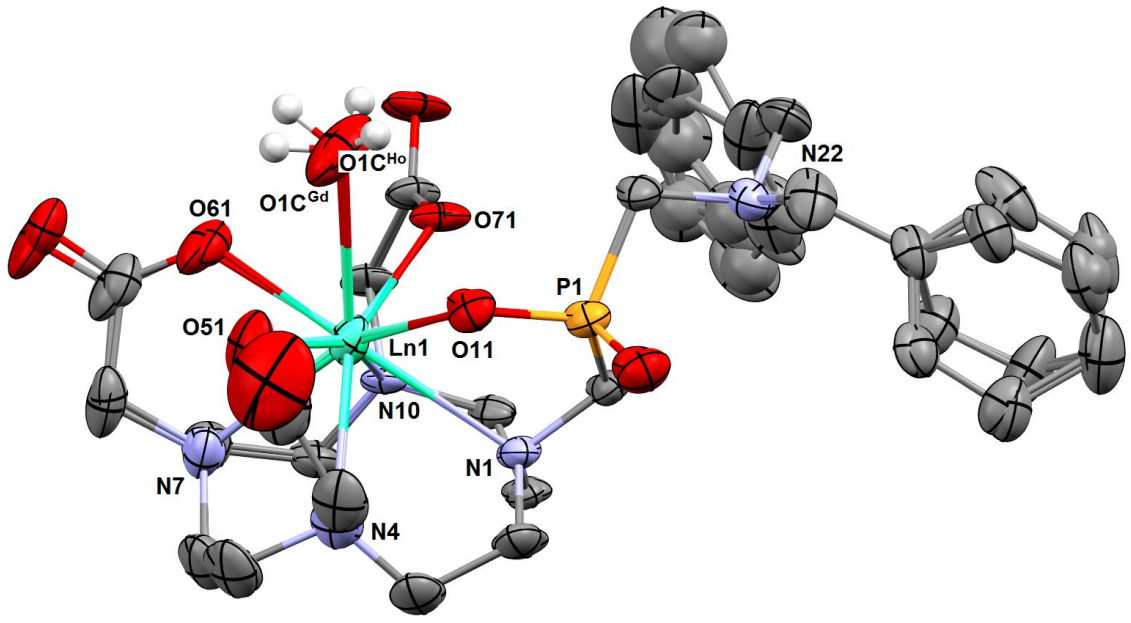



Figure S2. An overlay of the molecular structures of $[Gd(H_2O)(\textbf{do3ap}^{DBAm})]^-$ and $[Ho"(H_2O)_{0.5}"(\textbf{do3ap}^{DBAm})]^-$ anions found in the crystal structures of $Ca_{0.5}[Gd(H_2O)(\textbf{do3ap}^{DBAm})]\cdot 6H_2O$ and $Ca_{0.5}[Ho(\textbf{do3ap}^{DBAm})]\cdot 6H_2O$, showing the half-occupied water molecule apically pseudo-coordinated to Ho(III). For calculation of the overlay, lanthanide Ln1, phosphorus P1, and nitrogen N7 atom pairs from both structures were merged. Disordered phenyl rings are shown. Carbon-bound hydrogen atoms are omitted for clarity.

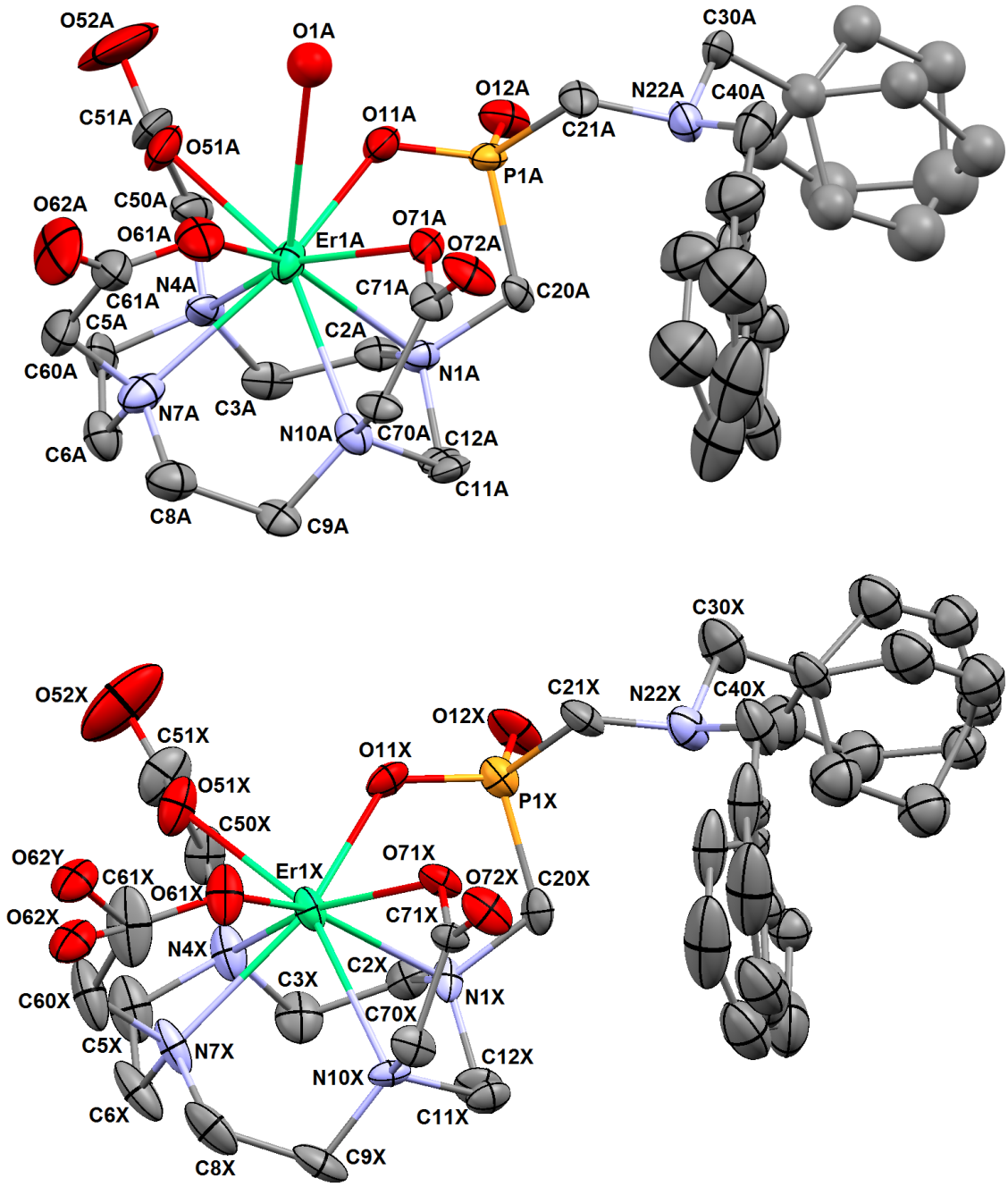



Figure S3. Molecular structure of the independent $[Er(H_2O)_{0.5}(\mathbf{do3ap}^{DBAm})]^-$ (top) and $[Er(\mathbf{do3ap}^{DBAm})]^-$ (bottom) units found in the crystal structure of $Na[Er(\mathbf{do3ap}^{DBAm})]\cdot 4.25H_2O$. Disordered phenyl rings are shown. Hydrogen atoms and labels of disordered phenyl rings are omitted for clarity.

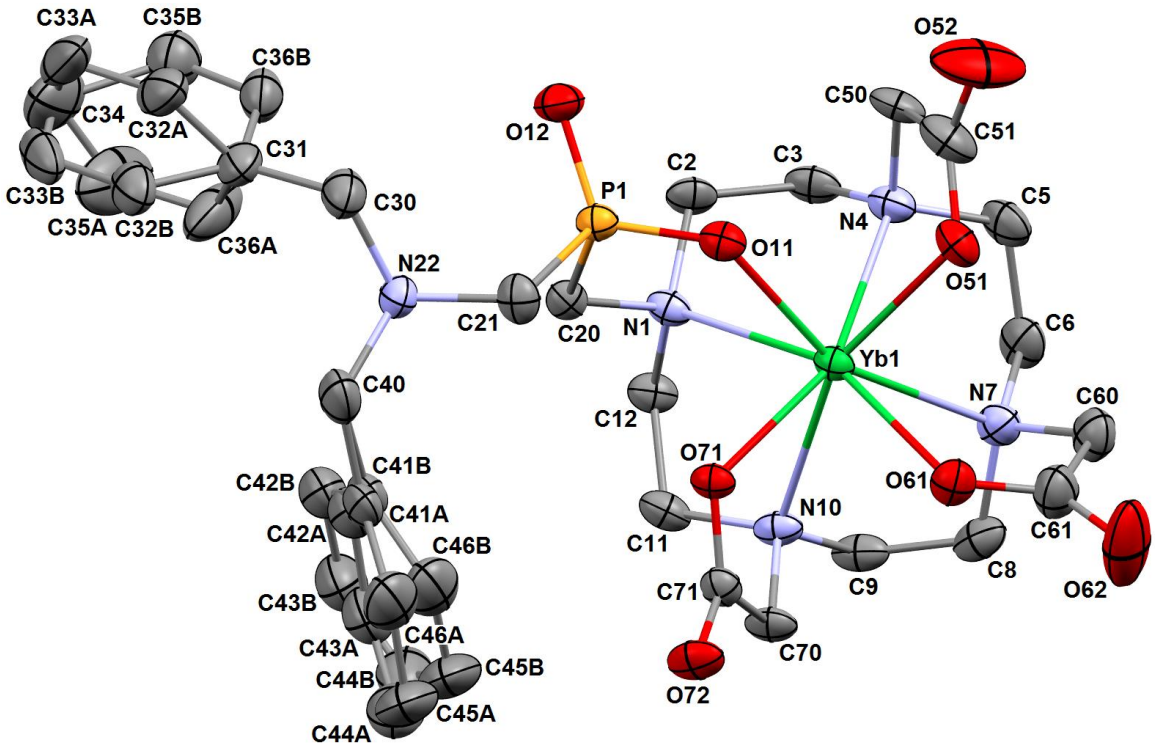


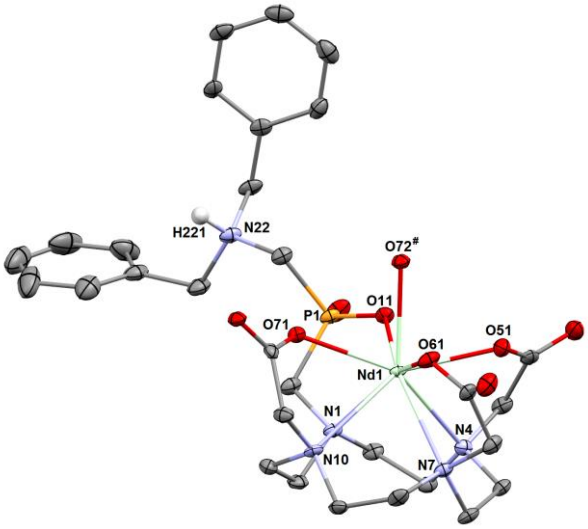

Figure S4. Molecular structure of the [Yb(**do3ap**$^{DBAm}$)]$^{-}$ anion found in the crystal structure of Na[Yb(**do3ap**$^{DBAm}$)]·6$H_2O$. Disordered phenyl rings are shown. Hydrogen atoms are omitted for clarity.

Table S2. Selected geometric parameters found in the crystal structures of lanthanide(III)–$H_4$**do3ap**$^{DBAm}$ (Ln–$H_4$**L1**) complexes.

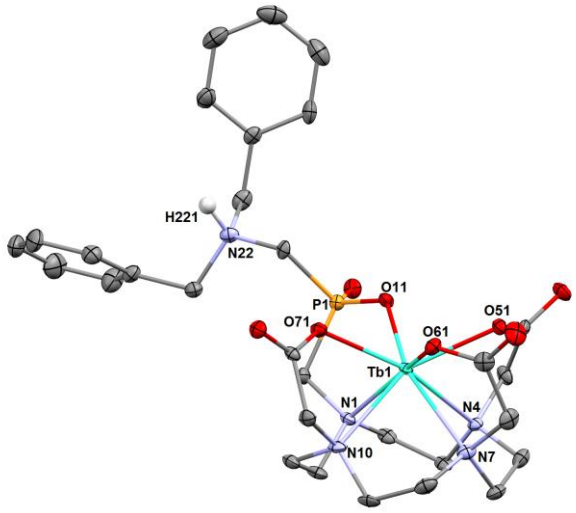
| Compound | [Ce(H**L1**)]·0.5$NH_4Cl$·6.5$H_2O$ | [Pr(H**L1**)]·0.5$NH_4Cl$·6.5$H_2O$ | [Nd(H**L1**)]·3$H_2O$ | ($NH_4$)[Nd($H_2O$)(**L1**)]·3$H_2O$ | ($NH_4$)[Sm($H_2O$)(**L1**)]·3$H_2O$ | ($NH_4$)[Eu($H_2O$)(**L1**)]·3$H_2O$ | ($NH_4$)[Gd($H_2O$)(**L1**)]·3$H_2O$ (ref.[55]) | $Ca_{0.5}$[Gd($H_2O$)(**L1**)]·6$H_2O$ | ($NH_4$)[Tb($H_2O$)(**L1**)]·3$H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Distances / Å | | | | |
| | | | | | Nitrogen plane | | | | |
| N1···N4 | 2.961(3) | 2.959(3) | 2.952(5) | 2.964(14) | 2.942(8) | 2.971(7) | 2.966(6) | 2.946(7) | 2.953(7) |
| N4···N7 | 2.968(3) | 2.956(3) | 2.952(5) | 2.975(16) | 2.953(8) | 2.944(7) | 2.932(6) | 2.953(8) | 2.927(7) |
| N7···N10 | 2.953(3) | 2.947(3) | 2.938(5) | 2.945(15) | 2.897(9) | 2.922(8) | 2.918(7) | 2.916(7) | 2.899(8) |
| N10···N1 | 2.984(3) | 2.984(3) | 2.970(5) | 3.014(14) | 2.983(8) | 2.968(7) | 2.960(6) | 2.954(7) | 2.964(7) |
| N1···N7 | 4.185(3) | 4.174(3) | 4.166(5) | 4.223(14) | 4.207(9) | 4.198(7) | 4.189(6) | 4.180(7) | 4.176(7) |
| N4···N10 | 4.205(3) | 4.202(3) | 4.186(5) | 4.190(15) | 4.119(8) | 4.148(7) | 4.137(6) | 4.141(7) | 4.128(7) |
| | | | | | Oxygen plane | | | | |
| O11···O51 | 3.289(3) | 3.242(3) | 3.223(4) | 3.053(13) | 2.997(7) | 2.992(6) | 2.983(5) | 2.956(7) | 2.959(6) |
| O51···O61 | 3.197(3) | 3.187(3) | 3.143(4) | 3.279(15) | 3.225(8) | 3.213(7) | 3.197(6) | 3.115(8) | 3.170(6) |
| O61···O71 | 3.655(2) | 3.614(3) | 3.559(4) | 3.248(14) | 3.185(8) | 3.175(7) | 3.159(6) | 3.170(7) | 3.120(6) |
| O71···O11 | 3.213(2) | 3.201(3) | 3.210(4) | 3.285(12) | 3.235(7) | 3.227(6) | 3.207(5) | 3.132(6) | 3.182(6) |
| O11···O61 | 4.723(2) | 4.693(3) | 4.653(4) | 4.526(13) | 4.476(7) | 4.433(6) | 4.414(5) | 4.362(7) | 4.377(6) |
| O51···O71 | 4.715(2) | 4.666(3) | 4.629(4) | 4.568(14) | 4.462(7) | 4.480(6) | 4.456(5) | 4.385(7) | 4.413(6) |
| | | | | | Angles / ° | | | | |
| | | | | | Nitrogen plane | | | | |
| N10···N1···N4 | 90.05(8) | 89.99(8) | 90.0(1) | 89.0(4) | 88.1(2) | 88.6(2) | 88.5(2) | 89.2(2) | 88.5(2) |
| N1···N4···N7 | 89.79(8) | 89.76(8) | 89.8(1) | 90.6(4) | 91.1(2) | 90.5(2) | 90.5(2) | 90.3(2) | 90.5(2) |
| N4···N7···N10 | 90.51(8) | 90.76(8) | 90.6(1) | 90.1(4) | 89.5(2) | 90.0(2) | 90.0(2) | 89.8(2) | 90.2(2) |
| N7···N10···N1 | 89.63(8) | 89.46(8) | 89.7(1) | 90.3(4) | 91.3(2) | 90.9(2) | 90.9(2) | 90.8(2) | 90.8(2) |
| | | | | | Oxygen plane | | | | |
| O71···O11···O51 | 92.95(6) | 92.80(6) | 92.0(1) | 92.2(3) | 91.4(2) | 92.1(2) | 92.0(1) | 92.1(2) | 91.8(2) |
| O11···O51···O61 | 93.46(6) | 93.76(7) | 93.9(1) | 91.2(4) | 91.9(2) | 91.1(2) | 91.1(1) | 91.8(2) | 91.1(2) |
| O51···O61···O71 | 86.67(6) | 86.39(6) | 87.1(1) | 88.9(3) | 88.2(2) | 89.1(2) | 89.0(1) | 88.5(2) | 89.1(2) |
| O61···O71···O11 | 86.63(6) | 86.82(6) | 86.7(1) | 87.7(3) | 88.4(2) | 87.7(2) | 87.8(1) | 87.6(2) | 88.0(2) |
| $N_4$-plane vs. $O_4$-plane | 2.00(9) | 2.3(1) | 1.5(1) | 1.0(4) | 1.2(3) | 1.0(2) | 0.9(2) | 1.1(3) | 0.9(2) |

Table S2. Selected geometric parameters found in the crystal structures of lanthanide(III)–$H_4$**do3ap**$^{DBAm}$ (Ln–$H_4$**L1**) complexes – continuation.

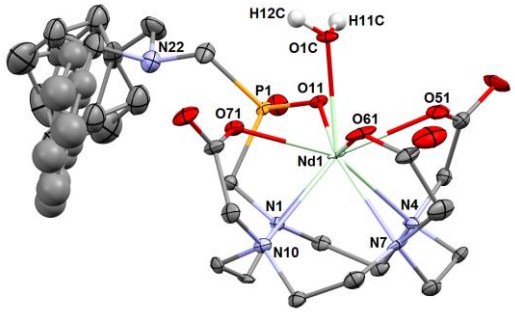
| Compound | [Tb(H**L1**)] ·$NH_4Cl$·$H_2O$ | Na[Dy($H_2O$)(**L1**)] ·4$H_2O$ (ref.[55]) | | $Ca_{0.5}$[Ho(**L1**)] ·6$H_2O$ | Na[Er(**L1**)] ·4.25$H_2O$ | | ($NH_4$)[Er(**L1**)] ·4$H_2O$ | Na[Yb(**L1**)] ·6$H_2O$ | ($NH_4$)[Sc(**L1**)] ·4$H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Distances / Å | | | | | |
| | | | | Nitrogen plane | | | | | |
| N1···N4 | 2.913(5) | 2.932(4) | 2.935(4) | 2.926(15) | 2.934(18) | 2.935(19) | 2.957(4) | 2.920(6) | 2.898(2) |
| N4···N7 | 2.924(6) | 2.926(4) | 2.925(4) | 2.946(16) | 2.885(23) | 2.947(19) | 2.920(4) | 2.913(7) | 2.862(2) |
| N7···N10 | 2.939(7) | 2.909(4) | 2.911(4) | 2.891(15) | 2.884(21) | 2.903(19) | 2.928(4) | 2.896(6) | 2.869(2) |
| N10···N1 | 2.983(7) | 2.968(4) | 2.951(4) | 2.933(14) | 2.902(19) | 2.964(18) | 2.950(4) | 2.925(6) | 2.893(2) |
| N1···N7 | 4.206(6) | 4.172(4) | 4.168(4) | 4.175(16) | 4.151(22) | 4.174(18) | 4.174(4) | 4.157(6) | 4.096(2) |
| N4···N10 | 4.107(7) | 4.124(4) | 4.121(4) | 4.096(14) | 4.053(19) | 4.134(19) | 4.137(4) | 4.083(6) | 4.050(2) |
| | | | | Oxygen plane | | | | | |
| O11···O51 | 2.969(5) | 2.940(3) | 2.955(3) | 2.862(14) | 2.897(18) | 2.798(17) | 2.829(3) | 2.794(5) | 2.664(2) |
| O51···O61 | 2.890(5) | 3.061(4) | 3.099(3) | 2.998(15) | 2.910(23) | 2.899(17) | 2.847(3) | 2.842(5) | 2.670(2) |
| O61···O71 | 2.941(4) | 3.213(4) | 3.109(3) | 2.977(14) | 3.013(17) | 2.869(16) | 2.855(3) | 2.853(5) | 2.656(2) |
| O71···O11 | 2.969(5) | 3.094(3) | 3.084(3) | 2.992(13) | 2.991(16) | 2.897(14) | 2.891(3) | 2.854(5) | 2.683(2) |
| O11···O61 | 4.066(5) | 4.349(3) | 4.316(3) | 4.151(14) | 4.160(19) | 3.997(16) | 3.988(3) | 3.961(5) | 3.719(2) |
| O51···O71 | 4.248(5) | 4.347(3) | 4.341(3) | 4.209(13) | 4.189(17) | 4.103(15) | 4.086(3) | 4.053(5) | 3.825(2) |
| | | | | Angles / ° | | | | | |
| | | | | Nitrogen plane | | | | | |
| N10···N1···N4 | 88.3(2) | 88.7(1) | 88.9(1) | 88.7(4) | 88.0(7) | 89.0(5) | 88.9(1) | 88.6(2) | 88.76(5) |
| N1···N4···N7 | 92.2(2) | 90.8(1) | 90.7(1) | 90.6(4) | 91.0(5) | 90.4(6) | 90.5(1) | 90.9(2) | 90.66(5) |
| N4···N7···N10 | 89.0(2) | 90.0(1) | 89.8(1) | 89.1(4) | 89.3(6) | 89.9(5) | 90.1(1) | 89.3(2) | 89.93(5) |
| N7···N10···N1 | 90.5(2) | 90.5(1) | 90.6(1) | 91.6(4) | 91.7(6) | 90.7(5) | 90.5(1) | 91.2(2) | 90.62(5) |
| | | | | Oxygen plane | | | | | |
| O71···O11···O51 | 91.4(1) | 92.15(9) | 91.88(9) | 91.9(4) | 90.7(5) | 92.2(5) | 91.17(8) | 91.7(2) | 91.35(5) |
| O11···O51···O61 | 87.9(2) | 92.88(9) | 90.91(9) | 90.2(4) | 91.5(5) | 89.1(4) | 89.28(8) | 89.3(2) | 88.43(5) |
| O51···O61···O71 | 93.5(1) | 87.69(9) | 88.75(9) | 89.6(4) | 90.0(5) | 90.7(5) | 91.55(8) | 90.8(2) | 91.83(5) |
| O61···O71···O11 | 87.0(1) | 87.17(9) | 88.37(9) | 88.1(4) | 87.7(5) | 87.8(4) | 87.92(8) | 87.9(1) | 88.32(5) |
| $N_4$-plane···$O_4$-plane | 2.9(2) | 0.9(1) | 1.0(1) | 1.0(5) | 1.0(6) | 1.5(7) | 1.8(1) | 1.2(2) | 1.5(7) |



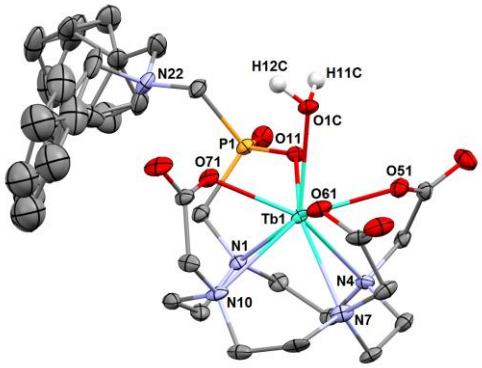

[Nd(O$^{\#}$)(H**do3ap**$^{DBAm}$)]·3$H_2O$




[Tb(H**do3ap**$^{DBAm}$)]·$NH_4Cl$·$H_2O$

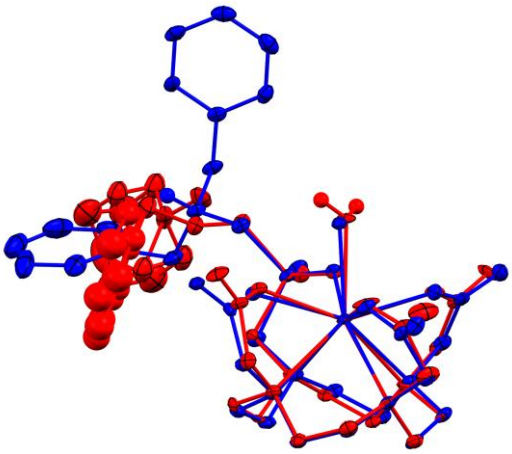



($NH_4$)[Nd($H_2O$)(**do3ap**$^{DBAm}$)]·3$H_2O$

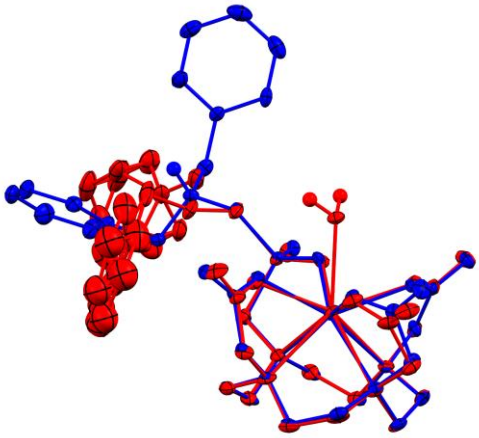



($NH_4$)[Tb($H_2O$)(**do3ap**$^{DBAm}$)]·3$H_2O$

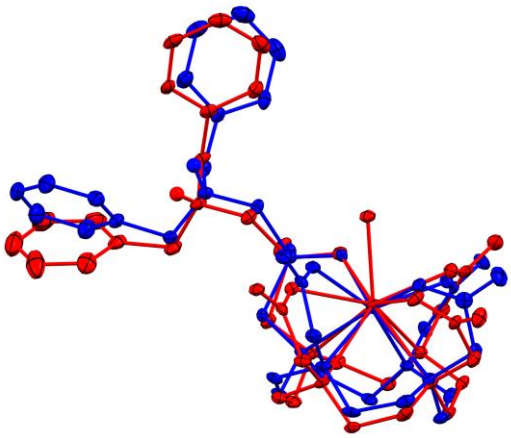
Figure S5. Molecular structures of Nd(III) and Tb(III) complex species in different protonation states found in the crystal structures of [Nd(O$^{\#}$)(H**do3ap**$^{DBAm}$)]·3$H_2O$ (O$^{\#}$ = apically coordinated oxygen atom belonging to the neighbouring unit in the dimeric species), [Tb(H**do3ap**$^{DBAm}$)]·$NH_4Cl$·$H_2O$ and ($NH_4$)[Ln($H_2O$)(**do3ap**$^{DBAm}$)]·3$H_2O$ (Ln = Nd, Tb). Carbon-bound hydrogen atoms are omitted and only selected atoms are labelled for clarity. Only a half of the dimer present in [Nd(O$^{\#}$)(H**do3ap**$^{DBAm}$)]·3$H_2O$ with the apically coordinated oxygen atom (O72$^{\#}$) from the neighbouring unit is shown. In structures of the deprotonated species, the disorder of the benzyl groups is shown.



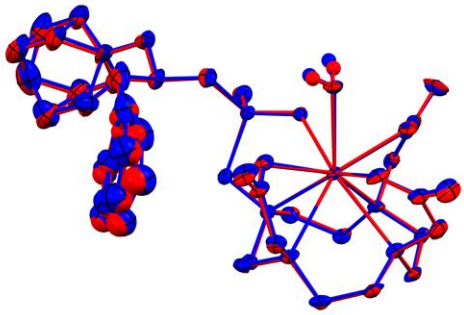
Overlay of [Nd($O^{\#}$)(H**do3ap**$^{DBAm}$)] (blue) and [Nd($H_2O$)(**do3ap**$^{DBAm}$)]$^-$ (red).



Overlay of [Tb(H**do3ap**$^{DBAm}$)] (blue) and [Tb($H_2O$)(**do3ap**$^{DBAm}$)]$^-$ (red).



Overlay of [Nd(H**do3ap**$^{DBAm}$)] (red) and [Tb(H**do3ap**$^{DBAm}$)] (blue).



Overlay of [Nd($H_2O$)(**do3ap**$^{DBAm}$)]$^-$ (red) and [Tb($H_2O$)(**do3ap**$^{DBAm}$)]$^-$ (blue).

Figure S6. Overlays of molecular structures of the Nd(III) and Tb(III) complex species in the different protonation states as found in the crystal structures of [Nd($O^{\#}$)(H**do3ap**$^{DBAm}$)]·3$H_2O$ ($O^{\#}$ = apically coordinated oxygen atom belonging to the neighbouring unit in the dimeric species), [Tb(H**do3ap**$^{DBAm}$)]·$NH_4Cl$·$H_2O$ and ($NH_4$)[Ln($H_2O$)(**do3ap**$^{DBAm}$)]·3$H_2O$ (Ln = Nd, Tb). Carbon-bound hydrogen atoms and atom labels are omitted for clarity. To overlay the molecules, distances between central Ln(III) ions, phosphorus atoms P1, and nitrogen atoms N7 were minimalized.

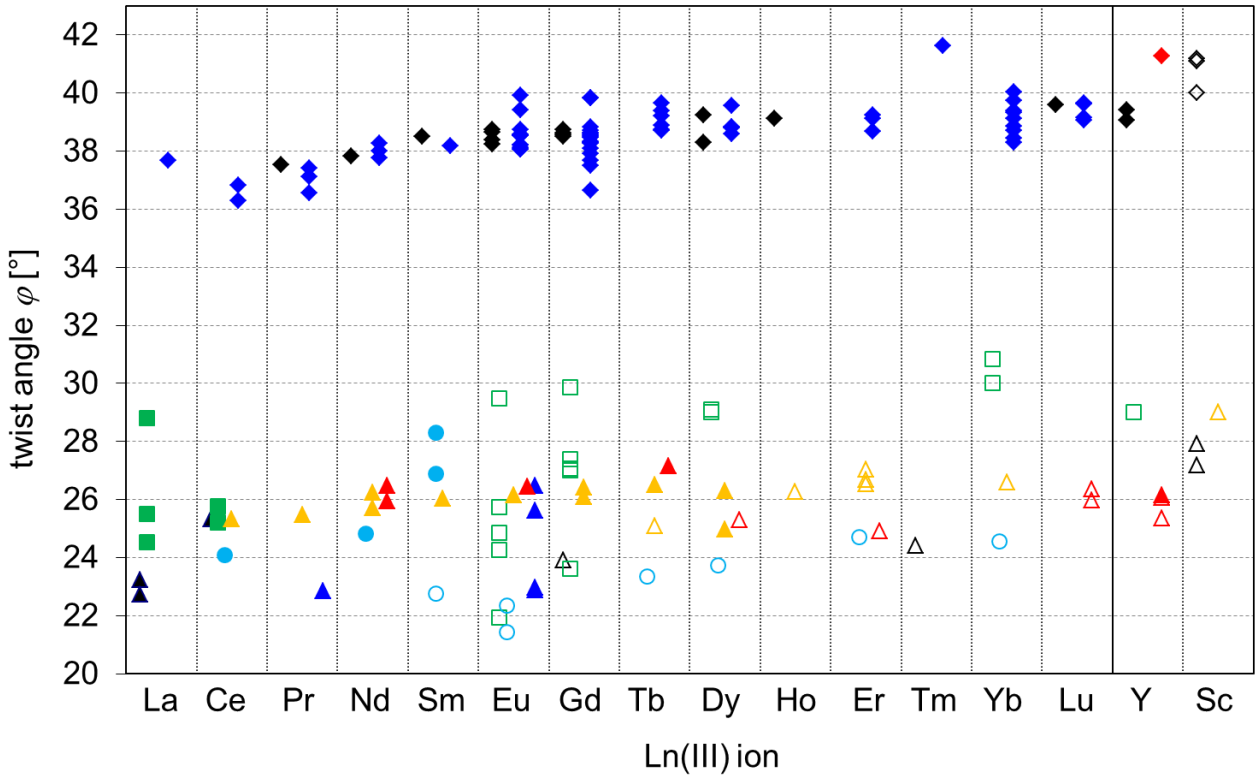



Figure S7. Dependence of mean twist angle $\varphi$ of the pendant arms in Ln(III)/Y(III)/Sc(III) complexes of selected ligands on metal ion. Ligand colour codes: $H_4$**dota**, **dotam**$^{(R)}$, $H_8$**dotp**/$H_4$**dotp**$^{R}$, *trans*-$H_6$**do2a2p**, $H_5$**do3ap**/$H_4$**do3ap**$^{R}$, $H_4$**do3ap**$^{DBAm}$. Isomer coding: diamonds are used for the SA/SA′ isomers ($H_4$**dota**, **dotam**$^{(R)}$ and $H_4$**do3ap**$^{R}$), and triangles ($H_4$**dota**, **dotam**$^{(R)}$, $H_5$**do3ap**/$H_4$**do3ap**$^{R}$ and $H_4$**do3ap**$^{DBAm}$), squares ($H_8$**dotp**/$H_4$**dotp**$^{R}$) and circles (*trans*-$H_6$**do2a2p**) for the TSA/TSA′ species. Full symbols mark nonacoordinated "hydrated" species (*i.e.* TSA/SA), and open symbols stay for octacoordinated "anhydrous" species (*i.e.* TSA′/SA′).

Table S3. Selected geometric parameters found in the crystal structures of lanthanide(III)–$H_4$**do3ap**$^{DBAm}$ and related complexes.

| CCDC code | ligand type | ion | configuration | distances / Å | | | | opening angles / ° | | twist angles / ° | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | M–$O_w$ | $QO_4$–$QN_4$ | M–$QO_4$ | M–$QN_4$ | O1-Ln-O3 | O2-Ln-O4 | N1-Q-O1 [a] | N2-Q-O2 [a] | N3-Q-O3 [a] | N4-Q-O4 [a] |
| nonjuv1 [b] | $H_4$**dota** | La | TSA | 2.569 [c] | 2.537 | 0.702 | 1.835 | 147.9 | 146.6 | 24.7 | 20.1 | 24.6 | 21.5 |
| nonjuv2 [b] | $H_4$**dota** | La | TSA | 2.538 [c] | 2.539 | 0.731 | 1.810 | 146.2 | 145.2 | 24.3 | 21.5 | 22.9 | 24.2 |
| luqbii | $H_4$**dota** | Ce | TSA | 2.598 | 2.520 | 0.755 | 1.765 | 145.0 | 143.5 | 24.9 | 25.9 | 25.7 | 24.9 |
| ogizou | $H_4$**dota** | Gd | TSA' | - [c] | 2.546 | 1.070 | 1.476 | 126.6 | 125.5 | 25.0 | 22.9 | 25.0 | 22.9 |
| luqcef | $H_4$**dota** | Tm | TSA' | - [c] | 2.530 | 1.064 | 1.466 | 124.0 | 124.7 | 24.7 | 24.6 | 24.0 | 24.3 |
| jogzem1 [b] | $H_4$**dota** | Sc | TSA' | - [c] | 2.473 | 1.172 | 1.301 | 116.4 | 116.4 | 27.9 | 27.9 | 27.9 | 27.9 |
| jogzem2 [b] | $H_4$**dota** | Sc | TSA' | - [c] | 2.525 | 1.209 | 1.316 | 122.3 | 122.3 | 27.2 | 27.2 | 27.2 | 27.2 |
| luqboo | $H_4$**dota** | Pr | SA | 2.530 | 2.366 | 0.671 | 1.695 | 149.1 | 146.8 | 38.5 | 36.6 | 39.0 | 36.1 |
| luqbuu | $H_4$**dota** | Nd | SA | 2.508 | 2.360 | 0.684 | 1.676 | 148.2 | 146.0 | 38.8 | 36.8 | 39.3 | 36.5 |
| ogizag | $H_4$**dota** | Sm | SA | 2.404 | 2.325 | 0.642 | 1.684 | 147.8 | 149.5 | 38.4 | 40.0 | 35.4 | 40.2 |
| cexkul | $H_4$**dota** | Eu | SA | 2.480 | 2.361 | 0.711 | 1.650 | 147.5 | 143.4 | 34.7 | 42.4 | 35.5 | 42.0 |
| cexkul01 | $H_4$**dota** | Eu | SA | 2.484 | 2.355 | 0.710 | 1.645 | 146.3 | 144.1 | 39.1 | 37.5 | 39.8 | 37.1 |
| coknas | $H_4$**dota** | Eu | SA | 2.475 | 2.347 | 0.724 | 1.623 | 143.9 | 145.4 | 37.4 | 38.8 | 37.7 | 39.1 |
| ogizek | $H_4$**dota** | Eu | SA | 2.389 | 2.320 | 0.646 | 1.675 | 147.7 | 149.1 | 38.5 | 40.5 | 35.6 | 40.5 |
| jopjih | $H_4$**dota** | Gd | SA | 2.458 | 2.353 | 0.720 | 1.634 | 143.6 | 145.4 | 37.8 | 39.2 | 37.5 | 39.9 |
| jopjih01 | $H_4$**dota** | Gd | SA | 2.463 | 2.347 | 0.715 | 1.632 | 145.9 | 143.7 | 39.1 | 37.2 | 40.1 | 37.6 |
| cokmul | $H_4$**dota** | Gd | SA | 2.455 | 2.345 | 0.729 | 1.616 | 143.6 | 144.9 | 38.0 | 39.0 | 37.9 | 39.4 |
| ogizio | $H_4$**dota** | Gd | SA | 2.437 | 2.318 | 0.731 | 1.587 | 143.0 | 145.1 | 38.8 | 40.0 | 37.3 | 38.9 |
| luqcab | $H_4$**dota** | Dy | SA | 2.479 | 2.340 | 0.755 | 1.585 | 141.6 | 143.1 | 38.1 | 38.5 | 38.4 | 38.2 |
| unefid | $H_4$**dota** | Dy | SA | 2.466 | 2.340 | 0.721 | 1.649 | 144.8 | 143.1 | 39.9 | 38.4 | 40.7 | 38.0 |
| godkoz | $H_4$**dota** | Ho | SA | 2.443 | 2.335 | 0.728 | 1.608 | 144.6 | 142.6 | 39.9 | 38.2 | 40.5 | 37.9 |
| nojyiu | $H_4$**dota** | Lu | SA | 2.417 | 2.318 | 0.732 | 1.586 | 143.3 | 141.7 | 40.4 | 38.5 | 41.1 | 38.4 |
| latkog01 | $H_4$**dota** | Y | SA | 2.425 | 2.332 | 0.717 | 1.615 | 145.1 | 143.0 | 40.3 | 38.4 | 41.0 | 38.1 |
| latkog | $H_4$**dota** | Y | SA | 2.436 | 2.334 | 0.718 | 1.617 | 144.8 | 143.1 | 40.0 | 37.8 | 40.4 | 38.1 |
| luqcij1 [e] | $H_4$**dota** | Sc | SA' | - [d] | 2.334 | 1.007 | 1.328 | 124.1 | 124.1 | 41.1 | 41.1 | 41.1 | 41.1 |
| luqcij2 [e] | $H_4$**dota** | Sc | SA' | - [d] | 2.325 | 0.989 | 1.336 | 125.0 | 125.0 | 41.2 | 41.2 | 41.2 | 41.2 |
| luqcij3 [e] | $H_4$**dota** | Sc | SA' | - [d] | 2.349 | 1.019 | 1.330 | 123.7 | 123.7 | 40.0 | 40.0 | 40.0 | 40.0 |
| kejbeh | **dotam** | Pr | TSA | 2.516 | 2.529 | 0.793 | 1.736 | 143.3 | 140.9 | 24.7 | 21.1 | 23.8 | 22.0 |
| abofom | **dotam$^R$ (R: *p*-$NO_2$-Ph)** | Eu | TSA | 2.450 [f] | 2.455 | 0.831 | 1.624 | 141.1 | 138.3 | 25.3 | 25.9 | 25.0 | 26.2 |
| walvel | **dotam$^R$ (R: *m*-pyridyl)** | Eu | TSA | 2.370 | 2.450 | 0.811 | 1.639 | 141.8 | 139.6 | 28.6 | 25.8 | 26.3 | 25.2 |
| pekdob1 [b] | **dotam$^R$ (R: *p*-$CF_3$-benzyl)** | Eu | TSA | 2.532 | 2.544 | 0.881 | 1.663 | 135.3 | 138.0 | 21.6 | 24.1 | 21.6 | 24.1 |
| pekdob2 [b] | **dotam$^R$ (R: *p*-$CF_3$-benzyl)** | Eu | TSA | 2.532 | 2.503 | 0.840 | 1.663 | 140.3 | 136.5 | 23.7 | 22.2 | 23.7 | 22.2 |
| zacxac | **dotam** | Eu | TSA | 2.442 | - [g] | 0.793 | - [g] | 142.4 | 140.1 | - [g] | - [g] | - [g] | - [g] |
| kawmay | **dotam$^R$** | La | SA | - [h] | 2.345 | 0.538 | 1.807 | 155.2 | 155.2 | 37.7 | 37.7 | 37.7 | 37.7 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **(R: $HO(CH_2)_2O(CH_2)_2$–)** | | | | | | | | | | | | |
| ufiruw1 [b] | **dotam$^R$ (R: α-phenethyl)** | Ce | SA | 2.491 | 2.407 | 0.643 | 1.763 | 148.3 | 150.7 | 35.5 | 37.1 | 36.0 | 36.6 |
| ufiruw2 [b] | **dotam$^R$ (R: α-phenethyl)** | Ce | SA | 2.488 | 2.384 | 0.646 | 1.738 | 148.6 | 149.7 | 36.2 | 37.5 | 36.4 | 37.2 |
| ufisad1 [b] | **dotam$^R$ (R: α-phenethyl)** | Pr | SA | 2.463 | 2.390 | 0.658 | 1.732 | 147.6 | 149.6 | 35.7 | 36.9 | 36.7 | 37.0 |
| ufisad2 [b] | **dotam$^R$ (R: α-phenethyl)** | Pr | SA | 2.479 | 2.361 | 0.652 | 1.709 | 148.0 | 149.1 | 36.5 | 38.2 | 36.7 | 37.0 |
| eqozal | **dotam$^R$ (R: α-phenethyl)** | Pr | SA | 2.516 | 2.363 | 0.665 | 1.698 | 147.1 | 149.1 | 38.2 | 37.2 | 37.9 | 36.5 |
| eqozep | **dotam$^R$ (R: α-phenethyl)** | Nd | SA | 2.501 | 2.357 | 0.682 | 1.676 | 146.0 | 148.2 | 38.4 | 37.6 | 38.1 | 37.0 |
| banxiz | **dotam$^R$ (R: prop-2-yn-1-yl)** | Nd | SA | 2.472 | 2.354 | 0.697 | 1.657 | 147.7 | 146.0 | 38.7 | 37.6 | 39.4 | 37.4 |
| veckew | **dotam (deuterated amides)** | Nd | SA | 2.435 | 2.347 | 0.695 | 1.653 | 146.8 | 146.5 | 37.2 | 37.8 | 37.8 | 39.2 |
| eqozit | **dotam$^R$ (R: α-phenethyl)** | Sm | SA | 2.495 | 2.348 | 0.707 | 1.641 | 144.4 | 146.1 | 38.8 | 38.3 | 38.5 | 37.1 |
| xiwpic | **dotam$^R$ (R: $EtO_2CCH_2$–)** | Eu | SA | 2.414 | 2.343 | 0.758 | 1.585 | 141.1 | 143.2 | 37.8 | 39.8 | 36.5 | 40.0 |
| tuqtoo | **dotam$^R$ (R: α-phenethyl)** | Eu | SA | 2.425 | 2.349 | 0.676 | 1.673 | 144.8 | 148.8 | 37.0 | 40.1 | 37.0 | 40.1 |
| tuqtoo01 | **dotam$^R$ (R: α-phenethyl)** | Eu | SA | 2.425 | 2.349 | 0.676 | 1.673 | 144.8 | 148.8 | 37.0 | 40.1 | 37.0 | 40.1 |
| abofig | **dotam$^R$ (R: Ph)** | Eu | SA | 2.431 | 2.383 | 0.709 | 1.673 | 145.7 | 144.9 | 38.9 | 36.5 | 39.4 | 37.7 |
| mubgar | **dotam$^R$ (R: $MeO_2CCH_2$–)** | Eu | SA | 2.444 [i] | 2.287 | 0.671 | 1.616 | 147.1 | 147.1 | 39.9 | 39.9 | 39.9 | 39.9 |
| fibfeb | **dotam$^R$ (R: $EtO_2C(CH_3)CH$–)** | Eu | SA | 2.414 | 2.330 | 0.733 | 1.597 | 144.4 | 144.6 | 39.9 | 40.7 | 38.8 | 38.4 |
| tuqtii | **dotam$^R$ (R: α-phenethyl)** | Eu | SA | 2.438 | 2.366 | 0.717 | 1.649 | 145.2 | 144.6 | 38.4 | 39.0 | 37.6 | 37.2 |
| tuqtii01 | **dotam$^R$ (R: α-phenethyl)** | Eu | SA | 2.438 | 2.366 | 0.717 | 1.649 | 145.2 | 144.6 | 38.4 | 39.0 | 37.6 | 37.2 |
| eqozoz | **dotam$^R$ (R: α-phenethyl)** | Eu | SA | 2.482 | 2.352 | 0.716 | 1.637 | 143.7 | 145.9 | 38.8 | 38.1 | 38.6 | 37.4 |
| veckia | **dotam (deuterated amide)** | Eu | SA | 2.409 | 2.332 | 0.713 | 1.620 | 144.9 | 145.9 | 39.5 | 38.1 | 38.4 | 38.3 |
| veckia01 | **dotam** | Eu | SA | 2.406 | 2.340 | 0.712 | 1.629 | 145.6 | 145.0 | 37.7 | 37.8 | 38.3 | 39.1 |
| veckia02 | **dotam** | Eu | SA | 2.402 | 2.336 | 0.715 | 1.622 | 145.4 | 144.9 | 37.9 | 38.3 | 38.4 | 39.5 |
| zacxac | **dotam** | Eu | SA | 2.442 | - [g] | 0.793 | - [g] | 142.4 | 140.1 | - [g] | - [g] | - [g] | - [g] |
| zewsay | **dotam$^R$ (R: $HO_2CCH_2$–)** | Eu | SA | 2.365 [c] | 2.320 | 0.667 | 1.653 | 147.8 | 147.1 | 38.6 | 39.1 | 37.8 | 39.3 |
| ufirac1 [b] | **dotam$^R$ (R: α-phenethyl)** | Gd | SA | 2.351 | 2.336 | 0.724 | 1.611 | 144.1 | 144.3 | 38.9 | 36.4 | 38.9 | 36.4 |
| ufirac2 [b] | **dotam$^R$ (R: α-phenethyl)** | Gd | SA | 2.383 | 2.340 | 0.708 | 1.632 | 146.1 | 143.9 | 39.5 | 37.2 | 39.5 | 37.2 |
| ufiseh1 [b] | **dotam$^R$ (R: α-phenethyl)** | Gd | SA | 2.408 | 2.364 | 0.701 | 1.664 | 144.1 | 147.1 | 36.9 | 38.4 | 37.9 | 38.5 |
| ufiseh2 [b] | **dotam$^R$ (R: α-phenethyl)** | Gd | SA | 2.420 | 2.334 | 0.699 | 1.636 | 145.3 | 145.3 | 38.3 | 39.5 | 38.3 | 38.4 |
| eqozuf | **dotam$^R$ (R: α-phenethyl)** | Gd | SA | 2.460 | 2.350 | 0.723 | 1.627 | 143.2 | 145.4 | 39.0 | 38.4 | 38.6 | 37.8 |
| gegcie | **dotam$^R$ (R: Me)** | Gd | SA | 2.461 | 2.332 | 0.742 | 1.591 | 145.1 | 142.3 | 40.3 | 38.3 | 38.1 | 36.6 |
| ehovay | **dotam** | Gd | SA | 2.466 | 2.340 | 0.739 | 1.601 | 142.7 | 144.7 | 37.2 | 38.5 | 38.3 | 40.3 |
| ekezaw | **dotam$^R$ (R: prop-2-yn-1-yl)** | Gd | SA | 2.437 | 2.349 | 0.733 | 1.616 | 143.3 | 145.3 | 37.6 | 39.3 | 37.8 | 40.1 |
| kehzut | **dotam** | Gd | SA | 2.395 | 2.330 | 0.717 | 1.614 | 144.7 | 145.1 | 37.7 | 37.6 | 38.9 | 38.3 |
| kejbad1 [b] | **dotam** | Gd | SA | 2.395 | 2.328 | 0.732 | 1.597 | 142.7 | 145.3 | 38.2 | 39.7 | 37.3 | 39.2 |
| kejbad2 [b] | **dotam** | Gd | SA | 2.474 | 2.341 | 0.741 | 1.601 | 144.3 | 1423.0 | 38.4 | 38.9 | 38.8 | 37.1 |
| pehfug | **dotam$^R$ (R: $H_2O_3PCH_2$–)** | Gd | SA | 2.425 | 2.306 | 0.710 | 1.597 | 145.2 | 144.4 | 39.5 | 38.8 | 40.2 | 40.7 |
| pehgan | **dotam$^R$ (R: $H_2O_3PCH_2$–)** | Gd | SA | 2.395 | 2.299 | 0.671 | 1.628 | 147.8 | 146.7 | 41.2 | 38.4 | 41.2 | 38.4 |
| sircay | **dotam** | Gd | SA | 2.467 | 2.346 | 0.731 | 1.616 | 144.8 | 143.2 | 38.2 | 37.6 | 38.8 | 39.6 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sircec | **dotam** | Gd | SA | 2.461 | 2.360 | 0.737 | 1.624 | 144.4 | 143.2 | 38.1 | 37.3 | 38.3 | 39.5 |
| sircig | **dotam$^{R}$ (R: *α*-phenethyl)** | Gd | SA | 2.435 | 2.351 | 0.690 | 1.661 | 146.2 | 146.0 | 38.3 | 38.0 | 39.3 | 38.2 |
| sircom | **dotam$^{R}$ (R: *α*-phenethyl)** | Gd | SA | 2.380 | 2.372 | 0.655 | 1.717 | 148.9 | 146.5 | 37.5 | 35.9 | 37.5 | 35.9 |
| sircus | **dotam$^{R}$ (R: *α*-phenethyl)** | Gd | SA | 2.381 | 2.364 | 0.672 | 1.691 | 147.5 | 146.0 | 38.0 | 37.0 | 38.0 | 37.0 |
| sirdon | **dotam** | Gd | SA | 2.384 | 2.332 | 0.715 | 1.617 | 146.0 | 143.9 | 39.2 | 39.1 | 39.0 | 38.1 |
| ufireg | **dotam$^{R}$ (R: *α*-phenethyl)** | Tb | SA | 2.461 | 2.345 | 0.727 | 1.618 | 142.7 | 144.9 | 39.3 | 38.7 | 38.9 | 38.0 |
| ruznuv | **dotam$^{R}$ (R: $BnO_2C(CH_3)CH$–)** | Tb | SA | 2.380 | 2.312 | 0.714 | 1.599 | 144.6 | 145.2 | 39.2 | 40.8 | 37.7 | 40.9 |
| efumat | **dotam$^{R}$ (R: $PhC(O)CH_2$–)** | Tb | SA | 2.437 | 2.319 | 0.746 | 1.574 | 142.6 | 143.9 | 39.2 | 39.5 | 38.6 | 39.7 |
| banxof | **dotam$^{R}$ (R: prop-2-yn-1-yl)** | Tb | SA | 2.437 | 2.337 | 0.741 | 1.596 | 144.4 | 142.9 | 40.0 | 39.3 | 39.8 | 38.5 |
| bosjea | **dotam** | Tb | SA | 2.450 | 2.330 | 0.727 | 1.603 | 143.5 | 144.8 | 38.2 | 39.1 | 37.4 | 40.2 |
| tusput | **dotam** | Tb | SA | 2.382 | 2.330 | 0.732 | 1.599 | 144.7 | 143.0 | 39.8 | 38.8 | 38.8 | 38.2 |
| goybol | **dotam$^{R}$ (R: Me)** | Dy | SA | 2.427 | 2.353 | 0.754 | 1.599 | 144.7 | 140.4 | 39.6 | 38.1 | 40.4 | 36.3 |
| equbat | **dotam$^{R}$ (R: *α*-phenethyl)** | Dy | SA | 2.454 | 2.340 | 0.730 | 1.610 | 142.3 | 144.6 | 39.1 | 39.1 | 38.8 | 38.3 |
| tuqtuu | **dotam$^{R}$ (R: *α*-phenethyl)** | Dy | SA | 2.422 | 2.342 | 0.725 | 1.617 | 144.1 | 143.6 | 39.2 | 38.1 | 38.3 | 39.7 |
| tuqtuu01 | **dotam$^{R}$ (R: *α*-phenethyl)** | Dy | SA | 2.422 | 2.342 | 0.725 | 1.617 | 144.1 | 143.6 | 39.2 | 38.1 | 38.3 | 39.7 |
| banxev | **dotam$^{R}$ (R: prop-2-yn-1-yl)** | Dy | SA | 2.427 | 2.335 | 0.747 | 1.588 | 142.4 | 144.0 | 39.4 | 40.1 | 38.6 | 40.2 |
| ufisil1 | **dotam$^{R}$ (R: *α*-phenethyl)** | Er | SA | 2.374 | 2.356 | 0.716 | 1.640 | 142.9 | 145.6 | 38.5 | 38.8 | 38.6 | 38.8 |
| ufisil2 | **dotam$^{R}$ (R: *α*-phenethyl)** | Er | SA | 2.380 | 2.336 | 0.719 | 1.617 | 143.5 | 144.0 | 38.7 | 40.4 | 38.6 | 39.3 |
| ufirik | **dotam$^{R}$ (R: *α*-phenethyl)** | Er | SA | 2.432 | 2.335 | 0.743 | 1.593 | 141.4 | 143.5 | 39.4 | 39.4 | 39.0 | 38.8 |
| tavsiv | **dotam$^{R}$ (R: $CF_3CH_2$–)** | Tm | SA | 2.347 | 2.281 | 0.727 | 1.554 | 143.1 | 143.3 | 41.5 | 41.8 | 41.5 | 41.8 |
| xohvev | **dotam** | Yb | SA | 2.335 | 2.304 | 0.739 | 1.566 | 143.2 | 141.9 | 39.8 | 39.1 | 40.5 | 39.6 |
| fibtit | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.440 | 2.328 | 0.740 | 1.588 | 141.1 | 143.2 | 39.7 | 39.7 | 39.1 | 39.1 |
| banxul | **dotam$^{R}$ (R: prop-2-yn-1-yl)** | Yb | SA | 2.417 | 2.322 | 0.758 | 1.564 | 141.0 | 142.7 | 38.9 | 40.7 | 40.0 | 40.5 |
| sirdaz1 [e] | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.408 | 2.317 | 0.735 | 1.583 | 142.5 | 142.0 | 41.4 | 38.2 | 39.1 | 38.6 |
| sirdaz2 [e] | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.388 | 2.326 | 0.747 | 1.580 | 141.5 | 142.0 | 36.9 | 39.9 | 38.6 | 39.5 |
| sirdaz3 [e] | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.448 | 2.335 | 0.757 | 1.578 | 141.7 | 140.8 | 40.0 | 39.0 | 39.3 | 38.3 |
| sirded1 [b] | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.445 | 2.344 | 0.766 | 1.578 | 140.9 | 140.3 | 38.4 | 39.4 | 37.2 | 38.8 |
| sirded2 [b] | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.439 | 2.347 | 0.770 | 1.576 | 140.9 | 140.2 | 37.8 | 38.0 | 38.1 | 39.4 |
| sirdih | **dotam$^{R}$ (R: *α*-phenethyl)** | Yb | SA | 2.397 | 2.349 | 0.747 | 1.602 | 140.7 | 141.9 | 37.5 | 39.3 | 37.4 | 41.3 |
| abofus1 [b] | **dotam$^{R}$ (R: *p*-$NO_2$-Ph)** | Lu | SA | 2.346 | 2.271 | 0.760 | 1.511 | 142.0 | 141.5 | 39.6 | 39.5 | 39.5 | 39.9 |
| abofus2 [b] | **dotam$^{R}$ (R: *p*-$NO_2$-Ph)** | Lu | SA | 2.369 | 2.290 | 0.790 | 1.500 | 140.0 | 139.9 | 39.2 | 39.0 | 38.4 | 39.7 |
| ufiroq | **dotam$^{R}$ (R: *α*-phenethyl)** | Lu | SA | 2.426 | 2.329 | 0.747 | 1.583 | 140.8 | 142.7 | 39.8 | 40.1 | 39.2 | 39.4 |
| iwuqex | **dotam$^{R}$ (R: *m*-pyridylmethyl)** | Lu | SA | 2.381 | 2.364 | 0.741 | 1.623 | 143.9 | 141.5 | 39.2 | 39.9 | 38.6 | 38.9 |
| ciqyoq1 [b] | $H_4$**dotp$^{R}$ (R: Ph)** | La | TSA | 2.656 | 2.727 | 0.793 | 1.935 | 140.8 | 143.7 | 24.5 | 26.3 | 22.5 | 24.8 |
| ciqyoq2 [b] | $H_4$**dotp$^{R}$ (R: Ph)** | La | TSA | 2.628 | 2.692 | 0.789 | 1.903 | 143.3 | 141.4 | 23.7 | 25.8 | 25.4 | 27.2 |
| ruhmiq | $H_4$**dotp$^{R}$ (R: Bn)** | La | TSA | 2.664 | 2.661 | 0.812 | 1.850 | 142.3 | 140.4 | 29.6 | 28.1 | 29.3 | 28.3 |
| ciqyuw1 [b] | $H_4$**dotp$^{R}$ (R: Ph)** | Ce | TSA | 2.652 | 2.714 | 0.806 | 1.909 | 139.5 | 142.8 | 25.2 | 26.7 | 23.8 | 25.2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ciqyuw2 [b] | $H_4$**dotp$^R$ (R: Ph)** | Ce | TSA | 2.583 | 2.689 | 0.792 | 1.897 | 140.7 | 142.7 | 23.9 | 26.0 | 25.8 | 27.4 |
| ruhmem | $H_4$**dotp$^R$ (R: Bn)** | Eu | TSA' | - [d] | 2.646 | 0.970 | 1.676 | 130.0 | 131.4 | 28.8 | 29.9 | 29.1 | 30.2 |
| axamap1 [b] | $H_8$**dotp** | Eu | TSA' | - [d] | 2.727 | 1.032 | 1.695 | 126.5 | 128.4 | 24.9 | 26.1 | 26.1 | 25.9 |
| axamap2 [b] | $H_8$**dotp** | Eu | TSA' | - [d] | 2.749 | 1.058 | 1.692 | 122.9 | 128.9 | 23.8 | 24.8 | 23.3 | 25.2 |
| axamet1 [b] | $H_8$**dotp** | Eu | TSA' | - [d] | 2.795 | 1.067 | 1.728 | 125.9 | 125.9 | 24.9 | 24.9 | 24.9 | 24.9 |
| axamet2 [b] | $H_8$**dotp** | Eu | TSA' | - [d] | 2.792 | 1.067 | 1.724 | 125.4 | 125.4 | 21.9 | 21.9 | 21.9 | 21.9 |
| eqiyim1 [b] | $H_8$**dotp** | Gd | TSA' | - [d] | 2.718 | 1.057 | 1.661 | 125.6 | 125.6 | 27.0 | 27.0 | 27.0 | 27.0 |
| eqiyim2 [b] | $H_8$**dotp** | Gd | TSA' | - [d] | 2.685 | 1.042 | 1.643 | 126.4 | 126.4 | 23.6 | 23.6 | 23.6 | 23.6 |
| sonfad | $H_4$**dotp$^R$ (R: H)** | Gd | TSA' | - [d] | 2.656 | 1.050 | 1.605 | 124.6 | 127.4 | 29.2 | 30.5 | 29.2 | 30.5 |
| sonduv1 [b] | $H_4$**dotp$^R$ (R: OEt)** | Gd | TSA' | - [d] | 2.688 | 1.050 | 1.639 | 124.7 | 127.6 | 26.7 | 27.4 | 27.0 | 28.6 |
| sonduv2 [b] | $H_4$**dotp$^R$ (R: OEt)** | Gd | TSA' | - [d] | 2.701 | 1.049 | 1.652 | 127.2 | 124.9 | 27.7 | 26.1 | 28.2 | 26.3 |
| yeqded | $H_4$**dotp$^R$ (R: Bn)** | Dy | TSA' | - [d] | 2.625 | 0.978 | 1.647 | 130.3 | 128.3 | 29.8 | 28.6 | 29.2 | 28.9 |
| yeqded01 | $H_4$**dotp$^R$ (R: Bn)** | Dy | TSA' | - [d] | 2.626 | 0.984 | 1.642 | 127.5 | 129.2 | 28.7 | 29.6 | 27.9 | 29.9 |
| ruhmow1 [b] | $H_4$**dotp$^R$ (R: Bn)** | Yb | TSA' | - [d] | 2.606 | 1.002 | 1.604 | 126.3 | 127.7 | 31.9 | 30.9 | 31.2 | 29.4 |
| ruhmow2 [b] | $H_4$**dotp$^R$ (R: Bn)** | Yb | TSA' | - [d] | 2.626 | 1.015 | 1.612 | 124.8 | 127.8 | 29.3 | 29.4 | 32.9 | 28.5 |
| lijfal | $H_4$**dotp$^R$ (R: Bn)** | Y | TSA' | - [d] | 2.612 | 0.973 | 1.639 | 129.0 | 128.9 | 30.4 | 27.9 | 29.3 | 28.3 |
| babfob | *trans*-$H_6$**do2a2p** | Ce | TSA | 2.545 | 2.596 | 0.822 | 1.774 | 136.9 | 144.4 | 26.4 | 21.9 | 26.1 | 21.9 |
| babcog | *trans*-$H_6$**do2a2p** | Nd | TSA | 2.542 | 2.584 | 0.835 | 1.749 | 136.1 | 143.2 | 26.9 | 23.1 | 26.5 | 22.8 |
| babhap1 [b] | *trans*-$H_6$**do2a2p** | Sm | TSA | 2.555 | 2.516 | 0.801 | 1.715 | 137.4 | 143.8 | 30.0 | 27.1 | 29.1 | 27.0 |
| babhap2 [b] | *trans*-$H_6$**do2a2p** | Sm | TSA | 2.602 | 2.547 | 0.819 | 1.729 | 135.3 | 143.8 | 27.7 | 25.9 | 28.2 | 25.8 |
| babgui | *trans*-$H_6$**do2a2p** | Sm | TSA' | - [d] | 2.647 | 1.063 | 1.584 | 116.3 | 135.2 | 20.8 | 24.7 | 20.8 | 24.7 |
| babgiw1 [b] | *trans*-$H_6$**do2a2p** | Eu | TSA' | - [d] | 2.716 | 1.101 | 1.616 | 115.5 | 132.9 | 19.6 | 25.1 | 19.6 | 25.1 |
| babgiw2 [b] | *trans*-$H_6$**do2a2p** | Eu | TSA' | - [d] | 2.700 | 1.086 | 1.615 | 115.1 | 134.6 | 19.7 | 23.2 | 19.7 | 23.2 |
| babhet | *trans*-$H_6$**do2a2p** | Tb | TSA' | - [d] | 2.631 | 1.079 | 1.552 | 114.7 | 133.6 | 21.5 | 25.2 | 21.5 | 25.2 |
| babgao | *trans*-$H_6$**do2a2p** | Dy | TSA' | - [d] | 2.610 | 1.077 | 1.532 | 114.4 | 132.6 | 22.2 | 25.3 | 22.2 | 25.3 |
| babges | *trans*-$H_6$**do2a2p** | Er | TSA' | - [d] | 2.610 | 1.086 | 1.524 | 114.5 | 131.4 | 23.4 | 26.0 | 23.4 | 26.0 |
| babhix | *trans*-$H_6$**do2a2p** | Yb | TSA' | - [d] | 2.601 | 1.094 | 1.507 | 113.0 | 130.8 | 23.4 | 25.7 | 23.4 | 25.7 |
| lanqat1 [b] | $H_5$**do3ap** | Nd | TSA | 2.519 | 2.499 | 0.783 | 1.738 | 142.2 | 143.0 | 30.0 | 23.3 | 28.6 | 24.0 |
| lanqat2 [b] | $H_5$**do3ap** | Nd | TSA | 2.536 | 2.591 | 0.792 | 1.746 | 140.3 | 143.4 | 28.9 | 23.3 | 28.1 | 23.5 |
| ofayec | $H_4$**do3ap$^R$ (R: H)** | Eu | TSA | 2.555 | 2.524 | 0.871 | 1.653 | 134.6 | 139.5 | 25.8 | 25.6 | 26.6 | 27.8 |
| larlia | $H_5$**do3ap** | Tb | TSA | 2.678 | 2.514 | 0.853 | 1.663 | 135.8 | 138.6 | 26.9 | 27.2 | 27.4 | 27.1 |
| kejroh1 [j] | $H_4$**do3ap$^R$ (R: *p*-$NH_2$-Bn)** | Y | TSA | 2.486 | 2.504 | 0.763 | 1.742 | 140.3 | 142.6 | 27.1 | 24.5 | 25.7 | 27.2 |
| larkof | $H_5$**do3ap** | Dy | TSA' | - [d] | 2.564 | 1.035 | 1.531 | 123.5 | 129.5 | 25.5 | 24.7 | 25.7 | 25.2 |
| larkul | $H_5$**do3ap** | Er | TSA' | - [d] | 2.525 | 1.054 | 1.472 | 122.2 | 128.2 | 26.4 | 24.2 | 24.0 | 25.0 |
| larlas | $H_5$**do3ap** | Lu | TSA' | - [d] | 2.547 | 1.065 | 1.483 | 120.8 | 127.1 | 26.7 | 26.0 | 26.4 | 26.3 |
| larlew | $H_5$**do3ap** | Lu | TSA' | - [d c] | 2.489 | 1.068 | 1.468 | 120.5 | 126.9 | 26.6 | 25.9 | 25.9 | 25.5 |
| larlog | $H_5$**do3ap** | Y | TSA' | - [d] | 2.566 | 1.043 | 1.525 | 123.0 | 129.1 | 25.8 | 25.0 | 25.4 | 25.3 |
| kejroh3 [j] | $H_4$**do3ap$^R$ (R: *p*-$NH_2$-Bn)** | Y | TSA' | - [d] | 2.562 | 1.030 | 1.533 | 122.4 | 130.4 | 25.1 | 27.7 | 24.5 | 27.0 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| kejroh2 [j] | $H_4$**do3ap$^{R}$ (R: *p*-$NH_2$-Bn)** | Y | SA | 2.486 | 2.348 | 0.763 | 1.586 | 140.3 | 142.6 | 42.2 | 40.0 | 40.8 | 42.2 |
| 1959625 | $H_4$**do3ap$^{DBAm}$** | Ce | TSA | 2.529 | 2.531 | 0.716 | 1.817 | 143.4 | 148.6 | 24.3 | 26.3 | 21.4 | 29.5 |
| 1959634 | $H_4$**do3ap$^{DBAm}$** | Pr | TSA | 2.537 | 2.529 | 0.730 | 1.801 | 142.9 | 147.3 | 24.7 | 26.0 | 21.8 | 29.4 |
| 1959633 | $H_4$**do3ap$^{DBAm}$** | Nd | TSA | 2.623 | 2.541 | 0.796 | 1.746 | 139.7 | 143.0 | 27.3 | 23.8 | 25.7 | 26.1 |
| 1959632 | $H_4$**do3ap$^{DBAm}$** | Nd | TSA | 2.476 | 2.510 | 0.718 | 1.794 | 142.9 | 148.0 | 25.8 | 27.0 | 22.5 | 29.6 |
| 1959636 | $H_4$**do3ap$^{DBAm}$** | Sm | TSA | 2.612 | 2.533 | 0.802 | 1.732 | 139.0 | 142.0 | 27.8 | 24.1 | 25.9 | 26.5 |
| 1959629 | $H_4$**do3ap$^{DBAm}$** | Eu | TSA | 2.594 | 2.521 | 0.804 | 1.718 | 138.7 | 141.9 | 28.3 | 23.9 | 26.3 | 26.2 |
| diydat [k] | $H_4$**do3ap$^{DBAm}$** | Gd | TSA | 2.583 | 2.517 | 0.807 | 1.710 | 138.5 | 141.5 | 28.5 | 24.1 | 26.6 | 26.4 |
| 1959630 | $H_4$**do3ap$^{DBAm}$** | Gd | TSA | 2.655 | 2.533 | 0.864 | 1.671 | 135.3 | 138.3 | 27.6 | 24.7 | 25.2 | 26.8 |
| 1959637 | $H_4$**do3ap$^{DBAm}$** | Tb | TSA | 2.591 | 2.505 | 0.809 | 1.697 | 138.2 | 141.0 | 28.4 | 24.3 | 26.7 | 26.6 |
| diycum [b,k] | $H_4$**do3ap$^{DBAm}$** | Dy | TSA | 2.623 | 2.542 | 0.856 | 1.687 | 135.2 | 138.6 | 26.0 | 23.8 | 23.5 | 26.7 |
| diycum [b,k] | $H_4$**do3ap$^{DBAm}$** | Dy | TSA | 2.747 | 2.509 | 0.834 | 1.675 | 136.2 | 139.4 | 27.3 | 24.9 | 26.1 | 26.9 |
| 1959638 | $H_4$**do3ap$^{DBAm}$** | Tb | TSA' | - [d] | 2.568 | 1.010 | 1.560 | 124.8 | 131.4 | 24.5 | 25.9 | 24.7 | 25.2 |
| 1959631 | $H_4$**do3ap$^{DBAm}$** | Ho | TSA' | 2.753 [l] | 2.533 | 0.950 | 1.584 | 129.0 | 133.2 | 27.4 | 25.2 | 26.0 | 26.6 |
| 1959626 | $H_4$**do3ap$^{DBAm}$** | Er | TSA' | - [d] | 2.533 | 1.052 | 1.481 | 123.2 | 126.7 | 27.7 | 26.5 | 27.0 | 26.9 |
| 1959628 [b] | $H_4$**do3ap$^{DBAm}$** | Er | TSA' | 2.803 [l] | 2.545 | 0.947 | 1.599 | 129.7 | 132.7 | 27.9 | 26.1 | 25.7 | 27.1 |
| 1959628 [b] | $H_4$**do3ap$^{DBAm}$** | Er | TSA' | - [d] | 2.502 | 1.007 | 1.496 | 124.4 | 129.9 | 27.2 | 25.7 | 26.4 | 26.9 |
| 1959627 | $H_4$**do3ap$^{DBAm}$** | Yb | TSA' | - [d] | 2.534 | 1.050 | 1.485 | 121.7 | 127.7 | 27.1 | 26.1 | 26.3 | 26.9 |
| 1959635 | $H_4$**do3ap$^{DBAm}$** | Sc | TSA' | - [d] | 2.457 | 1.040 | 1.417 | 120.6 | 123.9 | 29.2 | 28.6 | 29.2 | 29.0 |

[a]Q represents pair of centroids, $QN_4$-$QO_4$. [b]Two structurally independent molecules present in the crystal structure. [c]Carboxylate oxygen atom from neighbouring unit coordinated in the apical position. [d]No apically coordinated water/oxygen atom. [e]Three structurally independent molecules present in the crystal structure. [f]Methanol oxygen atom coordinated in the apical position. [g]Not applicable due to disorder. [h]Apical coordination of chloride. [i]Trifluoromethylsulfonate oxygen atom coordinated in the apical position. [j]Two structurally independent molecules present in the crystal structure, one of them disordered in TSA/SA arrangement. [k]ref.[55]. [l]"Semi-coordinated" water molecule.

*Crystal structures refinement details*

In general, all non-hydrogen atoms were refined anisotropically. Only some disordered groups/atoms (typically carbon atoms of benzyl groups and oxygen atoms of water molecules of crystallization) were treated isotropically. Almost all hydrogen atoms were localized in difference density map; however, those bound to the carbon atoms were placed in theoretical positions and hydrogen atoms bound to heteroatoms (O, N) were usually kept in original positions using $U_{eq}$(H) = 1.2 $U_{eq}$(X) to keep the number of refinement parameters low. Alterations from these general procedures are described below.

In the crystal structures of [Ln(H**L1**)]·0.5$NH_4Cl$·6.5$H_2O$ (Ln = Ce, Pr), one formula unit forms the structurally independent unit. Chloride atom was best refined with half occupancy to get reliable thermal factor, and its charge is compensated by half-occupied ammonium ion, of which nitrogen atom shares position with oxygen atom of half-occupied water molecule. In these fragments, four tetrahedrally-located hydrogen atoms of ammonium cation were found, two of them were defined as shared with water molecule, and EXYZ/EADP commands for corresponding N/O atoms were used. Two water molecules of crystallization were best refined with oxygen atoms disordered over two close positions and sharing corresponding hydrogen atoms.

In the crystal structure of [Nd(H**L1**)]·3$H_2O$, one formula unit forms the structurally independent unit. Two water molecules of crystallization were best refined with oxygen atoms disordered over two and three close positions, respectively. Positions of corresponding hydrogen atoms cannot be reliably determined.

One formula unit forms the structurally independent unit also in the crystal structures of ($NH_4$)[Ln($H_2O$)(do3ap$^{DBAm}$)]·3$H_2O$ (Ln = Nd, Sm, Eu, Tb). Similarly to isostructural Gd(III)-complex reported previously,[55] the same kind of disorder of benzylic side groups was found. One of phenyl rings was best refined to be staggered in two positions with pivot and "*para*" carbon atoms common for both possibilities. The other phenyl ring was best refined as regular hexagon (AFIX 66) disordered slit over two or three positions, which are nearly parallel. However, in Sm(III)-complex, probably more complicated disorder is present, but it cannot be reliably modelled. As the result of such complication, large maxima in difference density map are present. However, all hydrogen atoms belonging to coordinated water molecule, ammonium cation as well as to water molecules of crystallization were found in the difference density map, making rich system of hydrogen bonds.

In the structure of $Ca_{0.5}$[Ho(**L1**)]·6$H_2O$, one formula unit forms the structurally independent unit. Occupancy of Ca(II) ion was set to 50% as the ion is close to its symmetrically related position; such disorder is reflected also in Ca(II)-coordinated water molecules, which were refined also with occupancy 50%. However, more complicated disorder is present, which results in large electronic density map maxima/minima close to disordered water molecules. Occupancy of water molecule present in apical position of the Ho(III) complex was set to 50% to keep its thermal factor reliable. In benzylic side groups, similar disorder as described above was found (one phenyl staggered in two positions, other phenyl slid in two positions).

In the structure of $Ca_{0.5}$[Gd($H_2O$)(**L1**)]·6$H_2O$, one formula unit forms the structurally independent unit. The Ca(II) occupies special position with 50% occupancy factor, and is coordinated with water molecules forming distorted octahedron. Two of such water molecules are placed in special position, two other molecules are disordered over two close positions (but large difference density map maxima close to these positions point to more complicated disorder), corresponding hydrogen atoms cannot be found. Hydrogen atoms of coordinated water molecule and of other three water molecules of crystallization were located in the difference density map and form hydrogen bond

network. One side-group phenyl was refined staggered in two positions and other phenyl was slid in two positions in similar disorder as described above.

In the crystal structures of [Tb(H**L1**)]·$NH_4Cl$·$H_2O$, $(NH_4)$[Er(**L1**)]·$4H_2O$ and $(NH_4)$[Sc(**L1**)]·$4H_2O$, formula unit corresponds to the independent part and all hydrogen atoms were located in the difference density map. No disorder was found.

In the crystal structure of Na[Er(**L1**)]·$4.25H_2O$, two formula units form the independent part of the unit cell. In both independent complex molecules, disorder of phenyl rings was found (one phenyl staggered, other phenyl slid). Sodium aquaions are disordered as well. The disorder was best refined by splitting Na(I) into two close positions with half-occupancy. Remaining large maxima in difference density map were attributed to water molecules of crystallization, however, some of them lie very close to each other, and needed to be refined with half-occupancy. Hydrogen atoms could not be located.

In the crystal structure of Na[Yb(**L1**)]·$6H_2O$, one formula unit forms the structurally independent unit. Disorder of phenyl rings was found similar to previous cases (one phenyl staggered, other phenyl slid). Some of water molecules coordinated to Na(I) counter ion were best refined disordered in two close positions; corresponding hydrogen atoms could not be found.

All the data for the structures reported have been deposited with the Cambridge Crystallographic Data Centre. Experimental crystal data are outlined in Table S4.

Table S4. Experimental crystallographic data for structures of lanthanide(III)–$H_4$**do3ap**$^{DBAm}$ (Ln–$H_4$**L1**) complexes.

| Compound | [Ce(H**L1**)]·0.5$NH_4Cl$ ·6.5$H_2O$ | [Pr(H**L1**)]·0.5$NH_4Cl$ ·6.5$H_2O$ | [Nd(H**L1**)] ·3$H_2O$ | ($NH_4$)[Nd($H_2O$) (**L1**)]·3$H_2O$ | ($NH_4$)[Sm($H_2O$) (**L1**)]·3$H_2O$ | ($NH_4$)[Eu($H_2O$) (**L1**)]·3$H_2O$ | $Ca_{0.5}$[Gd($H_2O$) (**L1**)]·6$H_2O$ |
|---|---|---|---|---|---|---|---|
| Formula | $C_{30}H_{56}CeCl_{0.5}N_{5.5}O_{14.5}P$ | $C_{30}H_{56}Cl_{0.5}N_{5.5}O_{14.5}PPr$ | $C_{30}H_{47}N_5NdO_{11}P$ | $C_{30}H_{52}N_6NdO_{12}P$ | $C_{30}H_{52}N_6O_{12}PSm$ | $C_{30}H_{52}EuN_6O_{12}P$ | $C_{30}H_{54}Ca_{0.5}GdN_5O_{15}P$ |
| $M_r$ | 914.61 | 915.40 | 828.93 | 863.98 | 870.09 | 871.70 | 933.04 |
| Shape | bar | prism | bar | plate | prism | prism | plate |
| Colour | colourless | slightly green | colourless | colourless | colourless | colourless | colourless |
| Crystal system | triclinic | triclinic | triclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *P*−1 | *P*−1 | *P*−1 | *C*2/c | *C*2/c | *C*2/c | *P*2/c |
| *a* / Å | 11.7568(8) | 11.7803(8) | 10.5893(5) | 47.142(2) | 47.041(8) | 47.136(3) | 24.2222(7) |
| *b* / Å | 12.4231(9) | 12.4274(9) | 12.4277(6) | 10.3053(4) | 10.2877(14) | 10.3082(5) | 10.1613(2) |
| *c* / Å | 14.5497(10) | 14.5862(11) | 14.6008(8) | 15.3151(7) | 15.205(2) | 15.2253(8) | 15.4093(4) |
| *α* / ° | 68.256(2) | 68.147(2) | 112.071(2) | 90 | 90 | 90 | 90 |
| *β* / ° | 79.612(2) | 79.566(2) | 92.429(2) | 90.722(2) | 90.6500(10) | 90.685(2) | 95.4550(10) |
| *γ* / ° | 78.900(2) | 78.962(2) | 109.292(2) | 90 | 90 | 90 | 90 |
| *U* / Å$^3$ | 1923.0(2) | 1931.1(2) | 1649.94(15) | 7439.7(5) | 7357.9(19) | 7397.3(7) | 3775.50(16) |
| *Z* | 2 | 2 | 2 | 8 | 8 | 8 | 4 |
| $D_{calc}$ / g cm$^{-3}$ | 1.580 | 1.574 | 1.669 | 1.543 | 1.571 | 1.565 | 1.641 |
| *μ* / mm$^{-1}$ | 1.332 | 1.409 | 1.690 | 1.505 | 1.706 | 1.806 | 1.941 |
| Unique refl. | 8828 | 8886 | 7581 | 7322 | 8668 | 8492 | 8663 |
| Obsd. refl. | 8293 | 8518 | 6521 | 6678 | 8435 | 8117 | 7451 |
| $R_1$ ($I>2\sigma(I)$) | 0.0271 | 0.0286 | 0.0433 | 0.1067 | 0.0626 | 0.0567 | 0.0616 |
| $R_2$ (all data) | 0.0301 | 0.0300 | 0.0613 | 0.1147 | 0.0637 | 0.0590 | 0.0714 |
| $wR_2$ ($I>2\sigma(I)$) | 0.0718 | 0.0776 | 0.0742 | 0.2324 | 0.1671 | 0.1358 | 0.1484 |
| $wR_2$ (all data) | 0.0732 | 0.0785 | 0.0798 | 0.2357 | 0.1674 | 0.1369 | 0.1548 |
| CCDC-number | 1959625 | 1959634 | 1959632 | 1959633 | 1959636 | 1959629 | 1959630 |

| Compound | $(NH_4)$[Tb($H_2O$)(L1)]·3$H_2O$ | [Tb(HL1)]·$NH_4Cl$·$H_2O$ | $Ca_{0.5}$[Ho(L1)]·6$H_2O$ | Na[Er(L1)]·4.25$H_2O$ | $(NH_4)$[Er(L1)]·4$H_2O$ | Na[Yb(L1)]·6$H_2O$ | $(NH_4)$[Sc(L1)]·4$H_2O$ |
|---|---|---|---|---|---|---|---|
| Formula | $C_{30}H_{52}N_6O_{12}PTb$ | $C_{30}H_{47}ClN_6O_9PTb$ | $C_{30}H_{52}Ca_{0.5}HoN_5O_{14}P$ | $C_{30}H_{48.5}ErN_5NaO_{12.25}P$ | $C_{30}H_{52}ErN_6O_{12}P$ | $C_{30}H_{52}N_5NaO_{14}PYb$ | $C_{30}H_{52}N_6O_{12}PSc$ |
| $M_r$ | 878.66 | 861.07 | 922.70 | 896.46 | 887.00 | 933.76 | 764.70 |
| Shape | prism | plate | plate | plate | plate | plate | prism |
| Colour | colourless | colourless | colourless | slightly pink | slightly pink | colourless | colourless |
| Crystal system | monoclinic | monoclinic | monoclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | *C*2/c | *P*n | *P*2/c | *P*−1 | $P2_1/c$ | *C*2/c | $P2_1/c$ |
| *a* / Å | 47.048(2) | 9.9701(2) | 24.1798(13) | 10.2212(10) | 24.3204(4) | 49.3984(12) | 24.0303(16) |
| *b* / Å | 10.2943(4) | 15.3519(3) | 10.1265(5) | 15.3230(13) | 10.42140(10) | 10.1801(2) | 10.3449(6) |
| *c* / Å | 15.2057(7) | 11.4210(3) | 15.2799(8) | 25.162(2) | 15.1910(2) | 15.3464(4) | 15.1430(11) |
| *α* / ° | 90 | 90 | 90 | 77.957(3) | 90 | 90 | 90 |
| *β* / ° | 90.717(2) | 94.9903(8) | 95.775(2) | 78.577(3) | 107.6020(10) | 102.544(2) | 107.497(3) |
| *γ* / ° | 90 | 90 | 90 | 89.761(3) | 90 | 90 | 90 |
| *U* / $Å^3$ | 7363.9(6) | 1741.47(7) | 3722.4(3) | 3774.9(6) | 3669.93(9) | 7533.2(3) | 3590.2(4) |
| *Z* | 8 | 2 | 4 | 4 | 4 | 8 | 4 |
| $D_{calc}$ / g $cm^{-3}$ | 1.585 | 1.642 | 1.646 | 1.577 | 1.605 | 1.647 | 1.415 |
| *μ* / $mm^{-1}$ | 2.031 | 2.213 | 2.309 | 2.341 | 2.397 | 2.608 | 0.318 |
| Unique refl. | 7234 | 6788 | 8553 | 14762 | 8434 | 7410 | 8266 |
| Obsd. refl. | 6599 | 6464 | 7679 | 13327 | 6985 | 6343 | 7311 |
| $R_1$ ($I>2\sigma(I)$) | 0.0522 | 0.0228 | 0.1022 | 0.0915 | 0.0300 | 0.0402 | 0.0389 |
| $R_2$ (all data) | 0.0566 | 0.0252 | 0.1103 | 0.1010 | 0.0404 | 0.0495 | 0.0455 |
| $wR_2$ ($I>2\sigma(I)$) | 0.1142 | 0.0484 | 0.2400 | 0.2019 | 0.0653 | 0.0990 | 0.0983 |
| $wR_2$ (all data) | 0.1159 | 0.0495 | 0.2429 | 0.2082 | 0.0702 | 0.1039 | 0.1028 |
| CCDC-number | 1959637 | 1959638 | 1959631 | 1959628 | 1959626 | 1959627 | 1959635 |

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