Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Solution structure of a europium-nicotianamine complex supports that phytosiderophores bind lanthanides

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Atomic cartesian coordinates (Å) of the PBE/LnPP1 GTH optimized structure of the $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^-$ complex. Only the water molecules coordinated to Eu^{3+} included.

element	mass	x	y	z
Eu	63.0	13.84599972	11.27400017	9.83600044
N	7.0	11.16800022	10.50300026	9.22299957
N	7.0	13.53100014	9.68099976	7.58300018
C	6.0	11.07499981	10.15999985	7.78700018
C	6.0	12.14700031	9.15999985	7.38800001
C	6.0	10.44499969	11.73600006	9.57999992
C	6.0	10.83300018	12.16499996	10.99300003
C	6.0	13.91300011	10.60400009	6.48999977
C	6.0	13.35499954	12.02099991	6.63800001
C	6.0	14.49300003	8.56000042	7.63700008
C	6.0	15.76700020	8.92500019	8.39999962
C	6.0	10.78299999	9.37399960	10.08899975
C	6.0	11.93299961	8.58800030	10.71899986
O	8.0	10.06599998	12.90699959	11.66499996
O	8.0	11.96300030	11.73999977	11.43999958
O	8.0	13.20100021	12.69099998	5.55399990
O	8.0	13.11600018	12.46700001	7.80000019
O	8.0	15.67899990	9.78100014	9.32999992
O	8.0	16.84700012	8.31200027	8.09500027
O	8.0	13.12100029	9.03899956	10.65100002
O	8.0	11.59700012	7.50400019	11.29800034
H	1.0	11.13399982	11.08199978	7.20599985
H	1.0	10.08199978	9.73299980	7.56500006
H	1.0	12.04899979	8.24800014	7.99100018
H	1.0	11.97999954	8.86400032	6.33900023
H	1.0	9.35200024	11.60000038	9.50800037
H	1.0	10.73499966	12.53299999	8.87699986
H	1.0	13.63099957	10.19699955	5.50400019
H	1.0	15.01000023	10.71700001	6.49100018
H	1.0	14.74199963	8.17199993	6.63800001
H	1.0	14.03499985	7.73199987	8.19799995
H	1.0	10.16899967	9.73400021	10.92599964
H	1.0	10.14900017	8.66699982	9.53199959
O	8.0	15.75000000	12.53199959	8.75599957
H	1.0	15.65999985	13.45699978	8.39299965
H	1.0	16.64100075	12.55799961	9.22900009
O	8.0	15.31000042	11.30000019	11.81200027
H	1.0	16.06100082	10.67199993	11.95400047
H	1.0	15.11699963	11.76000023	12.67500019
O	8.0	13.92599964	13.71700001	10.79699993
H	1.0	14.83300018	13.95699978	11.17199993
H	1.0	13.27200031	13.98400021	11.51299953

Atomic cartesian coordinates (Å) of the PBE/LnPP1 GTH optimized structure of the $[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$ complex. Only the water molecules coordinated to Eu^{3+} included.

element	mass	x	y	z
Eu	63.0	7.92100000	7.83099985	6.86999989
C	6.0	11.68400002	10.07100010	6.63500023
C	6.0	12.94900036	9.23299980	6.92299986
C	6.0	12.95199966	9.77600002	8.36299992
C	6.0	10.34599972	9.34799957	6.50099993
O	8.0	10.32299995	8.13300037	6.12400007
O	8.0	9.26700020	9.98299980	6.73899984
N	7.0	11.95600033	10.85700035	7.95100021
H	1.0	11.74699974	10.77799988	5.79600000
H	1.0	12.82600021	8.15200043	6.84800005
H	1.0	13.81999969	9.55700016	6.34499979
H	1.0	13.87199974	10.20600033	8.76500034
H	1.0	12.49400043	9.08399963	9.07499981
C	6.0	10.89299965	11.42700005	8.87500000
C	6.0	10.86200047	10.87899971	10.31499958
C	6.0	9.78999996	9.82600021	10.68799973
N	7.0	8.40999985	10.40299988	10.58600044
C	6.0	7.35200024	9.54500008	11.22599983
C	6.0	5.94099998	10.01700020	10.85400009
C	6.0	5.14799976	9.05900002	9.93299961
N	7.0	3.94400001	9.78999996	9.45499992
H	1.0	11.12300014	12.49300003	8.92300034
H	1.0	9.93400002	11.31799984	8.35799980
H	1.0	10.70600033	11.74300003	10.97900009
H	1.0	11.84200001	10.47900009	10.60799980
H	1.0	9.93000031	9.59000015	11.75300026
C	6.0	9.93900013	8.50100040	9.90900040
O	8.0	9.09599972	8.22700024	9.00300026
O	8.0	10.93599987	7.78900003	10.24100018
H	1.0	8.14700031	10.67700005	9.61100006
H	1.0	7.52699995	8.51000023	10.92800045
H	1.0	7.52500010	9.60000038	12.30599976
H	1.0	5.34100008	10.15900040	11.76200008
H	1.0	5.98899984	11.00199986	10.37199974
H	1.0	4.80000019	8.18500042	10.49899960
H	1.0	3.28099990	9.19499969	8.88599968
C	6.0	5.99599981	8.52400017	8.77700043
O	8.0	6.46999979	7.34899998	8.83699989
O	8.0	6.28399992	9.29199982	7.78399992
H	1.0	8.35599995	11.32400036	11.14200020
H	1.0	4.14499998	10.62199974	8.84500027
H	1.0	12.54800034	11.66100025	7.61299992
H	1.0	3.35700011	10.09000015	10.29199982
O	8.0	6.53399992	6.38100004	5.93200016
H	1.0	5.75299978	5.80200005	6.27400017
H	1.0	6.79400015	5.90700006	5.03900003
O	8.0	8.91699982	5.61100006	7.26200008
H	1.0	9.77900028	5.54600000	7.81899977
H	1.0	8.97900009	4.90999985	6.54799986
O	8.0	7.43599987	8.75699997	4.73299980
H	1.0	6.86399984	8.31700039	4.01700020
H	1.0	8.13700008	9.25399971	4.19099998

Atomic cartesian coordinates (Å) of the PBE/LnPP1 GTH optimized structure of the $[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$ complex. Only the water molecules coordinated to Eu^{3+} included.

element	mass	x	y	z
Eu	63.0	7.74599981	7.30700016	6.86899996
C	6.0	11.94299984	9.15699959	5.76700020
C	6.0	13.42399979	8.83100033	5.49900007
C	6.0	13.71700001	9.18299961	6.97200012
C	6.0	10.81200027	8.21599960	5.36600018
O	8.0	10.93700027	7.44000006	4.37599993
O	8.0	9.79199982	8.31099987	6.13399982
N	7.0	12.22200012	9.08100033	7.27799988
H	1.0	11.68999958	10.19799995	5.52199984
H	1.0	13.56000042	7.77299976	5.26399994
H	1.0	13.92500019	9.44600010	4.74900007
H	1.0	14.03299999	10.22000027	7.11800003
H	1.0	14.31000042	8.50599957	7.59200001
C	6.0	11.56700039	10.04100037	8.21700001
C	6.0	11.68700027	9.60299969	9.68999958
C	6.0	10.46000004	8.90799999	10.32499981
N	7.0	9.26599979	9.80700016	10.21399975
C	6.0	8.18099976	9.56499958	11.23400021
C	6.0	6.90700006	10.33399963	10.85000038
C	6.0	5.83300018	9.48299980	10.14700031
N	7.0	4.75699997	10.39299965	9.63500023
H	1.0	12.05900002	11.00800037	8.06900024
H	1.0	10.53100014	10.13099957	7.87400007
H	1.0	11.89200020	10.50100040	10.28499985
H	1.0	12.56700039	8.95600033	9.82600021
H	1.0	10.65799999	8.78800011	11.39700031
C	6.0	10.17199993	7.51800013	9.73400021
O	8.0	9.35999966	7.43499994	8.75100040
O	8.0	10.84300041	6.56300020	10.22900009
H	1.0	8.86200047	9.73299980	9.26399994
H	1.0	8.02600002	8.47900009	11.31900024
H	1.0	8.58100033	9.92399979	12.18900013
H	1.0	6.46099997	10.76099968	11.75599957
H	1.0	7.16499996	11.18500042	10.20600033
H	1.0	5.36199999	8.80300045	10.86299992
H	1.0	4.07399988	9.91499996	9.00100040
C	6.0	6.42600012	8.65100002	9.01299953
O	8.0	6.38700008	7.37300014	9.08500004
O	8.0	6.99700022	9.26900005	8.05300045
H	1.0	4.21000004	10.69900036	10.47900009
H	1.0	5.14699984	11.20400047	9.07199955
H	1.0	9.59399986	10.82100010	10.31799984
H	1.0	12.03199959	8.08800030	7.55900002
O	8.0	8.57499981	6.21000004	4.98299980
H	1.0	9.42800045	6.52799988	4.57700014
H	1.0	8.32699966	5.29500008	4.62900019
O	8.0	5.69299984	6.48099995	6.12699986
H	1.0	5.34600019	5.55100012	6.06699991
H	1.0	5.13399982	6.98099995	5.44799995
O	8.0	7.95699978	4.90899992	7.60900021
H	1.0	8.63899994	4.66499996	8.29699993
H	1.0	7.11800003	4.40500021	7.82600021
O	8.0	7.08699989	8.92300034	5.24599981
H	1.0	6.59700012	9.79100037	5.35900021
H	1.0	7.30100012	8.81799984	4.27799988

Atomic cartesian coordinates (Å) of the PBE/LnPP1 GTH optimized structure of the $[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$ complex. Only the water molecules coordinated to Eu^{3+} included.

element	mass	x	y	z
Eu	63.0	7.83129978	7.52320004	6.34560013
C	6.0	11.88360023	9.41580009	5.63219976
C	6.0	13.38370037	9.16790009	5.38539982
C	6.0	13.55720043	8.98709965	6.90950012
C	6.0	10.75479984	8.66749954	4.92409992
O	8.0	10.85369968	8.22949982	3.76410007
O	8.0	9.70930004	8.57579994	5.68450022
N	7.0	12.03409958	8.92609978	7.07900000
H	1.0	11.62430000	10.48309994	5.66860008
H	1.0	13.58530045	8.26679993	4.80350018
H	1.0	13.92459965	10.01200008	4.95209980
H	1.0	13.94999981	9.86660004	7.43219995
H	1.0	14.03649998	8.07260036	7.27159977
C	6.0	11.37849998	9.73139954	8.15019989
C	6.0	11.48130035	9.10359955	9.54290009
C	6.0	10.27200031	8.32229996	10.07789993
N	7.0	8.99740028	9.12030029	10.12749958
C	6.0	8.00010014	8.42249966	11.01169968
C	6.0	6.65189981	9.11250019	11.14379978
C	6.0	5.71350002	9.07540035	9.92329979
N	7.0	4.37939978	9.54959965	10.41030025
H	1.0	11.86870003	10.71370029	8.13059998
H	1.0	10.34399986	9.86940002	7.82429981
H	1.0	11.71350002	9.91549969	10.24940014
H	1.0	12.34379959	8.41860008	9.59379959
H	1.0	10.49670029	8.05519962	11.11579990
C	6.0	9.96150017	7.02689981	9.30249977
O	8.0	9.27789974	7.17490005	8.23180008
O	8.0	10.40450001	5.94999981	9.79100037
H	1.0	8.62619972	9.19880009	9.15789986
H	1.0	7.88420010	7.39510012	10.64439964
H	1.0	8.45820045	8.36639977	12.00580025
H	1.0	6.15990019	8.57670021	11.96899986
H	1.0	6.77370024	10.15419960	11.46450043
H	1.0	6.02909994	9.78349972	9.15079975
H	1.0	3.59069991	9.47159958	9.70699978
C	6.0	5.63969994	7.66340017	9.30749989
O	8.0	4.89750004	6.82110023	9.88749981
O	8.0	6.39260006	7.44089985	8.30230045
H	1.0	4.44159985	10.56569958	10.67230034
H	1.0	4.07040024	9.07339954	11.28299999
H	1.0	9.08990002	10.13379955	10.48400021
H	1.0	11.74800014	7.92269993	7.08220005
O	8.0	8.47669983	6.74340010	3.94989991
H	1.0	9.43630028	6.91219997	3.78259993
H	1.0	8.34189987	5.77360010	3.83759999
O	8.0	6.12809992	6.03749990	5.60330009
H	1.0	6.18370008	5.03889990	5.66830015
H	1.0	5.15630007	6.23899984	5.72760010
O	8.0	7.95650005	9.88059998	7.35349989
H	1.0	7.20930004	10.48060036	7.60589981
H	1.0	8.51340008	10.46339989	6.74609995
O	8.0	9.18299961	5.26090002	6.29589987
H	1.0	9.29119968	4.67880011	7.09399986
H	1.0	8.95069981	4.65560007	5.53200006
O	8.0	6.38229990	8.83510017	5.06879997
H	1.0	6.16870022	9.81770039	5.10239983
H	1.0	5.79600000	8.45740032	4.35410023

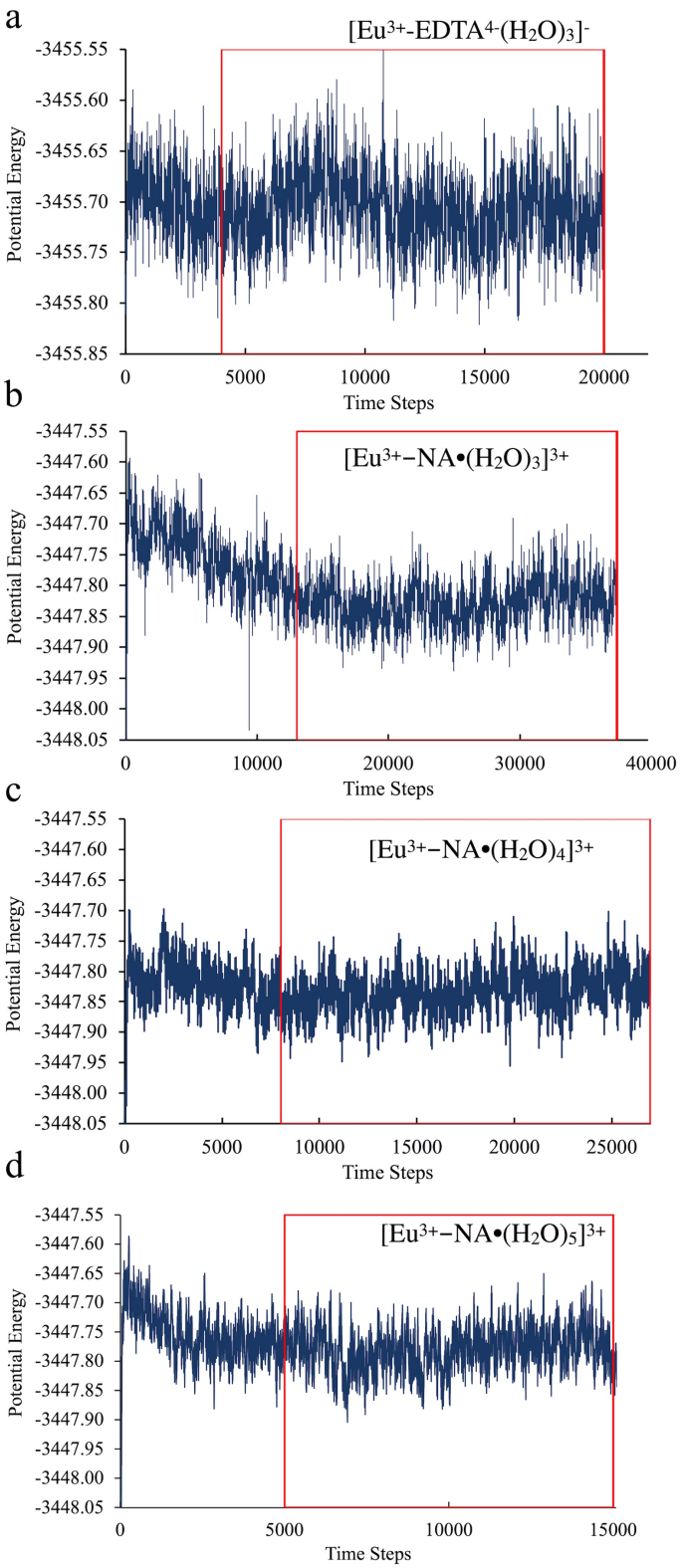

Figure S1. Potential energy (hartree) plots for AIMD trajectories of simulated complexes. a) $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^-$ complex, b) $[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$ complex, c) $[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$, d) $[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$ complex. Red boxes indicate the equilibrated portions of AIMD trajectories that were used to obtain the radial distribution functions and further analysis.

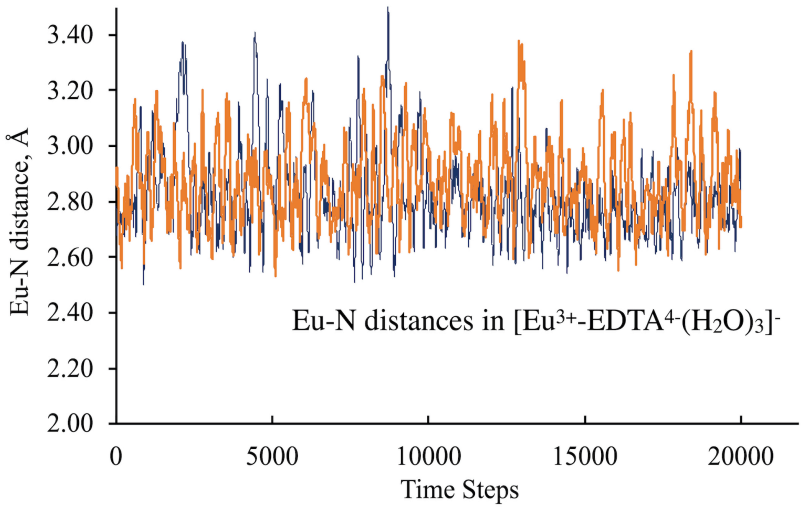

Figure S2. Plot of Eu-N bond distances during the AIMD trajectory of the $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^-$ complex. Orange and blue curves represent the Eu-N distances for two individual nitrogen atoms along the AIMD trajectory.

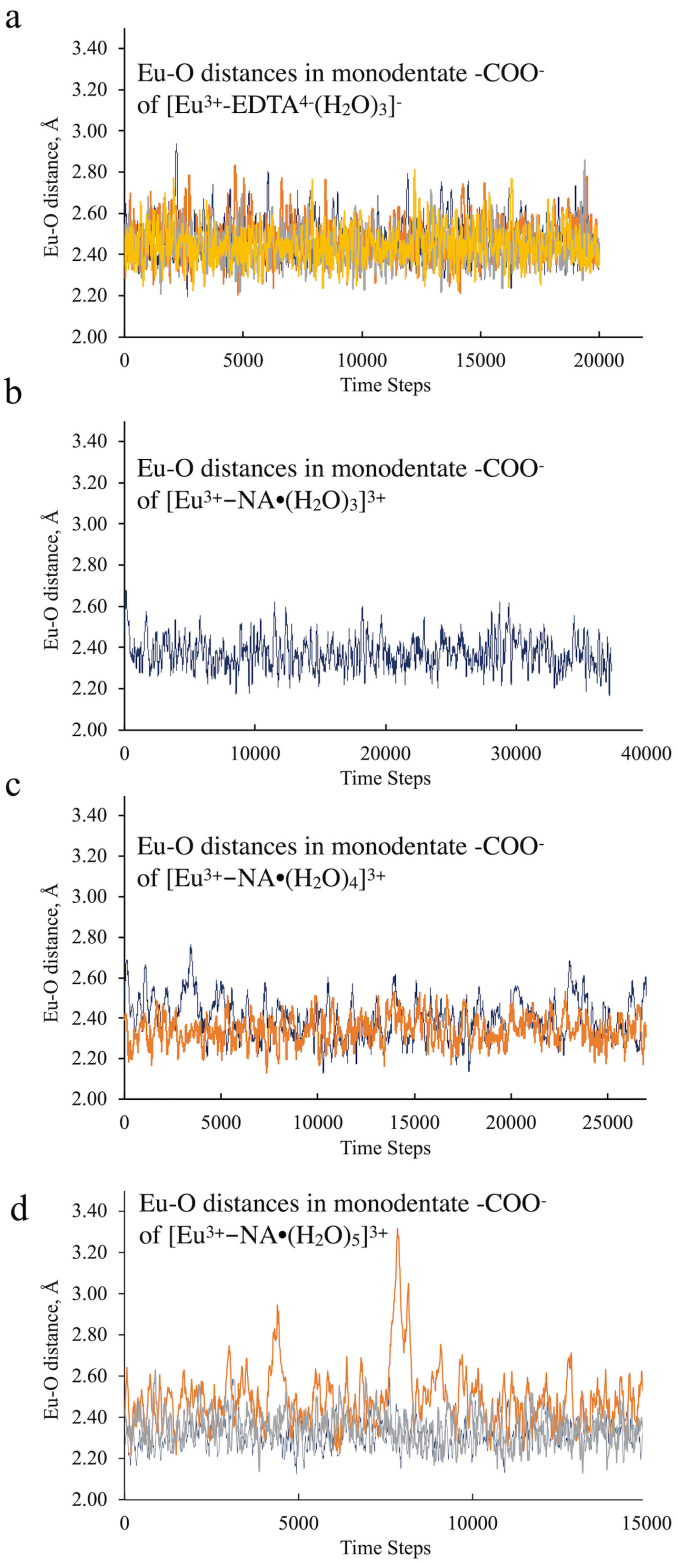

Figure S3. Plots of Eu-O bond distances, for monodentate carboxylates, during the AIMD trajectories of a) $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^-$ complex, b) $[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$ complex, c) $[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$ complex, d) $[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$ complex. Orange, blue, yellow and grey curves represent the Eu-O distances for individual oxygen atoms along the AIMD trajectory.

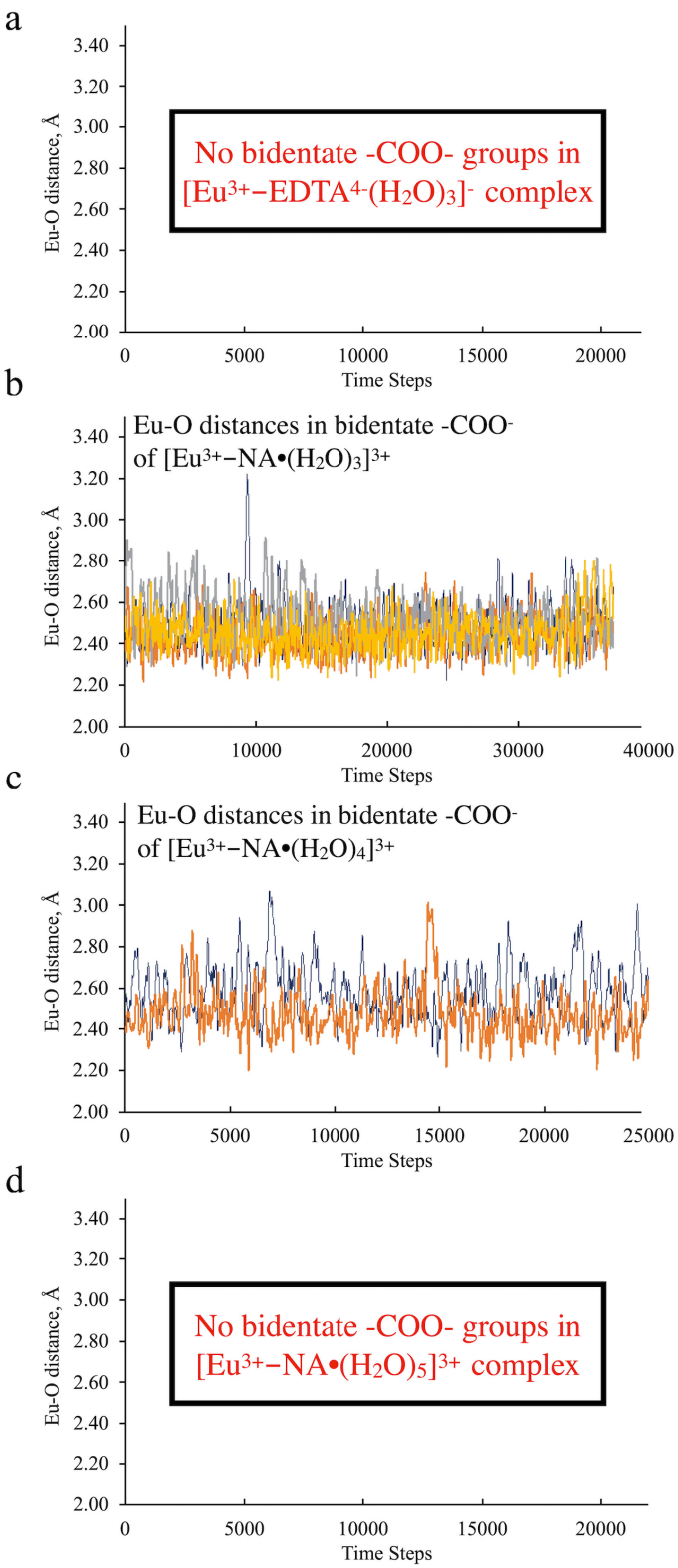

Figure S4. Plots of Eu-O bond distances, for bi-dentate carboxylates, during the AIMD trajectories of b) $[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$ complex, c) $[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$ complex, d) $[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$ complex. Orange, blue, yellow and grey curves represent the Eu-O distances for individual oxygen atoms along the AIMD trajectory.

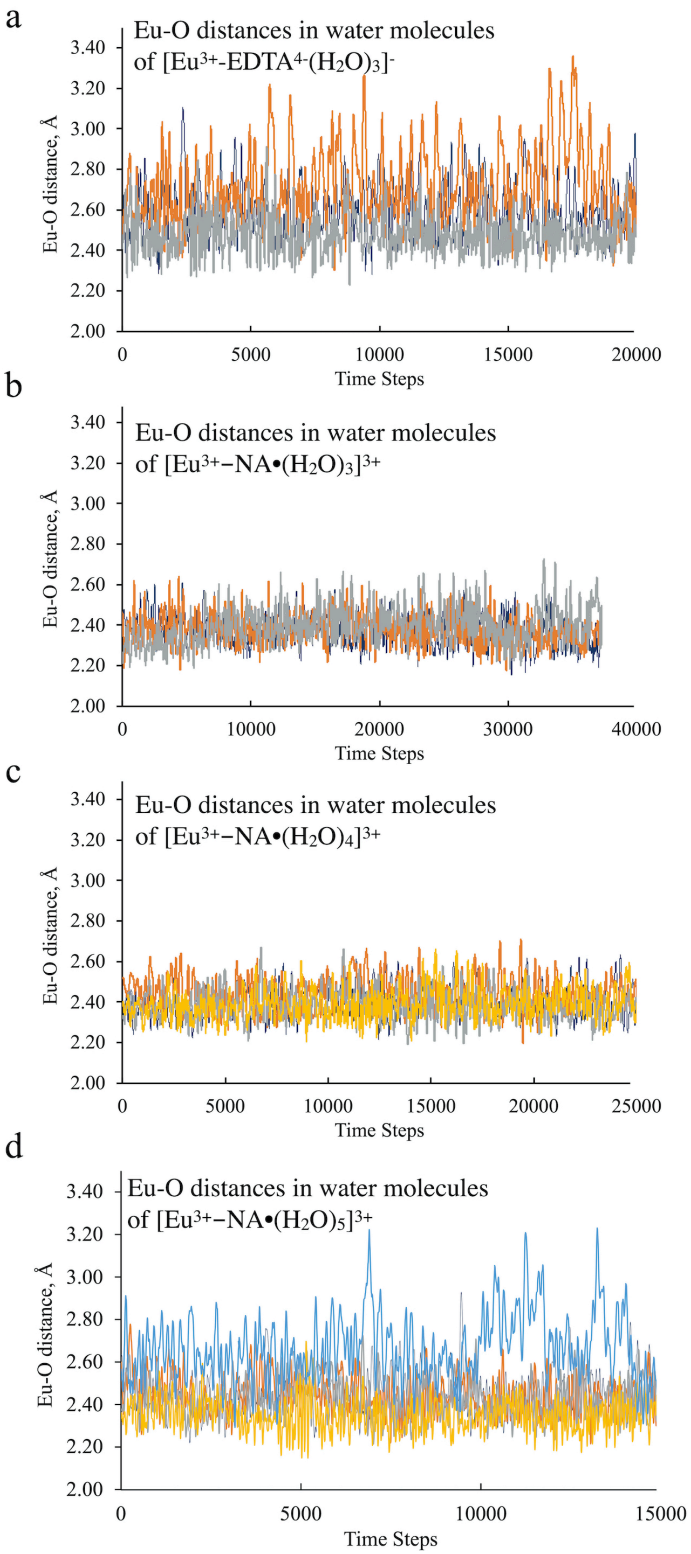

Figure S5. Plots of Eu-O bond distances, for water molecules, during the AIMD trajectories of a) $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^{-}$ complex, b) $[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$ complex, c) $[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$ complex, d) $[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$. Orange, blue, yellow and grey curves represent the Eu-O distances for individual oxygen atoms along the AIMD trajectory.

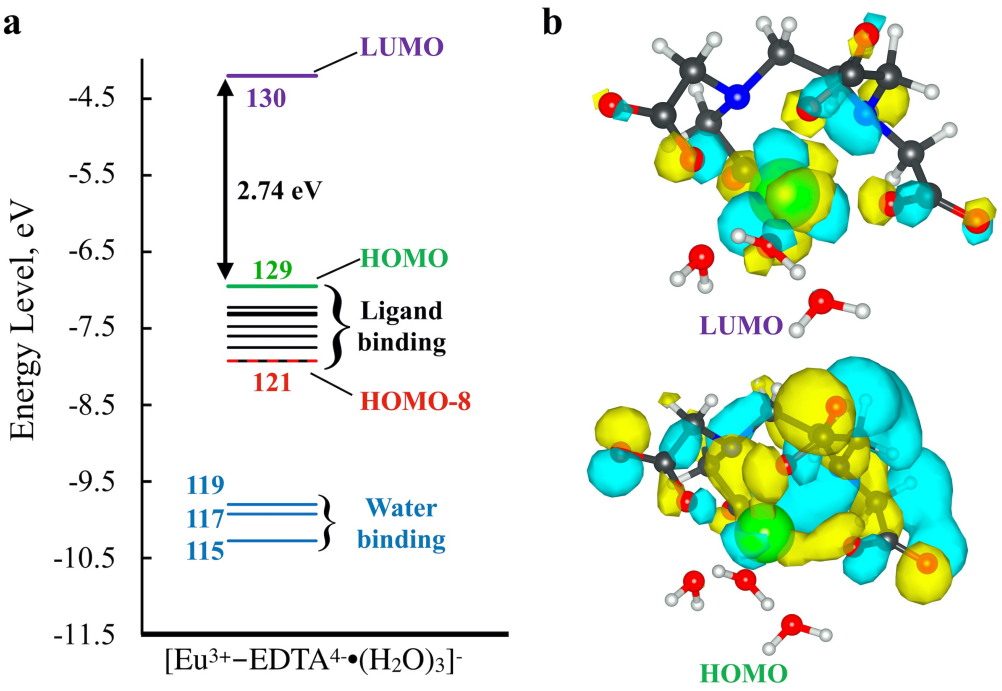

Figure S6. Valence molecular orbitales (MOs) of the $[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^-$ complex. a) MO diagrams. b) HOMO and LUMO orbitals, the orbital wave functions are positive in the yellow regions and negative in the cyan.

Table S1: Binding energies

Complex	Binding Energies (kJ/mol)	Relative Binding Energies
$[Eu^{3+}\text{-}NA\cdot(H_2O)_3]^{3+}$	-1025	0.78
$[Eu^{3+}\text{-}NA\cdot(H_2O)_4]^{3+}$	-1068	0.81
$[Eu^{3+}\text{-}NA\cdot(H_2O)_5]^{3+}$	-1059	0.80
$[Eu^{3+}\text{-}EDTA^{4-}\cdot(H_2O)_3]^{-}$	-1322	1.00