Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Combined NMR, DFT and X-ray studies highlight structural and hydration changes of [Ln(AAZTA)]$^-$ complexes across the series

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Contents:

1. ^{1}H NMR spectra

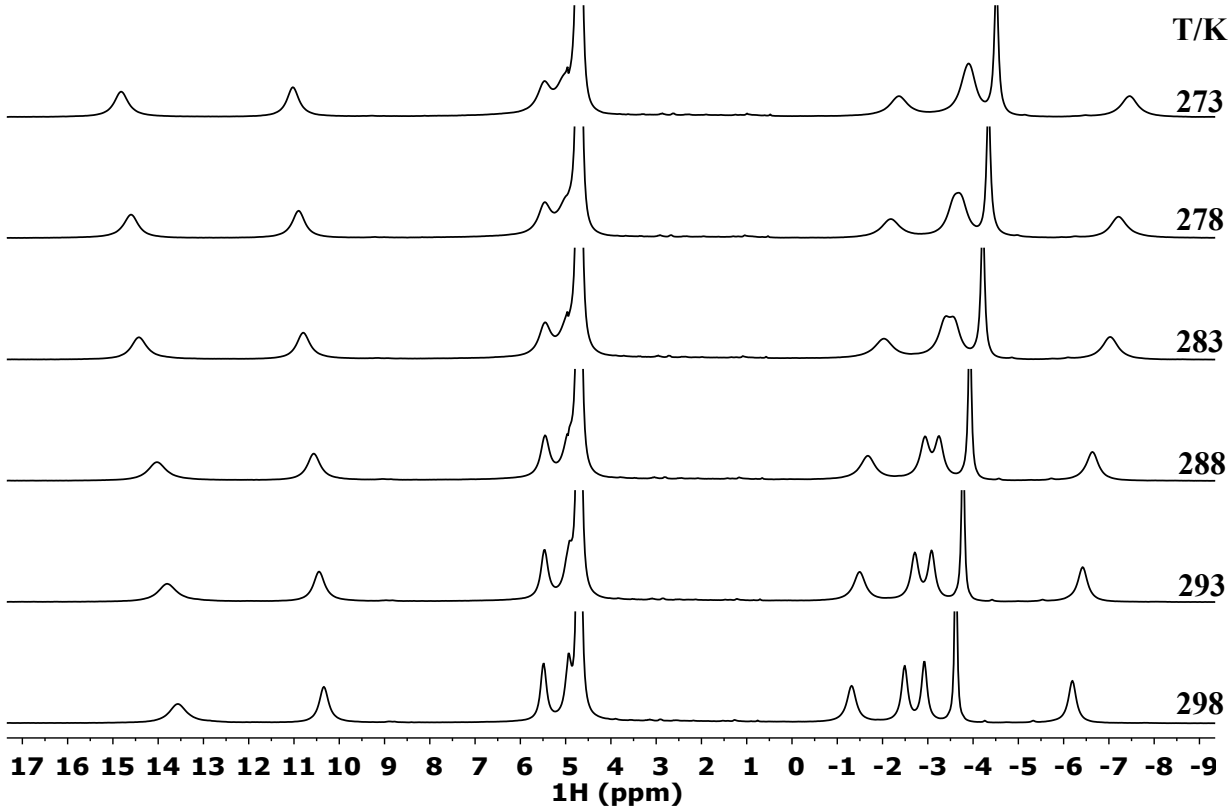

Figure S1. ^{1}H NMR spectra of $[Nd(AAZTA)]^-$ ([NdL]=25 mM, pH=7.0, D_2O, 9.4 T).

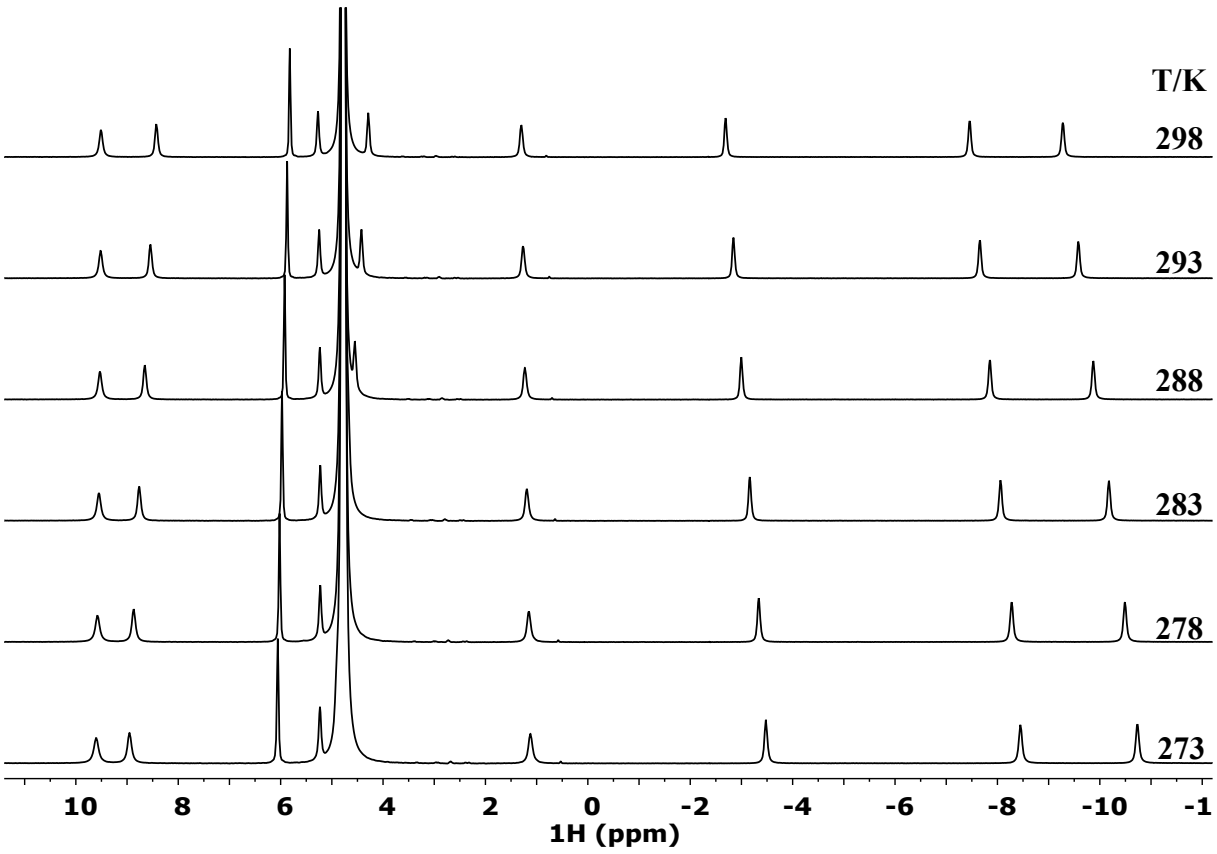

Figure S2. ^{1}H-NMR spectra of $[Eu(AAZTA)]^-$ ([EuL]=10 mM, pH=7.0, 14.1 T)

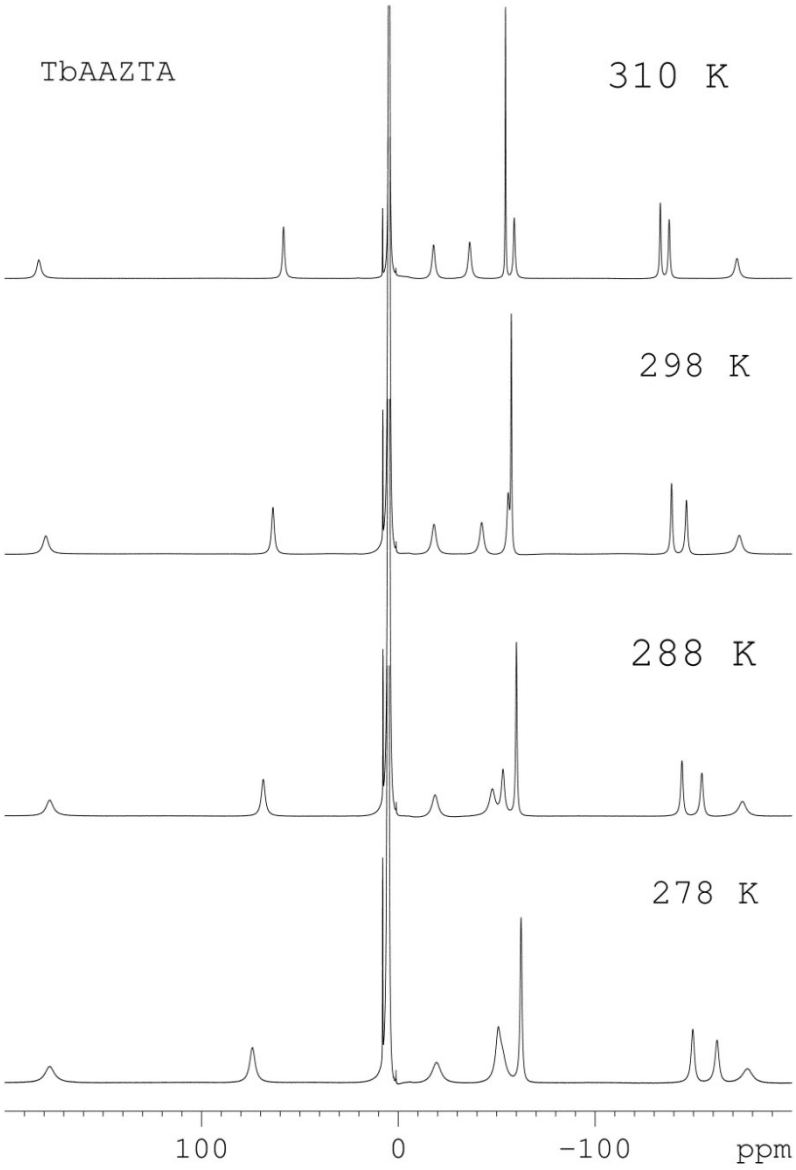

Figure S3. ^{1}H NMR spectra (14.1 T) of $[Tb(AAZTA)(H_2O)_2]^-$ recorded in D_2O at pH =7.0.

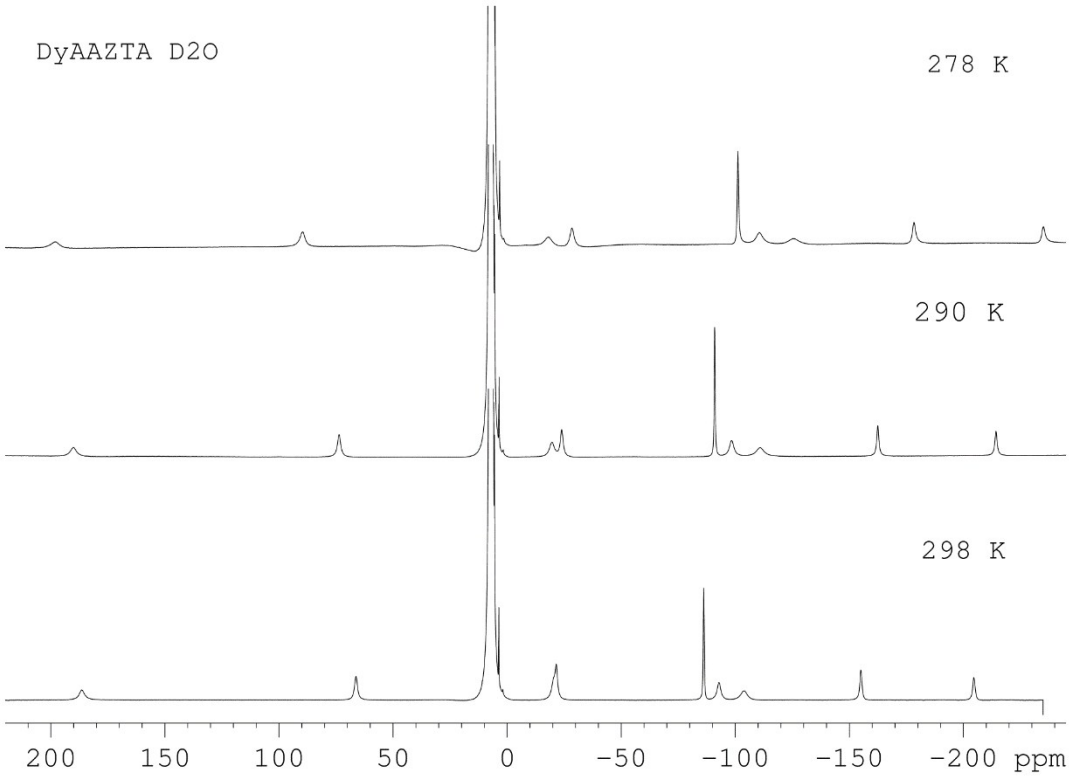

Figure S4. ^{1}H NMR spectra (14.1 T) of $[Dy(AAZTA)(H_2O)_2]^-$ recorded in D_2O at pH =7.0.

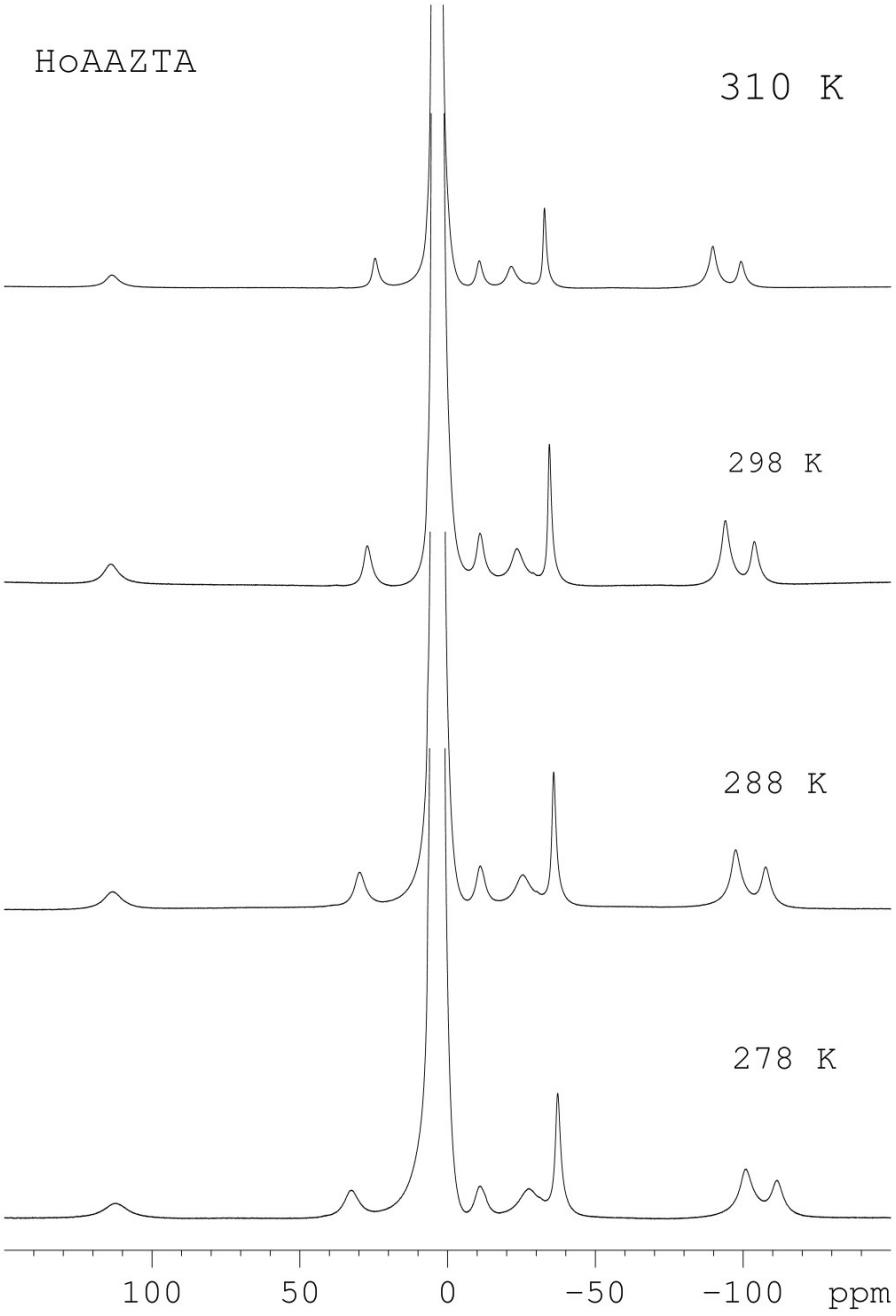

Figure S5. ^{1}H NMR spectra (14.1 T) of $[Ho(AAZTA)(H_2O)_2]^-$ recorded in D_2O at pH =7.0.

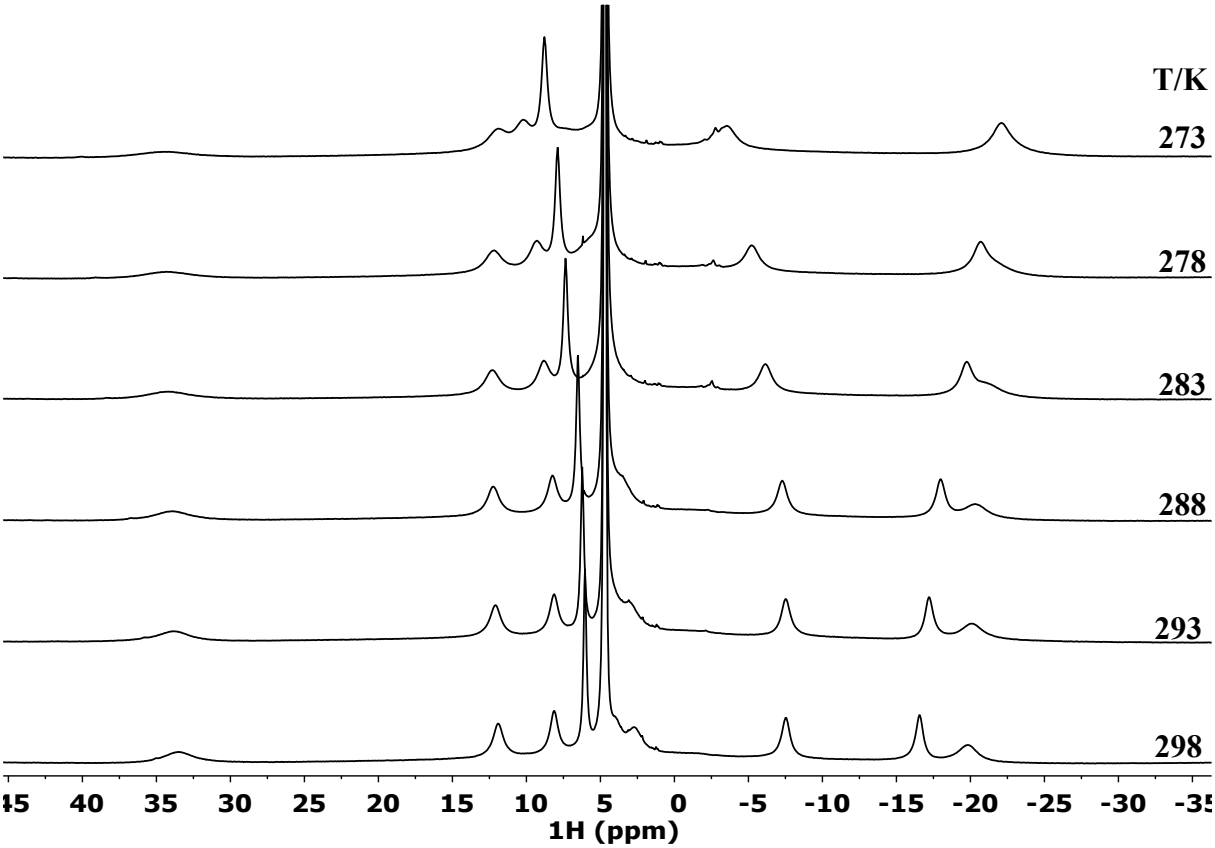

Figure S6. ^{1}H NMR spectra of $[Er(AAZTA)]^{-}$ ([ErL]=25 mM, pH=7.0, D_2O, 9.4 T)

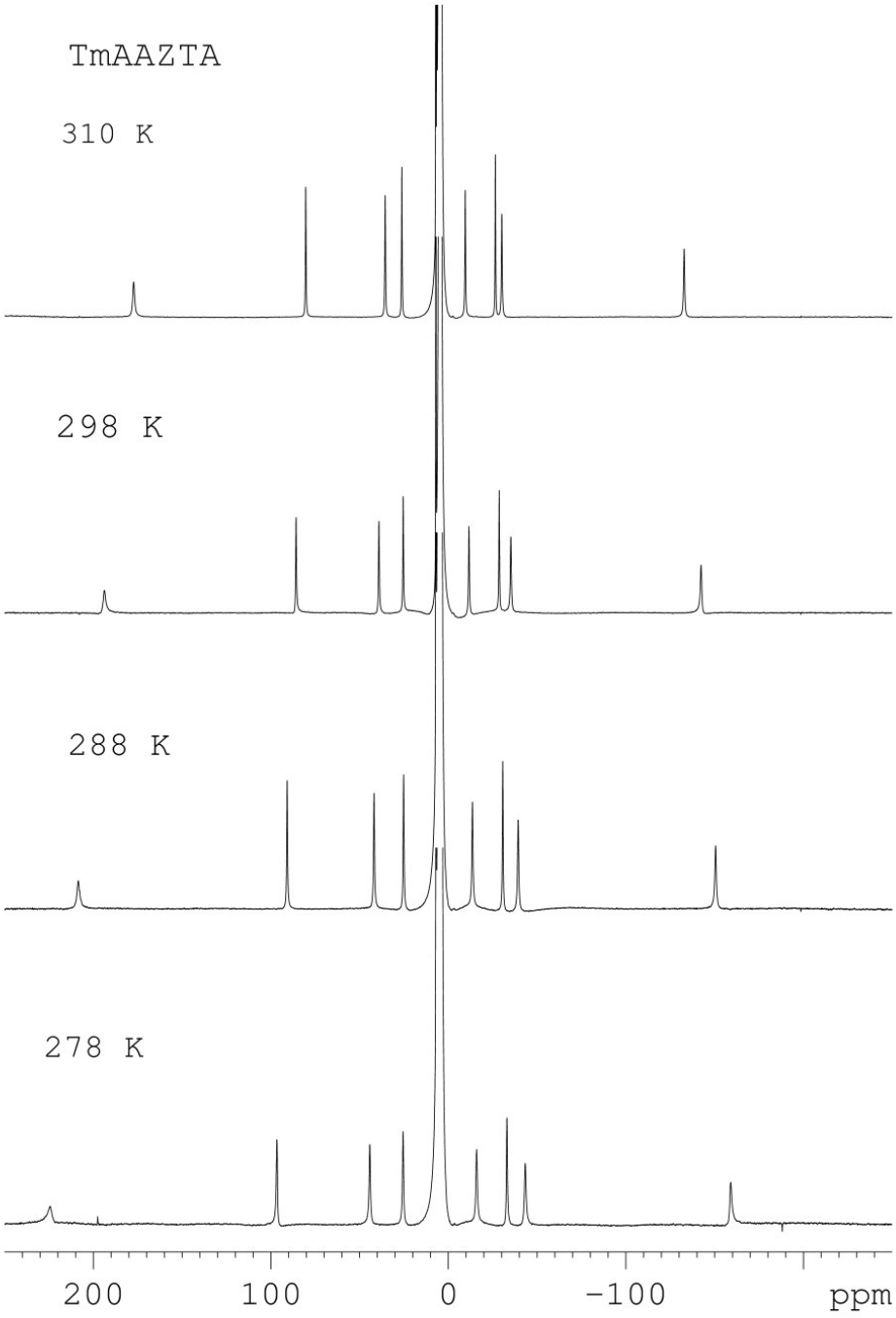

Figure S7. ^{1}H NMR spectra (14.1 T) of $[Tm(AAZTA)(H_2O)_2]^-$ recorded in D_2O at pH =7.0.

2. X-ray diffractions studies of $\{(C(NH_2)_3)[Er(AAZTA)(H_2O)]\}\cdot 2H_2O$

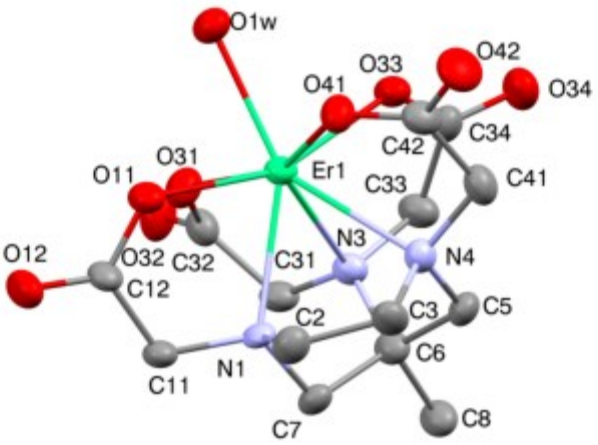

Figure S8. ORTEP view of $[Er(AAZTA)(H_2O)]^-$ at 40% probability level with numbering scheme. Hydrogen atoms are omitted for clarity.

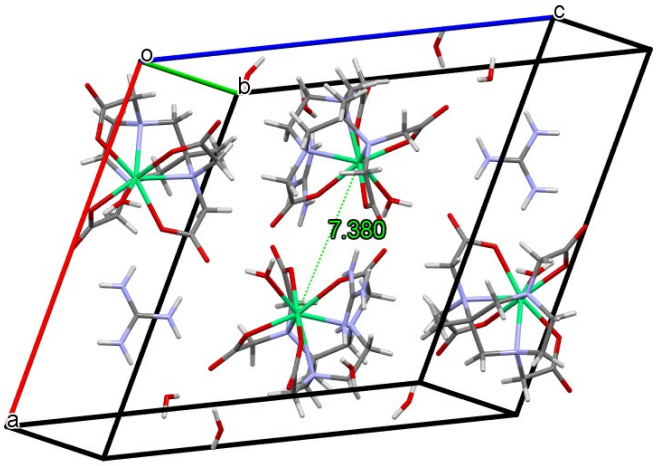

Figure S9. Packing diagram of $\{(C(NH_2)_3)[Er(AAZTA)(H_2O)]\}\cdot 2H_2O$

3. Supplementary tables

Table S1. Experimental details of X-ray structure determination

Crystal data {$(C(NH_2)_3)$[Er(AAZTA)(H_2O)]}·2H_2O	
Chemical formula	$C_{14}H_{21}ErN_3O_9 \cdot CH_6N_3 \cdot 2(H_2O)$
M_r	638.72
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	118
a, b, c (Å)	15.6276 (6), 8.3137 (3), 18.8019 (8)
β (°)	113.632 (2)
V (Å^3)	2237.95 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.82
Crystal size (mm)	0.39 × 0.06 × 0.04
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Numerical *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.63, 0.86
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	90321, 5546, 3427
R_{int}	0.206
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.179, 1.09
No. of reflections	5546
No. of parameters	318
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 47.5278P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	3.51, -1.96

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.2178 (8)	0.1386 (17)	0.3968 (7)	0.045 (3)
H2A	0.239127	0.231001	0.374925	0.054*
H2B	0.205731	0.047222	0.360263	0.054*
C3	0.1297 (8)	0.1824 (16)	0.4051 (7)	0.044 (3)
H3A	0.098456	0.27057	0.368452	0.052*
H3B	0.087179	0.088434	0.390799	0.052*
C5	0.1337 (8)	0.0959 (15)	0.5308 (7)	0.039 (3)
H5A	0.081225	0.027863	0.49688	0.047*
H5B	0.11773	0.137418	0.573345	0.047*
C6	0.2217 (9)	-0.0058 (14)	0.5651 (7)	0.040 (3)
C7	0.2583 (8)	-0.0508 (14)	0.5018 (6)	0.035 (3)
H7A	0.309877	-0.129433	0.523555	0.042*
H7B	0.207393	-0.102579	0.457465	0.042*
C8	0.1976 (10)	-0.1634 (15)	0.5947 (8)	0.050 (3)
H8A	0.169932	-0.139849	0.63206	0.074*
H8B	0.254535	-0.227177	0.620207	0.074*
H8C	0.152853	-0.224321	0.551001	0.074*
C11	0.3795 (8)	0.0659 (13)	0.4637 (7)	0.037 (3)
H11C	0.367243	-0.005251	0.418461	0.045*
H11D	0.424706	0.010931	0.510346	0.045*
C12	0.4214 (9)	0.2226 (13)	0.4517 (7)	0.038 (3)
C31	0.3842 (9)	0.0078 (14)	0.6658 (7)	0.044 (3)
H31C	0.389462	-0.078431	0.631444	0.052*
H31D	0.386219	-0.042853	0.714064	0.052*
C32	0.4652 (9)	0.1220 (15)	0.6851 (7)	0.041 (3)
C33	0.2649 (10)	0.1505 (15)	0.6889 (7)	0.046 (3)
H33A	0.318285	0.139763	0.739771	0.055*
H33B	0.214198	0.080011	0.689705	0.055*
C34	0.2311 (8)	0.3222 (16)	0.6795 (7)	0.042 (3)
C41	0.0855 (9)	0.3709 (16)	0.4813 (8)	0.046 (3)
H41A	0.084791	0.390242	0.532984	0.055*
H41B	0.020851	0.348346	0.444021	0.055*
C42	0.1232 (9)	0.5190 (15)	0.4553 (7)	0.044 (3)
C50	0.3019 (9)	0.7033 (15)	0.3300 (7)	0.042 (3)
N1	0.2924 (7)	0.0933 (10)	0.4734 (6)	0.035 (2)
N3	0.2945 (7)	0.0919 (12)	0.6269 (5)	0.037 (2)

N4	0.1459 (6)	0.2340 (12)	0.4849 (5)	0.036 (2)
N51	0.2219 (8)	0.6618 (16)	0.3342 (7)	0.061 (3)
H51A	0.221475	0.587872	0.36756	0.073*
H51B	0.169448	0.708284	0.303669	0.073*
N52	0.3805 (8)	0.6355 (14)	0.3750 (7)	0.054 (3)
H52A	0.432941	0.662974	0.371183	0.065*
H52B	0.381053	0.562436	0.40898	0.065*
N53	0.3008 (9)	0.8133 (14)	0.2787 (6)	0.056 (3)
H53A	0.353095	0.841033	0.274828	0.067*
H53B	0.247769	0.858735	0.24857	0.067*
O1W	0.4018 (6)	0.5712 (11)	0.6020 (5)	0.046 (2)
O2W	0.0791 (9)	0.8624 (15)	0.2230 (8)	0.084 (4)
O3W	0.0280 (9)	0.3468 (18)	0.1881 (9)	0.097 (4)
O11	0.3925 (6)	0.3538 (9)	0.4726 (5)	0.0403 (19)
O12	0.4805 (7)	0.2214 (11)	0.4237 (6)	0.056 (3)
O31	0.4533 (6)	0.2363 (11)	0.6370 (5)	0.047 (2)
O32	0.5388 (6)	0.0980 (13)	0.7415 (5)	0.056 (3)
O33	0.2575 (6)	0.4154 (10)	0.6404 (5)	0.0410 (19)
O34	0.1807 (7)	0.3594 (12)	0.7145 (5)	0.056 (2)
O41	0.2089 (5)	0.5158 (10)	0.4678 (5)	0.042 (2)
O42	0.0690 (7)	0.6343 (12)	0.4250 (6)	0.062 (3)
Er1	0.31276 (4)	0.33906 (6)	0.55217 (3)	0.03263 (19)
H11A	0.437 (7)	0.624 (14)	0.585 (7)	0.049*
H11B	0.420 (9)	0.583 (16)	0.6513 (18)	0.049*
H21A	0.022 (3)	0.833 (16)	0.204 (7)	0.049*
H21B	0.091 (9)	0.964 (4)	0.225 (8)	0.049*
H31A	0.077 (6)	0.286 (14)	0.206 (8)	0.049*
H31B	-0.016 (6)	0.381 (16)	0.201 (7)	0.049*

Table S3. Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.044 (7)	0.052 (8)	0.036 (6)	-0.006 (6)	0.013 (5)	-0.002 (6)
C3	0.042 (7)	0.050 (8)	0.035 (6)	-0.004 (6)	0.012 (5)	-0.013 (6)
C5	0.034 (6)	0.040 (6)	0.046 (7)	-0.010 (5)	0.018 (5)	-0.003 (5)
C6	0.049 (7)	0.033 (6)	0.043 (7)	-0.001 (5)	0.024 (6)	0.004 (5)
C7	0.038 (6)	0.035 (6)	0.032 (6)	-0.011 (5)	0.013 (5)	-0.004 (5)
C8	0.061 (8)	0.038 (7)	0.061 (8)	-0.001 (7)	0.037 (7)	0.005 (7)
C11	0.044 (7)	0.025 (5)	0.044 (7)	-0.002 (5)	0.020 (6)	-0.004 (5)
C12	0.045 (7)	0.024 (5)	0.046 (7)	0.007 (5)	0.021 (6)	0.004 (5)
C31	0.055 (8)	0.029 (6)	0.048 (7)	0.000 (6)	0.022 (6)	0.000 (5)

C32	0.044 (7)	0.042 (7)	0.044 (7)	0.007 (5)	0.024 (6)	0.006 (5)
C33	0.061 (8)	0.038 (7)	0.042 (7)	0.003 (6)	0.025 (6)	0.000 (6)
C34	0.037 (6)	0.049 (7)	0.040 (6)	-0.007 (6)	0.016 (5)	-0.003 (6)
C41	0.040 (7)	0.054 (8)	0.046 (7)	0.008 (6)	0.020 (6)	0.002 (6)
C42	0.045 (7)	0.035 (6)	0.043 (7)	0.010 (6)	0.009 (6)	0.004 (5)
C50	0.046 (7)	0.044 (7)	0.037 (7)	-0.007 (6)	0.017 (6)	-0.003 (5)
N1	0.044 (6)	0.020 (4)	0.046 (6)	-0.009 (4)	0.024 (5)	-0.002 (4)
N3	0.045 (6)	0.034 (5)	0.034 (5)	-0.001 (4)	0.018 (5)	-0.001 (4)
N4	0.032 (5)	0.039 (5)	0.035 (5)	0.000 (4)	0.012 (4)	0.000 (4)
N51	0.057 (7)	0.074 (9)	0.058 (7)	0.001 (7)	0.029 (6)	0.022 (7)
N52	0.050 (7)	0.052 (7)	0.057 (7)	-0.002 (6)	0.019 (6)	0.009 (6)
N53	0.065 (8)	0.056 (7)	0.045 (6)	0.007 (6)	0.020 (6)	0.020 (6)
O1W	0.050 (5)	0.042 (5)	0.047 (5)	-0.010 (4)	0.022 (5)	-0.001 (4)
O2W	0.067 (7)	0.062 (8)	0.091 (9)	-0.015 (7)	-0.002 (7)	0.019 (7)
O3W	0.076 (9)	0.094 (10)	0.127 (12)	0.014 (8)	0.047 (9)	-0.039 (9)
O11	0.052 (5)	0.028 (4)	0.046 (5)	0.000 (4)	0.024 (4)	0.003 (4)
O12	0.071 (7)	0.047 (5)	0.073 (7)	0.000 (5)	0.052 (6)	-0.002 (5)
O31	0.041 (5)	0.046 (5)	0.050 (5)	-0.002 (4)	0.015 (4)	0.012 (4)
O32	0.037 (5)	0.081 (7)	0.045 (5)	0.001 (5)	0.011 (4)	0.018 (5)
O33	0.051 (5)	0.033 (4)	0.044 (5)	-0.005 (4)	0.024 (4)	-0.004 (4)
O34	0.055 (6)	0.066 (6)	0.056 (6)	-0.003 (5)	0.033 (5)	-0.008 (5)
O41	0.039 (5)	0.039 (5)	0.050 (5)	0.004 (4)	0.019 (4)	0.013 (4)
O42	0.056 (6)	0.050 (6)	0.071 (7)	0.023 (5)	0.016 (5)	0.016 (5)
Er1	0.0380 (3)	0.0262 (3)	0.0339 (3)	0.0003 (2)	0.0146 (2)	0.0003 (2)

Table S4. Geometric parameters (Å, º)

C2—C3	1.491 (17)	C33—H33A	0.99
C2—N1	1.494 (15)	C33—H33B	0.99
C2—H2A	0.99	C34—O33	1.246 (14)
C2—H2B	0.99	C34—O34	1.251 (14)
C3—N4	1.482 (14)	C41—N4	1.463 (15)
C3—H3A	0.99	C41—C42	1.528 (18)
C3—H3B	0.99	C41—H41A	0.99
C5—N4	1.494 (15)	C41—H41B	0.99
C5—C6	1.520 (17)	C42—O42	1.255 (14)
C5—H5A	0.99	C42—O41	1.264 (14)
C5—H5B	0.99	C50—N52	1.307 (16)
C6—N3	1.499 (15)	C50—N53	1.324 (15)
C6—C8	1.529 (16)	C50—N51	1.329 (16)
C6—C7	1.559 (16)	N1—Er1	2.468 (9)

C7—N1	1.494 (13)	N3—Er1	2.569 (10)
C7—H7A	0.99	N4—Er1	2.553 (9)
C7—H7B	0.99	N51—H51A	0.88
C8—H8A	0.98	N51—H51B	0.88
C8—H8B	0.98	N52—H52A	0.88
C8—H8C	0.98	N52—H52B	0.88
C11—N1	1.462 (14)	N53—H53A	0.88
C11—C12	1.516 (16)	N53—H53B	0.88
C11—H11C	0.99	O1W—Er1	2.344 (9)
C11—H11D	0.99	O1W—H11A	0.86 (2)
C12—O12	1.232 (14)	O1W—H11B	0.86 (2)
C12—O11	1.301 (13)	O2W—H21A	0.86 (2)
C31—N3	1.471 (15)	O2W—H21B	0.86 (2)
C31—C32	1.506 (17)	O3W—H31A	0.86 (2)
C31—H31C	0.99	O3W—H31B	0.86 (2)
C31—H31D	0.99	O11—Er1	2.302 (8)
C32—O32	1.229 (14)	O31—Er1	2.300 (8)
C32—O31	1.273 (14)	O33—Er1	2.247 (8)
C33—N3	1.498 (15)	O41—Er1	2.290 (8)
C33—C34	1.508 (18)		
C3—C2—N1	110.9 (10)	O42—C42—C41	118.9 (12)
C3—C2—H2A	109.5	O41—C42—C41	116.1 (10)
N1—C2—H2A	109.5	N52—C50—N53	120.2 (12)
C3—C2—H2B	109.5	N52—C50—N51	120.8 (12)
N1—C2—H2B	109.5	N53—C50—N51	119.0 (13)
H2A—C2—H2B	108.0	C11—N1—C2	109.0 (9)
N4—C3—C2	112.7 (10)	C11—N1—C7	113.7 (9)
N4—C3—H3A	109.0	C2—N1—C7	107.1 (9)
C2—C3—H3A	109.0	C11—N1—Er1	107.5 (6)
N4—C3—H3B	109.0	C2—N1—Er1	103.5 (7)
C2—C3—H3B	109.0	C7—N1—Er1	115.4 (6)
H3A—C3—H3B	107.8	C31—N3—C33	107.3 (9)
N4—C5—C6	111.6 (9)	C31—N3—C6	113.8 (9)
N4—C5—H5A	109.3	C33—N3—C6	113.8 (9)
C6—C5—H5A	109.3	C31—N3—Er1	111.1 (7)
N4—C5—H5B	109.3	C33—N3—Er1	107.6 (7)
C6—C5—H5B	109.3	C6—N3—Er1	103.0 (6)
H5A—C5—H5B	108.0	C41—N4—C3	109.4 (9)
N3—C6—C5	107.7 (10)	C41—N4—C5	113.3 (9)

N3—C6—C8	113.8 (10)	C3—N4—C5	110.7 (10)
C5—C6—C8	108.5 (10)	C41—N4—Er1	105.6 (7)
N3—C6—C7	109.0 (9)	C3—N4—Er1	109.1 (7)
C5—C6—C7	110.9 (10)	C5—N4—Er1	108.6 (6)
C8—C6—C7	107.0 (10)	C50—N51—H51A	120.0
N1—C7—C6	111.9 (9)	C50—N51—H51B	120.0
N1—C7—H7A	109.2	H51A—N51—H51B	120.0
C6—C7—H7A	109.2	C50—N52—H52A	120.0
N1—C7—H7B	109.2	C50—N52—H52B	120.0
C6—C7—H7B	109.2	H52A—N52—H52B	120.0
H7A—C7—H7B	107.9	C50—N53—H53A	120.0
C6—C8—H8A	109.5	C50—N53—H53B	120.0
C6—C8—H8B	109.5	H53A—N53—H53B	120.0
H8A—C8—H8B	109.5	Er1—O1W—H11A	130 (9)
C6—C8—H8C	109.5	Er1—O1W—H11B	114 (9)
H8A—C8—H8C	109.5	H11A—O1W—H11B	111 (10)
H8B—C8—H8C	109.5	H21A—O2W—H21B	118 (10)
N1—C11—C12	111.4 (9)	H31A—O3W—H31B	139 (10)
N1—C11—H11C	109.3	C12—O11—Er1	119.8 (7)
C12—C11—H11C	109.3	C32—O31—Er1	126.6 (8)
N1—C11—H11D	109.3	C34—O33—Er1	125.2 (8)
C12—C11—H11D	109.3	C42—O41—Er1	123.1 (8)
H11C—C11—H11D	108.0	O33—Er1—O41	87.4 (3)
O12—C12—O11	123.2 (11)	O33—Er1—O31	97.8 (3)
O12—C12—C11	120.0 (10)	O41—Er1—O31	158.9 (3)
O11—C12—C11	116.8 (10)	O33—Er1—O11	158.9 (3)
N3—C31—C32	111.2 (10)	O41—Er1—O11	86.2 (3)
N3—C31—H31C	109.4	O31—Er1—O11	81.7 (3)
C32—C31—H31C	109.4	O33—Er1—O1W	79.3 (3)
N3—C31—H31D	109.4	O41—Er1—O1W	83.7 (3)
C32—C31—H31D	109.4	O31—Er1—O1W	77.3 (3)
H31C—C31—H31D	108.0	O11—Er1—O1W	80.0 (3)
O32—C32—O31	123.6 (12)	O33—Er1—N1	132.9 (3)
O32—C32—C31	120.8 (11)	O41—Er1—N1	103.3 (3)
O31—C32—C31	115.5 (11)	O31—Er1—N1	88.1 (3)
N3—C33—C34	114.8 (10)	O11—Er1—N1	68.1 (3)
N3—C33—H33A	108.6	O1W—Er1—N1	146.6 (3)
C34—C33—H33A	108.6	O33—Er1—N4	81.0 (3)
N3—C33—H33B	108.6	O41—Er1—N4	65.0 (3)
C34—C33—H33B	108.6	O31—Er1—N4	135.9 (3)

H33A—C33—H33B	107.5	O11—Er1—N4	114.0 (3)
O33—C34—O34	125.7 (13)	O1W—Er1—N4	143.6 (3)
O33—C34—C33	118.4 (11)	N1—Er1—N4	63.8 (3)
O34—C34—C33	115.9 (11)	O33—Er1—N3	70.3 (3)
N4—C41—C42	108.5 (10)	O41—Er1—N3	133.6 (3)
N4—C41—H41A	110.0	O31—Er1—N3	66.9 (3)
C42—C41—H41A	110.0	O11—Er1—N3	127.3 (3)
N4—C41—H41B	110.0	O1W—Er1—N3	128.2 (3)
C42—C41—H41B	110.0	N1—Er1—N3	69.5 (3)
H41A—C41—H41B	108.4	N4—Er1—N3	71.5 (3)
O42—C42—O41	125.0 (12)		
N1—C2—C3—N4	23.1 (15)	C34—C33—N3—C6	-99.1 (12)
N4—C5—C6—N3	69.3 (12)	C34—C33—N3—Er1	14.4 (12)
N4—C5—C6—C8	-167.1 (10)	C5—C6—N3—C31	179.7 (9)
N4—C5—C6—C7	-49.9 (13)	C8—C6—N3—C31	59.4 (13)
N3—C6—C7—N1	-51.4 (12)	C7—C6—N3—C31	-59.9 (12)
C5—C6—C7—N1	67.0 (12)	C5—C6—N3—C33	56.3 (12)
C8—C6—C7—N1	-174.8 (10)	C8—C6—N3—C33	-64.1 (13)
N1—C11—C12—O12	-161.9 (11)	C7—C6—N3—C33	176.7 (9)
N1—C11—C12—O11	18.6 (15)	C5—C6—N3—Er1	-59.9 (9)
N3—C31—C32—O32	150.4 (11)	C8—C6—N3—Er1	179.7 (8)
N3—C31—C32—O31	-33.5 (15)	C7—C6—N3—Er1	60.5 (9)
N3—C33—C34—O33	-23.1 (17)	C42—C41—N4—C3	-72.7 (12)
N3—C33—C34—O34	159.1 (11)	C42—C41—N4—C5	163.2 (10)
N4—C41—C42—O42	157.7 (11)	C42—C41—N4—Er1	44.6 (11)
N4—C41—C42—O41	-23.6 (16)	C2—C3—N4—C41	139.5 (11)
C12—C11—N1—C2	72.7 (12)	C2—C3—N4—C5	-94.9 (12)
C12—C11—N1—C7	-167.9 (9)	C2—C3—N4—Er1	24.5 (13)
C12—C11—N1—Er1	-38.9 (11)	C6—C5—N4—C41	-153.5 (10)
C3—C2—N1—C11	-174.8 (10)	C6—C5—N4—C3	83.1 (12)
C3—C2—N1—C7	61.7 (12)	C6—C5—N4—Er1	-36.6 (11)
C3—C2—N1—Er1	-60.6 (11)	O12—C12—O11—Er1	-164.0 (10)
C6—C7—N1—C11	137.6 (10)	C11—C12—O11—Er1	15.5 (14)
C6—C7—N1—C2	-101.9 (11)	O32—C32—O31—Er1	-161.0 (10)
C6—C7—N1—Er1	12.7 (12)	C31—C32—O31—Er1	23.0 (15)
C32—C31—N3—C33	-89.5 (12)	O34—C34—O33—Er1	-162.0 (9)
C32—C31—N3—C6	143.6 (10)	C33—C34—O33—Er1	20.4 (15)
C32—C31—N3—Er1	27.9 (11)	O42—C42—O41—Er1	162.2 (10)
C34—C33—N3—C31	134.0 (11)	C41—C42—O41—Er1	-16.4 (15)

Table S5. Hydrogen-bond geometry (Å, º) for $\{(C(NH_2)_3)[Er(AAZTA)(H_2O)]\}\cdot 2H_2O$

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O11	0.99	2.57	3.093 (15)	113
C8—H8*C*···O42^{i}	0.98	2.5	3.452 (18)	165
C11—H11*D*···O12^{ii}	0.99	2.45	3.355 (15)	152
C41—H41*A*···O33	0.99	2.65	3.140 (16)	111
N51—H51*A*···O41	0.88	2.06	2.868 (14)	152
N51—H51*B*···O2*W*	0.88	2.05	2.897 (17)	160
N52—H52*A*···O31^{iii}	0.88	2.03	2.898 (14)	171
N52—H52*B*···O11	0.88	2.07	2.935 (14)	166
N53—H53*A*···O32^{iii}	0.88	1.9	2.781 (15)	176
N53—H53*B*···O2*W*	0.88	2.48	3.219 (18)	142
N53—H53*B*···O34^{iv}	0.88	2.54	3.251 (15)	138
O1*W*—H11*A*···O12^{iii}	0.86 (2)	1.87 (5)	2.702 (13)	162 (13)
O1*W*—H11*B*···O32^{v}	0.86 (2)	1.86 (3)	2.717 (13)	177 (14)
O2*W*—H21*B*···O34^{iv}	0.86 (2)	2.10 (8)	2.846 (15)	146 (12)
O3*W*—H31*A*···O34^{vi}	0.86 (2)	1.98 (5)	2.816 (16)	163 (13)
O3*W*—H31*B*···O2*W*^{vii}	0.86 (2)	2.04 (8)	2.80 (2)	147 (13)

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) *x*, -*y*+3/2, *z*-1/2; (v) -*x*+1, *y*+1/2, -*z*+3/2; (vi) *x*, -*y*+1/2, *z*-1/2; (vii) -*x*, *y*-1/2, -*z*+1/2.

Table S6. Ln O_{water} bond distances (Å) and electron densities and its Laplacian (a. u.) at the corresponding bond critical points, calculated for the $[Ln(AAZTA)(H_2O)_2]\cdot 4H_2O$ and $[Ln(AAZTA)(H_2O)]\cdot 5H_2O$ systems with DFT calculations.

	Ln-O	ρ_{BCP}	$\nabla\rho$
$[La(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.611	0.03500493930	0.1432741538
	2.624	0.03467832905	0.1512618902
$[La(AAZTA)(H_2O)]\cdot 5H_2O$	2.598	0.036300963	0.1533557496
$[Ce(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.560	0.03760916467	0.1682068989
	2.592	0.03592665522	0.1516139872
$[Ce(AAZTA)(H_2O)]\cdot 5H_2O$	2.568	0.03753178003	0.1618289766
$[Pr(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.540	0.03814684964	0.173228980
	2.567	0.03673300942	0.1583757664
$[Pr(AAZTA)(H_2O)]\cdot 5H_2O$	2.533	0.03920143369	0.01735435901
$[Nd(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.527	0.03819820109	0.1754681337
	2.545	0.03731517046	0.1639982882
$[Nd(AAZTA)(H_2O)]\cdot 5H_2O$	2.510	0.03996472222	0.1807057412
$[Sm(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.494	0.03894192373	0.1802286265
	2.512	0.03810495132	0.16882866
$[Sm(AAZTA)(H_2O)]\cdot 5H_2O$	2.489	0.03976364062	0.1804674222
$[Eu(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.479	0.03916931751	0.1836076875
	2.496	0.038374211	0.1722235276
$[Eu(AAZTA)(H_2O)]\cdot 5H_2O$	2.437	0.04306529114	0.2034586909
$[Gd(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.465	0.03930743248	0.1858398255
	2.485	0.03833201605	0.1732028612
$[Gd(AAZTA)(H_2O)]\cdot 5H_2O$	2.427	0.04291504055	0.2042399542
$[Tb(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.451	0.03971849386	0.1867130309
	2.467	0.03902859070	0.1758423594
$[Tb(AAZTA)(H_2O)]\cdot 5H_2O$	2.409	0.04366989278	0.2074364658
$[Dy(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.439	0.03990514223	0.1888405240
	2.453	0.0393111232	0.1784976310
$[Dy(AAZTA)(H_2O)]\cdot 5H_2O$	2.392	0.04431609492	0.2126427502
$[Ho(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.427	0.03999930725	0.1904265193
	2.438	0.03971429940	0.1817757724
$[Ho(AAZTA)(H_2O)]\cdot 5H_2O$	2.377	0.04481210738	0.2167555332
$[Er(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.416	0.04007177113	0.1919035161
	2.424	0.04005338093	0.1846530980
$[Er(AAZTA)(H_2O)]\cdot 5H_2O$	2.376	0.04442178730	0.2121310761
$[Tm(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.459	0.0359119615	0.1672750655
	2.409	0.04020380318	0.1912139599
$[Tm(AAZTA)(H_2O)]\cdot 5H_2O$	2.348	0.04551605757	0.2255356702
$[Yb(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.449	0.03593067118	0.1678571469
	2.396	0.04047515131	0.1934846812
$[Yb(AAZTA)(H_2O)]\cdot 5H_2O$	2.336	0.04579359982	0.2281132258
$[Lu(AAZTA)(H_2O)_2]\cdot 4H_2O$	2.444	0.03583817940	0.1671265583
	2.383	0.04106797335	0.1969205556
$[Lu(AAZTA)(H_2O)]\cdot 5H_2O$	2.326	0.04611971439	0.2301047561

Table S7. Optimized Cartesian coordinates (Å) of the $[Yb(AAZTA)(H_2O)_2]\cdot 4H_2O$ system obtained with DFT calculations.[a]

Center Number	Atomic Number		Coordinates (Angstroms) X	Y	Z
1	70	0	-0.261308	0.109512	0.204492
2	8	0	0.741151	1.803831	1.400490
3	7	0	2.033130	-0.872858	-0.129927
4	6	0	1.941506	-2.354892	-0.100976
5	1	0	2.720022	-2.773688	0.540476
6	1	0	2.110332	-2.779476	-1.090643
7	8	0	0.845758	4.013127	1.621186
8	7	0	0.168386	-0.461631	-2.290251
9	6	0	0.586782	-2.921542	0.364201
10	7	0	1.181368	1.827556	-1.253167
11	6	0	2.533746	-0.313591	-1.429673
12	6	0	2.525980	1.221770	-1.358934
13	1	0	3.122981	1.553576	-0.512043
14	1	0	3.034614	1.600714	-2.254886
15	6	0	0.573585	1.979336	-2.592729
16	1	0	1.355276	2.182210	-3.333458
17	1	0	-0.092616	2.839459	-2.579387
18	8	0	0.585491	-4.056012	0.829403
19	8	0	-0.434932	-2.186352	0.154753
20	6	0	-0.257673	0.758106	-2.999260
21	1	0	-0.191508	0.607273	-4.084735
22	1	0	-1.303365	0.928180	-2.744604
23	8	0	0.733058	-0.777021	2.196122
24	6	0	1.588247	-0.771306	-2.563979
25	1	0	1.915579	-0.288220	-3.492288
26	1	0	1.694942	-1.841676	-2.734370
27	8	0	2.614503	-0.964043	3.388057
28	6	0	2.797900	-0.460596	1.065364
29	1	0	2.945120	0.616776	1.083609
30	1	0	3.773392	-0.952098	1.120168
31	8	0	-1.540573	2.153963	-0.222691
32	6	0	2.005854	-0.772129	2.343442
33	6	0	1.244098	3.114733	-0.539813
34	1	0	0.478331	3.783428	-0.927859
35	1	0	2.210105	3.614773	-0.671837
36	8	0	-2.158189	-0.417603	-1.051304
37	6	0	0.939850	2.980905	0.955237
38	8	0	-2.959920	-2.254703	-2.004458
39	6	0	3.960189	-0.769423	-1.750431
40	1	0	4.671454	-0.350313	-1.035588
41	1	0	4.043089	-1.857478	-1.720472
42	6	0	-0.756745	-1.555682	-2.622815
43	1	0	-0.318944	-2.510441	-2.336160
44	1	0	-0.980302	-1.590923	-3.696780
45	6	0	-2.071661	-1.423226	-1.844374
46	8	0	-2.041376	0.027432	1.806143
47	1	0	4.250159	-0.436197	-2.748798
48	1	0	-1.846790	-0.541875	2.586571
49	1	0	-2.825785	-0.382656	1.375763
50	1	0	-1.718973	2.607177	0.627064
51	1	0	-2.408560	2.052974	-0.662192
52	8	0	-1.781469	2.955990	2.396823
53	1	0	-1.793738	2.001710	2.555624
54	1	0	-0.851841	3.220563	2.485665
55	8	0	-3.986067	1.521624	-1.282121

56	1	0	-4.165068	1.679896	-2.213225
57	1	0	-3.574798	0.636584	-1.241549
58	8	0	-4.126760	-1.401116	0.661788
59	8	0	-1.175499	-1.575899	3.814161
60	1	0	-4.386527	-2.212490	1.106795
61	1	0	-3.783999	-1.672191	-0.206586
62	1	0	-1.348623	-2.499301	3.608872
63	1	0	-0.313929	-1.374140	3.377487

[a]Energy data (hartree): E(RM062X) = -1809.36630501; Zero-point correction = 0.506999; Thermal correction to Energy = 0.545449; Thermal correction to Enthalpy = 0.546393; Thermal correction to Gibbs Free Energy = 0.439596; Sum of electronic and zero-point Energies = -1808.859306; Sum of electronic and thermal Energies = -1808.820856; Sum of electronic and thermal Enthalpies = -1808.819912; Sum of electronic and thermal Free Energies = -1808.926709

Table S8. Optimized Cartesian coordinates (Å) of the [Yb(AAZTA)(H_2O)]·5H_2O system obtained with DFT calculations.[b]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	70	0	0.062568	0.068747	0.380248
2	8	0	1.410403	-1.691895	0.859566
3	7	0	-2.448921	-0.123291	-0.052054
4	6	0	-3.028343	1.228179	0.145615
5	1	0	-3.342511	1.306722	1.190249
6	1	0	-3.917309	1.392574	-0.465433
7	8	0	1.984113	-3.833489	0.703237
8	7	0	-0.420100	0.478237	-2.145277
9	6	0	-2.037529	2.382005	-0.064077
10	7	0	-0.480909	-1.982101	-1.015928
11	6	0	-2.564738	-0.629815	-1.461453
12	6	0	-1.855448	-1.999476	-1.560157
13	1	0	-2.440203	-2.763119	-1.048202
14	1	0	-1.841110	-2.297655	-2.614343
15	6	0	0.506944	-1.852612	-2.106421
16	1	0	0.447783	-2.724484	-2.769825
17	1	0	1.504075	-1.840448	-1.665928
18	8	0	-2.442311	3.430899	-0.548633
19	8	0	-0.839614	2.145755	0.324663
20	6	0	0.303742	-0.565464	-2.911353
21	1	0	-0.232174	-0.761851	-3.845287
22	1	0	1.290560	-0.189266	-3.181413
23	8	0	-1.100874	-0.491211	2.259555
24	6	0	-1.875991	0.391184	-2.384993
25	1	0	-2.080060	0.111526	-3.425152
26	1	0	-2.322793	1.375033	-2.235920
27	8	0	-2.996291	-0.923456	3.353445
28	6	0	-3.027565	-1.020479	0.965969
29	1	0	-2.850231	-2.065629	0.713610
30	1	0	-4.107229	-0.886608	1.070992
31	8	0	3.616461	-0.916845	-2.021047
32	6	0	-2.356473	-0.790348	2.325646
33	6	0	-0.129801	-3.163258	-0.211805
34	1	0	-0.050399	-4.069668	-0.820599
35	1	0	-0.895045	-3.322594	0.553240
36	8	0	1.776722	1.058151	-0.827857
37	6	0	1.205955	-2.906961	0.508895
38	8	0	1.984225	3.117581	-1.651343

39	6	0	-4.013119	-0.819976	-1.922846
40	1	0	-4.568006	-1.444672	-1.220322
41	1	0	-4.535718	0.131003	-2.031947
42	6	0	0.150445	1.803375	-2.431534
43	1	0	-0.556711	2.586043	-2.155034
44	1	0	0.396625	1.931723	-3.491662
45	6	0	1.411234	2.036531	-1.591306
46	8	0	1.342801	1.110292	2.033781
47	1	0	-4.027231	-1.314875	-2.895880
48	1	0	0.978905	1.201868	2.938653
49	1	0	1.810373	1.930854	1.773460
50	1	0	3.900966	-1.383387	-1.214276
51	1	0	3.068054	-0.196585	-1.685947
52	8	0	4.344345	-1.998479	0.475287
53	1	0	4.235020	-1.087973	0.797193
54	1	0	3.553122	-2.474321	0.768349
55	8	0	4.170915	0.789993	0.620420
56	1	0	4.143514	1.520512	1.248047
57	1	0	3.377607	0.954405	0.081790
58	8	0	2.768843	3.221751	1.048760
59	8	0	-0.029132	0.876461	4.354454
60	1	0	2.644147	4.114487	1.382870
61	1	0	2.607692	3.268146	0.085549
62	1	0	-0.635020	1.592392	4.565999
63	1	0	-0.547682	0.262253	3.797209

[b] Energy data (hartree): E(RM062X) = -1809.36688189; Zero-point correction = 0.506540; Thermal correction to Energy = 0.545509; Thermal correction to Enthalpy = 0.546453; Thermal correction to Gibbs Free Energy = 0.438060; Sum of electronic and zero-point Energies = -1808.860342; Sum of electronic and thermal Energies = -1808.821373; Sum of electronic and thermal Enthalpies = -1808.820428; Sum of electronic and thermal Free Energies = -1808.928822.