Supporting Information

Lanthanide Complexes of Aminopolycarboxylates Reveal Deuteration of Aminoacetate Carbons In Alkaline Aqueous Media

Sebastian Friedrich,[a] Lukas Waurick,[a] Björn Drobot,[a] Robin Steudtner,[a] Katharina Müller,[a] Astrid Barkleit,[a] Thorsten Stumpf,[a] and Jerome Kretzschmar [a,*]

[a] Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstr. 400, 01328 Dresden, Germany.

* Corresponding author.
E-mail address: *j.kretzschmar@hzdr.de*

Experimental procedure

All solutions were prepared in D_2O, using $LaCl_3 \cdot 7H_2O$ (99.999 %, Sigma, 60 mM), $SmCl_3 \cdot 6H_2O$ (>99 %, Sigma, 60 mM), $Lu(NO_3)_3 \cdot 5H_2O$ (99.99 %, Alfa Aesar, 60 mM), H_3NTA (Sigma, ≥99 %, 60 mM) $H_2Na_2EDTA \cdot 2H_2O$ (Roth, ≥99%, 60 mM) and H_4EGTA (Roth, ≥99%, 60 mM). Stock solutions of NTA, EDTA, and EGTA were adjusted to pD 10 using 0.1 M NaOD. All deuterated chemicals (D_2O, 99.9% D; DCl 37%, 99% D; NaOD 38%, 99% D) were purchased from Deutero, Kastellaun, Germany. For ^2H NMR measurements, the deuterated ligands were dissolved in Milli-Q H_2O (18.2 MΩ cm, Millipore, Merck, Darmstadt, Germany) and, where necessary, pH adjusted using HCl and NaOH. For doing so, we used a VWR pHenomenal® MU 6100 L pH meter equipped with a WTW SenTix Mic pH electrode, applying a five-point calibration using buffers at pH 1.679, 4.006, 6.865, 9.180, and 12.47 (standard DIN/NIST buffer solutions, WTW). pH was corrected for deuterium according to the common relationship of adding +0.4 units to the pH-meter reading D_2O.[1]

For the complexones NTA, EDTA, and EGTA, the effect of three different lanthanides was investigated. For EDTA and EGTA working solutions, to 2.5 mL of metal solution another 2.5 mL of ligand solution was added to yield 30 mM of ligand and 30 mM of metal, respectively. For NTA working solutions, to 1.25 mL of metal solution, 2.5 mL of NTA solution and 1.25 mL of D_2O were added to yield 30 mM of ligand and 15 mM of metal. The thus obtained 1:2 Ln(III)–NTA complex is more resistant to hydrolysis and Ln(III) hydroxide precipitation. All solutions were prepared in heavy water as deuterium source, pD was adjusted to 12.5 ± 0.1 using 12 M NaOD, and then shaken overhead for two months at room temperature. As proof-of-concept, we performed an exemplary experiment at increased reaction temperature. As anticipated, the reaction accelerates. Using Sm(III) and EGTA, compared to the 14% of unreacted aminoacetate methylene carbons after 8 weeks at room temperature (cf. Figure 2), at 70 °C in a continuously heated water bath a comparable conversion was achieved after 17 days (see Figure S1 and Table S1, below). Afterwards, the samples were centrifuged and the solutions separated from the precipitates. Then the reaction was quenched by acidification using 12 M DCl to reach pD 7 ± 2, and further acidified to pH 2 ± 0.5 then using 12 M HCl. At this low pH, the aminopolycarboxylates slowly crystallize in their zwitterionic forms (one deprotonated carboxylate per protonated amino group).[2] The crystals were separated from the mother liquor by filtration and dried on air.

For DTPA deuteration, only Lu(III) was used as catalyst. The procedure was modified regarding separation of the selectively deuterated ligand. This was necessary owing to the structural peculiarity of DTPA's central nitrogen bearing only one aminoacetate residue (instead of two), causing this nitrogen to be more basic and its singular aminoacetic acid residue (sites e+f in Figure S10) to be less acidic, apparently shifting the pH_{iso} to values where pH was high enough to complex Lu present in the reaction mixture, rendering crystallization of DTPA difficult as it required a higher pH in order to obtain the hardly soluble zwitterionic species. Consequently, before quenching the reaction, the pD was further increased to pD >13, causing Lu(III) to dissociate from the DTPA complex and to precipitate as $Lu(OD)_3$, which was removed from the suspension by centrifugation. The supernatant was then acidified following the procedure described above.

Details on further supporting experiments, such as reaction mixture intermediate sampling and spectroscopic analyses, as well as reference spectra (of, e.g., the non-deuterated ligands), are stated with the figures below.

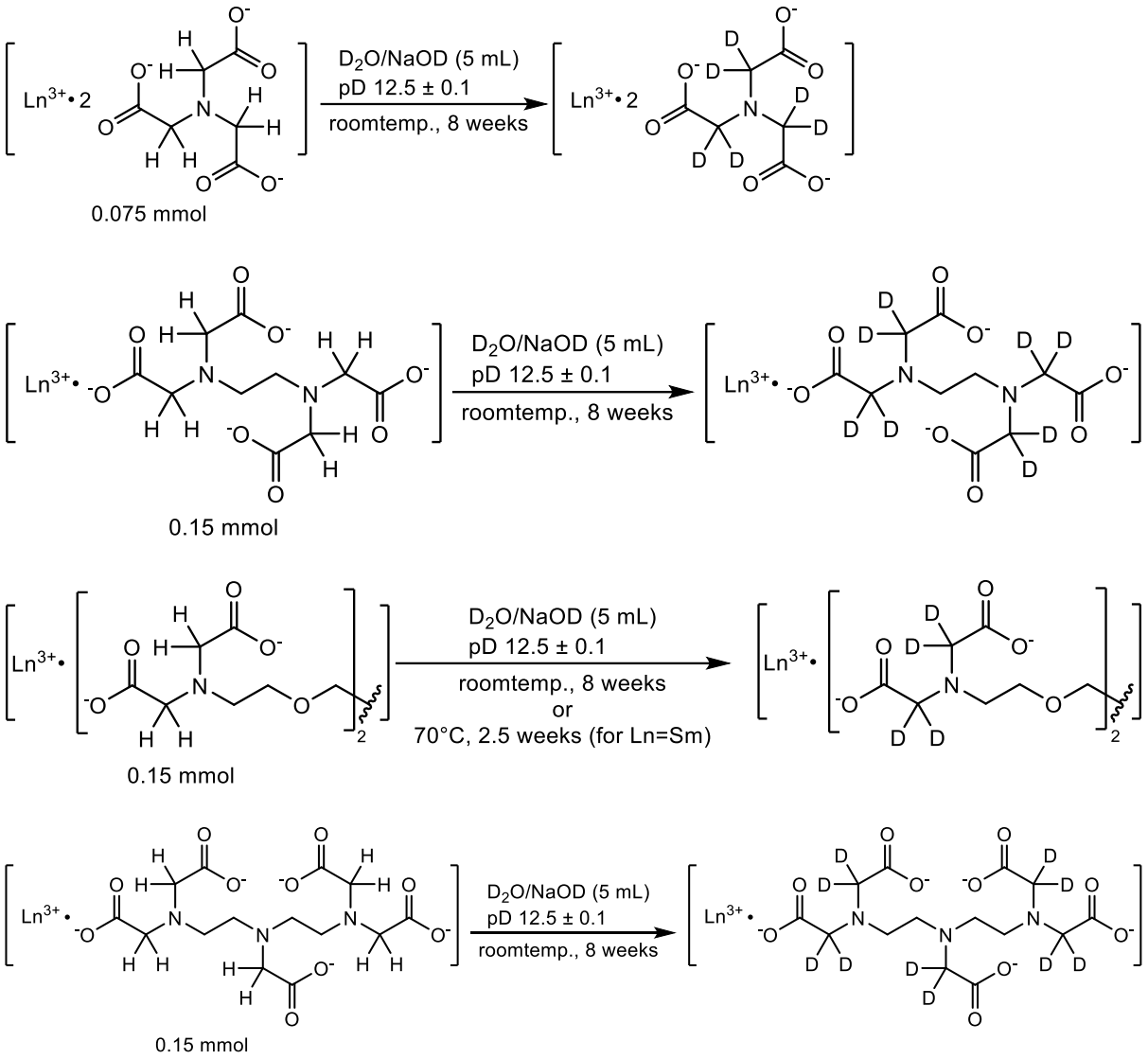


Figure S1. Schematic representation of the general experimental procedure.

Table S1. Ligands, lanthanide ions, their respective concentrations used in the experiments and the corresponding fractions of aminoacetate CH_2/CHD/CD_2 corresponding to 8 weeks of reaction time at room temperature.

Ligand	**Ln^{3+}**	**[Ligand] (mM)**	**[Ln^{3+}] (mM)**	**Fractions of CH_2/CHD/CD_2**
EGTA	La	30	30	45/23/32
	Sm	30	30	14/26/60*
	Lu	30	30	0/2/98
EDTA	Lu	30	30	0/10/90
DTPA	Lu	30	30	0/3/97

*Comparable yields were obtained after 17 days of reaction time at 70 °C.

Analytical methods

NMR spectroscopy

NMR spectra were obtained at (25 ± 0.2) °C with an Agilent DD2-600 system, operating at 14.1 T, with corresponding ^{1}H, ^{2}H, and ^{13}C resonance frequencies of 599.82, 92.07, and 150.81 MHz, using a 5 mm oneNMR™ probe. Chemical shifts are reported in parts per million relative to external TMS (^{1}H/^{13}C) and bulk water for ^{2}H. ^{1}H NMR spectra were obtained by accumulating a varying number of scans depending on concentrations of the individual samples, applying 2 s of acquisition time and relaxation delay, respectively, and a 2 s pre-saturation pulse on the HDO resonance for water signal suppression followed by a π/6 excitation pulse of 2.7 µs. ^{13}C spectra were obtained by accumulating at least 512 individual spectra upon applying 30 s relaxation delay after the 2.6 µs π/6 excitation pulse and 1 s acquisition time with inverse-gated ^{1}H decoupling. ^{2}H NMR spectra were acquired using the deuterium lock channel. Owing to the reduced power in the lock transmitter, the excitation pulse is 80 µs, and the center of the spectrum (tof/o1p) was opted as 3.25 ppm, being close to the aminoacetate CD_2 resonances, to ensure sufficient excitation. The relaxation delay was 10 s, and at least 64 scans were recorded. Prior to ^{2}H measurement, samples were manually shimmed (z1 – z3) detecting the ligands ^{1}H signals of the non-deuterated methylene groups.

Raman spectroscopy

To 3 mg of the original material (EGTA-d_0 and EGTA-d_8) 300 mg of desiccated potassium bromide (KBr, 99.99%, Sigma-Aldrich) were added, pulverized and mixed upon vigorous grinding in a ball mill, and then pressed by a hydraulic press under vacuum to yield the corresponding KBr disc. Raman spectra were acquired using a Raman microscope (LabRAM system, Horiba Jobin Yvon, Lyon, France), equipped with an external 473 nm laser (Cobolt Blues, 25 mW). The laser beam was coupled with an Olympus BX-40 microscope and directed through an objective with 10-fold magnification. Raman signals were guided through a 200 µm pinhole to a spectrometer with 300 lines per mm grating and 200 µm entrance slit width before eventually reaching a Peltier-cooled (−70 °C) CCD detector. Data acquisition was in the range 4475 – 200 cm^{-1}, with an exposition time of 10 s, 30 accumulations. Optional baseline correction was carried out with LabSpec 5 software (Horiba Jobin Yvon).

Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

The samples in D_2O were prepared by mixing the corresponding volumes of Eu(III) and EGTA-d_0/d_8 stock solutions in D_2O, followed by lyophilization to replace H by D as originating from $EuCl_3 \cdot 6H_2O$ as well as from the ligand's protonated functional groups, and humidity. The resulting solids were transferred to a glovebox under nitrogen atmosphere in sealed cuvettes, and re-dissolved in D_2O. Then each sample was measured seven times in total, spread over several days to overcome variability in external circumstances such as laser performance. In this time, the cuvettes remained sealed the whole time. Solutions were stirred in 10 mm path length Hellma Analytics 4 mL quartz cells. The cuvette was placed in a cuvette holder which was connected via a light guide to a spectrograph (Andor, Belfast, UK, SR-303i-A). For recording the spectra, an ICCD (Andor iStar, DH320T-18U-63) was used. The excitation wavelength (Ekspla, Vilnius, Lithuania, NT230, ∼5 ns pulse) was 394 nm (grating: 300 lines per mm). TRLFS data were analyzed using parallel factor analysis (PARAFAC), a state-of-the-art mathematical tool, which is a generalization of principle component analysis to higher order arrays, as described elsewhere.[3]

Quantum chemical calculations

Geometry optimizations of the 1:1 complexes of La^{3+} and Lu^{3+} with EDTA and EGTA, as well as the free ligands considered as fully deprotonated in their carboxyl and amino groups (L^{4-}), were performed using *Turbomole 7.3.1* at the Density Functional Theory (DFT) level.[4] Deprotonated ligand and complex species, respectively, obtained by removing a proton from an aminoacetate methylene group (L_{-H}^{5-}), were also optimized in the same way to evaluate deprotonation energies. The initial starting structures were based on available crystal structures.[5] Solvent effects were modeled using the COSMO approach with implicit water solvation (ε = 80.3).[6] Calculations employed the PBE0 hybrid functional with def2-SVP and def2-TZVPP basis sets, along with effective core potentials for La and Lu (La: ECP-46, Lu: ECP-28).[7–12] Dispersion interactions were accounted for using Grimme's DFT-D3 correction.[13] Numerical frequency analyses confirmed the absence of imaginary frequencies for def2-SVP-optimized structures, indicating successful convergence to local minima. These structures were subsequently re-optimized with the def2-TZVPP basis set. Single-point CCSD(T) calculations were carried out with *Orca 6.0* to refine the electronic energies.[14–17] Relativistic effects were included using the X2C method. CBS extrapolation was performed using X2C-SVPALL and X2C-TZVPALL basis sets to further enhance accuracy.[18] To correct for solvent and zero-point vibrational effects, additional DFT single-point calculations (PBE0/def2-TZVPP, CPCM solvent model) were conducted with *Orca 6.0*.[7–12,14–17,19] Gibbs free energies (G_{prot} and G_{deprot}) were obtained by combining CCSD(T) electronic energies with DFT-derived vibrational and solvation corrections. Deprotonation free energies were calculated according to:

$$\Delta G_{deprot} = G_{deprot} + G_{H^+} - G_{prot} \quad (1)$$

$$G_{H^+} = G_{H^+}^{gas} + \Delta G_{H^+}^{aq} \quad (2)$$

The Gibbs free energy of the proton was computed as the sum of the standard gas-phase value ($G_{H^+}^{gas} = -6.28$ kcal/mol) and the widely adopted literature experimental solvation free energy ($\Delta G_{H^+}^{aq} = -265.9$ kcal/mol).[20]

Supplementary Results

Luminescence decay time measurements

In aqueous systems, non-radiative deactivation of Ln(III) and An(III) luminescence is primarily due to OH oscillators from coordinating water. OD oscillators instead have a much smaller oscillator strength considerably increasing the luminescence decay time, τ, from 111 ± 0.3[21] for $[Eu(H_2O)_9]^{3+}$ to 2630 µs[22] for $[Eu(D_2O)_9]^{3+}$. To study the contribution of the CH/CD oscillators to quenching processes, we performed TRLFS on the Eu(III) complexes of both EGTA-d_0 and EGTA-d_8, each in H_2O and D_2O, respectively. In the EGTA complex, eight of the nine coordinating water molecules are displaced by the octadentate ligand.[2] The results of seven independent measurements are summarized in Table S1.

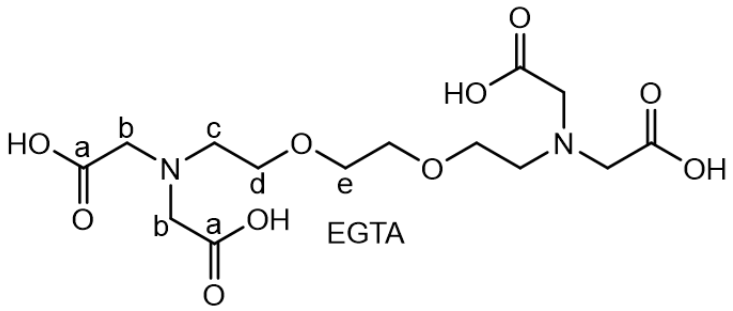
For $[Eu(EGTA\text{-}d_0)(H_2O)]^-$, τ matches the (586 ± 5) µs reported in the literature.[2] Replacing the aminoacetate CH_2 by CD_2 groups, $[Eu(EGTA\text{-}d_8)(H_2O)]^-$ exhibits a slightly but significantly higher τ. A somewhat larger effect occurs in D_2O solution.

Exchanging H_2O by D_2O as the one coordinating solvent molecule still causes the largest impact on the decay time. Notably, the organic ligand itself acts as a quencher as seen from the shortening of τ of $[Eu(D_2O)_9]^{3+}$, with the non-deuterated ligand causing a somewhat stronger response.

Table S2. Luminescence decay times in µs of the Eu(III) complexes using EGTA-d_0 and EGTA-d_8 as ligands (L) each in H_2O and D_2O, with solutions 100 µM in Eu(III) and 110 µM in the ligand, respectively.

Run	$[Eu(L\text{-}d_0)(H_2O)]^-$	$[Eu(L\text{-}d_8)(H_2O)]^-$	$[Eu(L\text{-}d_0)(D_2O)]^-$	$[Eu(L\text{-}d_8)(D_2O)]^-$
1	559	604	1943	2208
2	562	621	1902	2299
3	574	611	1989	2222
4	582	627	1953	2191
5	592	618	1933	2255
6	604	611	1912	2170
7	596	629	1917	2204
mean ± SD	581 ± 17	617 ± 9	1935 ± 30	2221 ± 43

EGTA



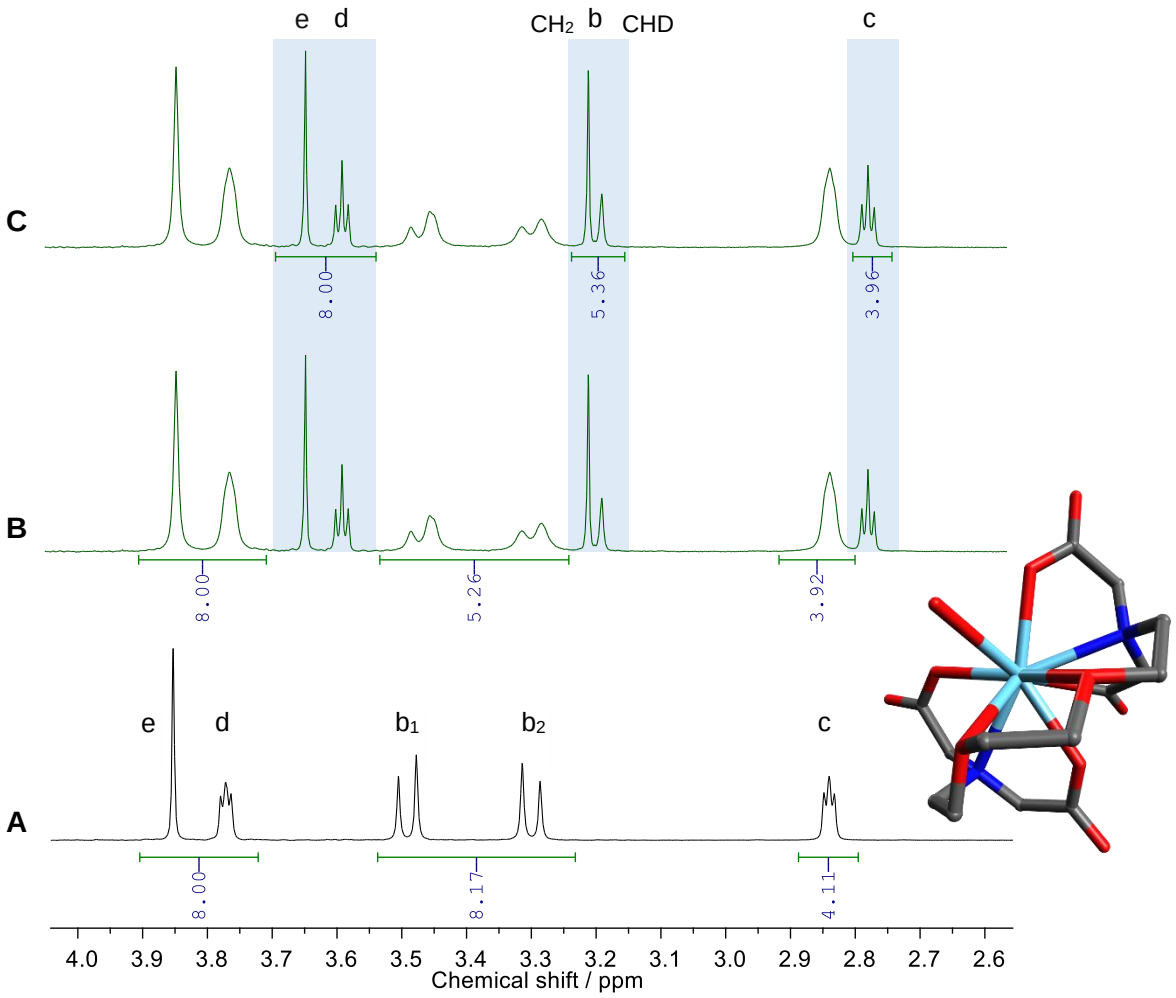


Figure S2. ^{1}H NMR spectra of D_2O solutions containing EGTA and La(III): (A) at pD 11, and (B+C) at pD 12.6. (A) represents $[La(EGTA)]^{-}$ before and (B+C) after incomplete H–D exchange at the aminoacetate methylene groups. At pD 12.6 some of the La(III) is removed from the solution due to hydrolysis, thereby releasing ligand (highlighted in blue). The degree of deuteration is reflected in both the free and the La(III)-bound ligand, viz. integral of 5.3 instead of 8 according to the four aminoacetate methylene groups.

Note that La(III) prefers a coordination number of 9, rendering one water molecule present in the first coordination sphere. Associated with that, owing to conformational change (intramolecular reorientation) being fast on the NMR time scale (^{1}H, 600 MHz, 25 °C), the four aminoacetate residues (as well as all other hydrogens within one methylene group (c, d, and e, except b) become indistinctive. The diastereotopicity of the aminoacetate hydrogens (b_1/b_2) is evident, revealing a *geminal* coupling $|^{2}J|$ of ~16 Hz.

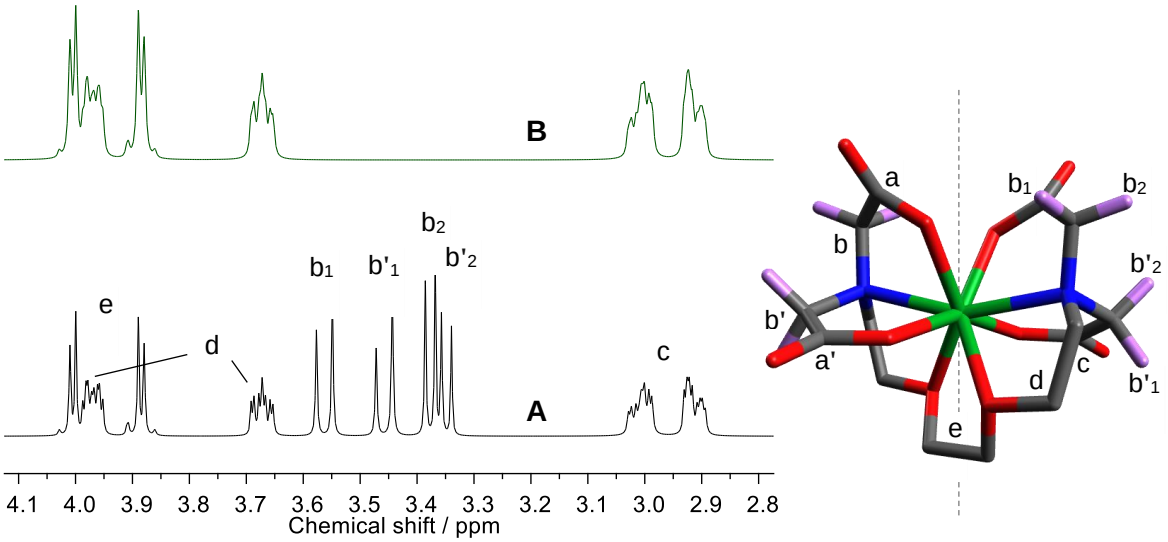


Figure S3. ^{1}H NMR spectra of the [Lu(EGTA)]$^{-}$ complex in D_2O: (A) before and (B) after H–D exchange at the aminoacetate methylene groups (corresponding to Figure 5B), along with signal assignment. Owing to the C_2 symmetry (C_2 rotational axis indicated by the grey line), the four aminoacetate residues (a+b and a'+b') are pairwise equivalent, each bearing two (spectroscopically distinct) diastereotopic hydrogens, hence denoted b_1/b_2 and b'_1/b'_2 (showing *geminal* coupling $|^2J|$ of ~17 Hz). Conformational change (intramolecular reorientation) is slow on the NMR time scale (^{1}H, 600 MHz, 25 °C).

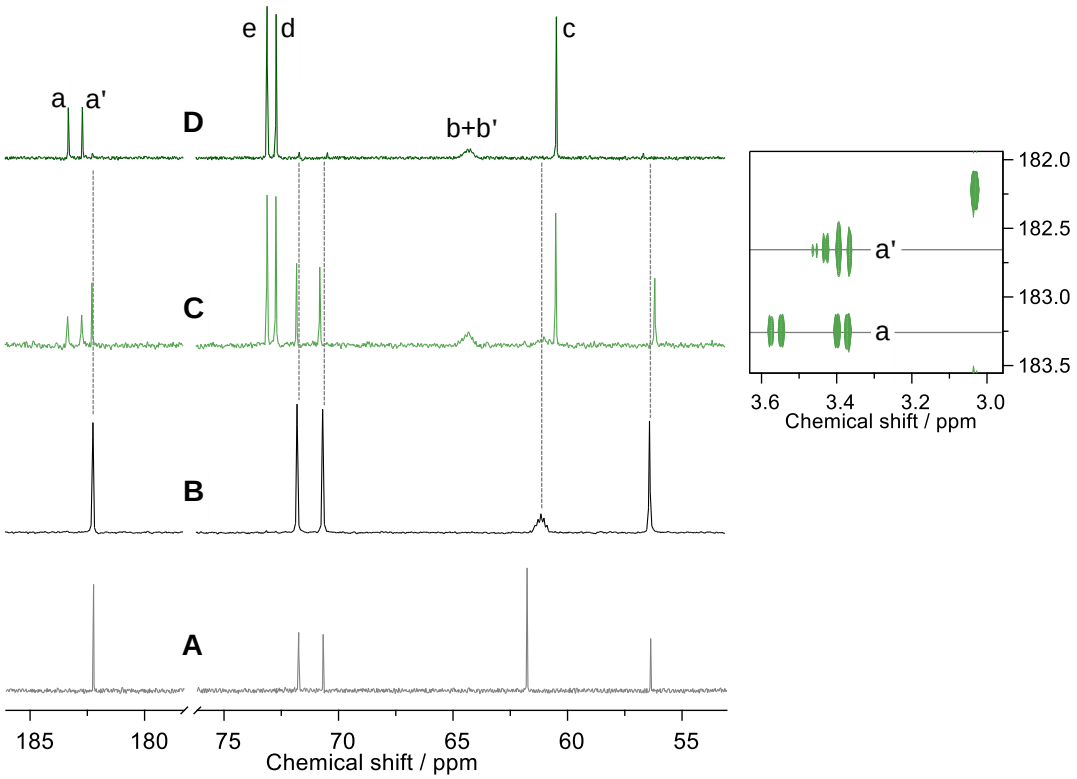


Figure S4. ^{13}C NMR spectra of D_2O pD 12 solutions of EGTA-d_0 (A) as well as EGTA-d_8 in absence (B) and in presence of 0.67 (C) and 0.99 equivalents (D) of Lu(III). The H,C-HMBC spectrum corresponding to (C) shows the carboxyl carbon signals, where a and a' refer to the two distinct aminoacetate residues in [Lu(EGTA)]$^{-}$. All complex-associated signals are downfield from their free-ligand counterparts. The aminoacetate methylene carbon signals are also distinct but cannot be resolved owing to the high multiplicity, and show an isotopic upfield shift of ~ 0.66 ppm, cf. singlet in (A) *vs*. quintet in (B).

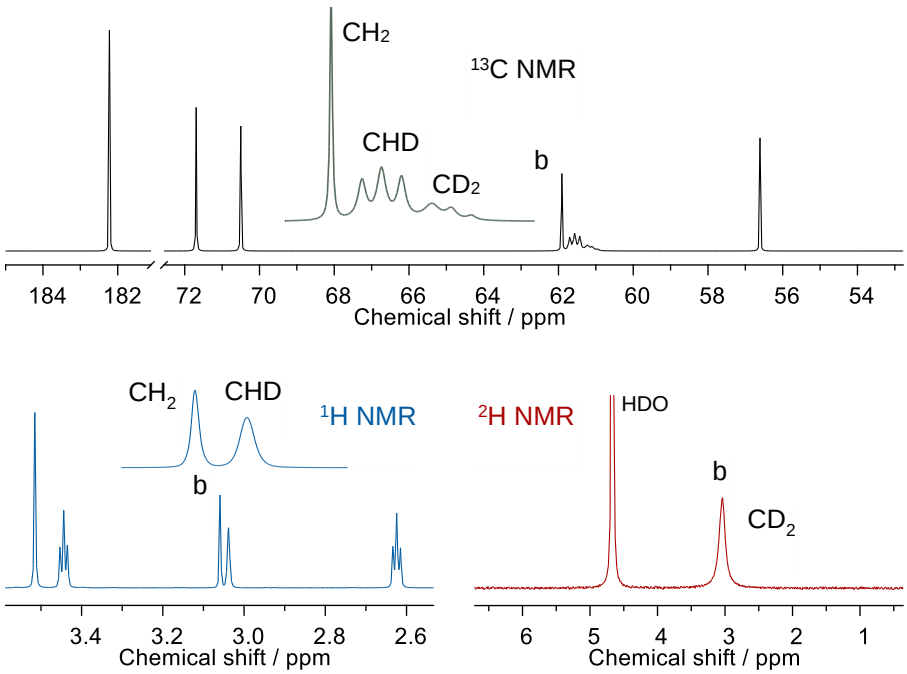


Figure S5. The reaction mixture of EGTA and Lu(III) was sampled after two weeks. To the taken aliquot NaOD was added in order to remove the metal upon precipitation as hydroxide. After centrifugation and discarding the precipitate, the clear supernatant was lyophilized and re-dissolved in 0.1 M NaOH in H_2O. ^{1}H and ^{13}C NMR spectra exhibit the aminoacetate methylene groups' distinct isotopomers: not yet deuterated CH_2, singly deuterated CHD, and doubly deuterated CD_2. In the ^{13}C spectrum, the latter two feature the distinct ^{2}H characteristics: spin coupling patterns of a triplet and quintet to one and two spin-1 nuclei with $^{1}J_{C,D}$ of ~22 Hz, respectively, along with an isotopic upfield-shift of ~ 0.33 ppm per ^{2}H replacing ^{1}H. In the ^{2}H NMR spectrum, owing to the linewidth of 10 Hz, individual signals of the CHD and CD_2 groups cannot be resolved, and neither can the geminal coupling $^{2}J_{H,D}$ that is expected to be of the order of 2–3 Hz. Correspondingly, the CHD's ^{1}H NMR signal is also broadened: 4.1 Hz instead of the CH_2's 2.1 Hz (without apodization). The isotopic shift is −0.02 ppm.

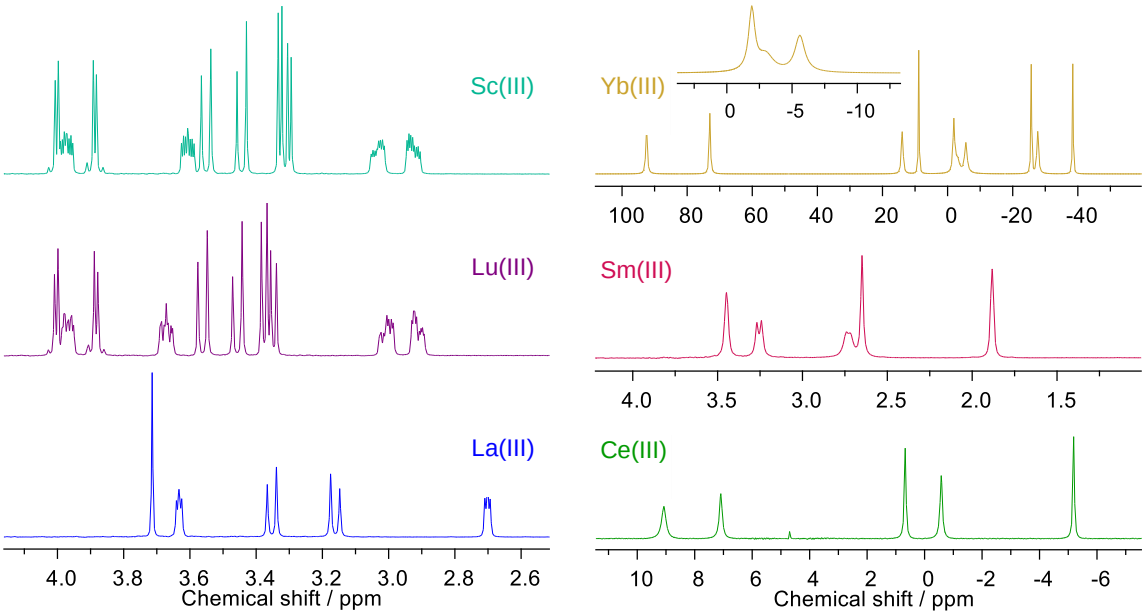


Figure S6. ^{1}H NMR spectra of EGTA complexes of different trivalent metal ions in D_2O at pD 9, where La(III), Sm(III), and Lu(III) are subject of the deuteration reaction, while the others were used as reference spectra for outlining the changes in symmetry and dynamics encountered from spectra of the La(III) and Lu(III) complexes.[23] Ions with small radii, corresponding to 8-fold coordination by all of EGTA's binding sites, reveal 10 signals in total. That is, Sc(III), Yb(III), and Lu(III). By contrast, spectra of complexes with ions of larger radius and preferred coordination number of 9[24] reveal only 5 signals upon easily facilitated intramolecular reorientation of the ligand, averaging otherwise distinct sites. Note the spectral effects on the resonances for the paramagnetic ions on the right compared to those of the diamagnetic ions on the left.

EDTA

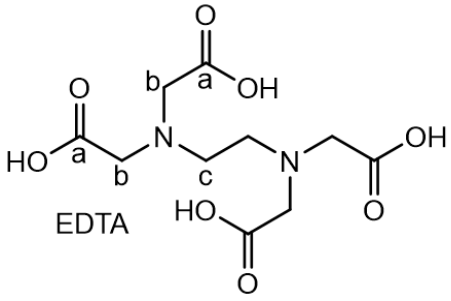


Figure S7. Generic structure of aminopolycarboxylate ligand EDTA along with atomic labeling for further assignment. Sites b refer to the aminoacetate methylene groups.

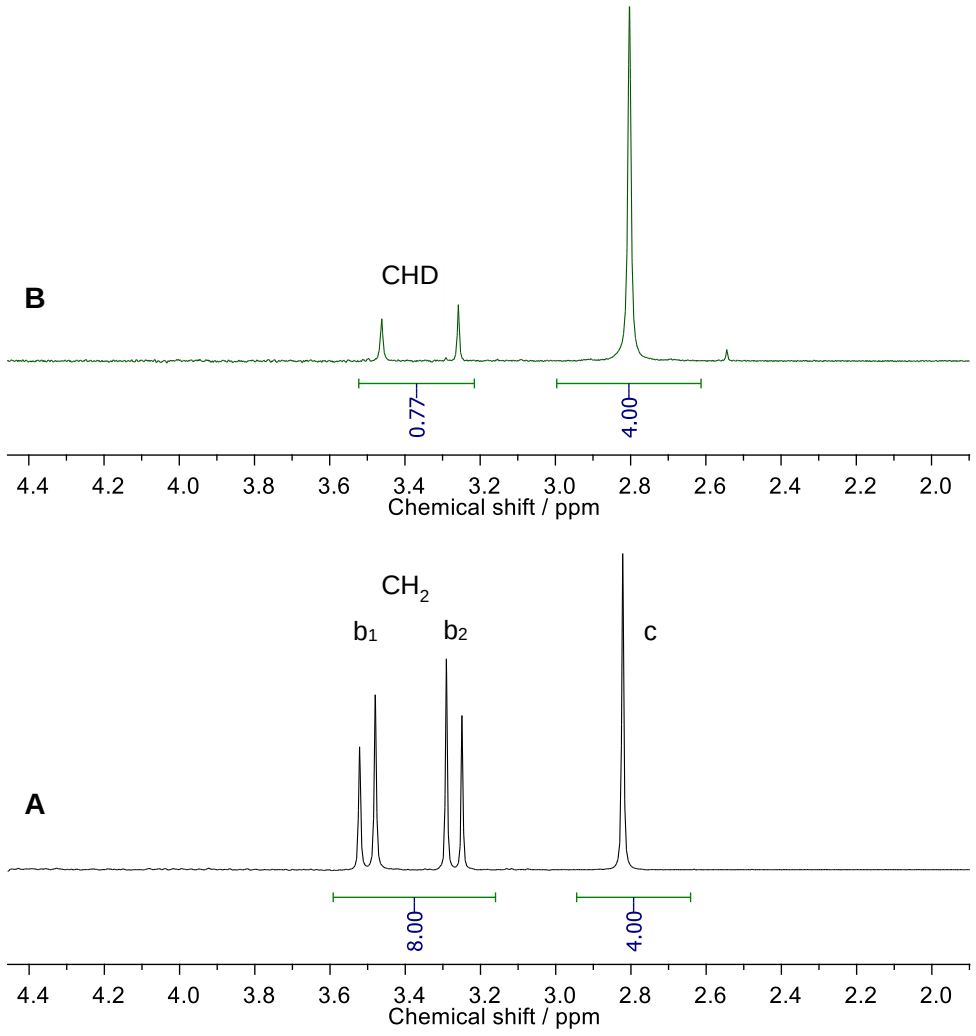


Figure S8. ^{1}H NMR spectra (D_2O, pD 10) of the Lu(III) complexes of non-deuterated EDTA (A) and after deuteration of EDTA's aminoacetate methylene groups (signals b). A remainder of 0.77 H instead of 8 corresponds to a deuteration degree of >90% in these sites: the ligand can thus be considered as EDTA-d_7.

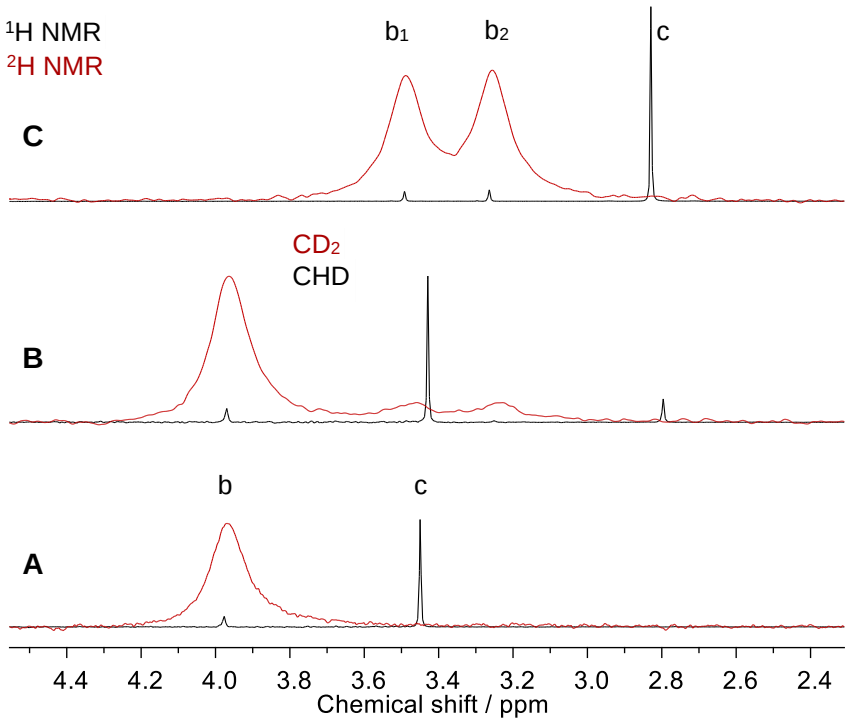


Figure S9. Deuterated EDTA (-d_7) in absence (A) and in presence of Lu(III) (B+C): ^{1}H NMR (black spectra) in D_2O and ^{2}H NMR (red spectra) in H_2O. The pH/pD values were ~1.5 in (A) and (B), and 7.3 in (C). Spectra of free and Lu(III)-bound EDTA-d_7 are represented by (A) and (C), respectively. (B) is a combination of free and (a small fraction of) Lu(III)-bound ligand, depicting the commencing complexation. The ethylene diamine signals (c) are not deuterated, showing no corresponding ^{2}H signal.

DTPA

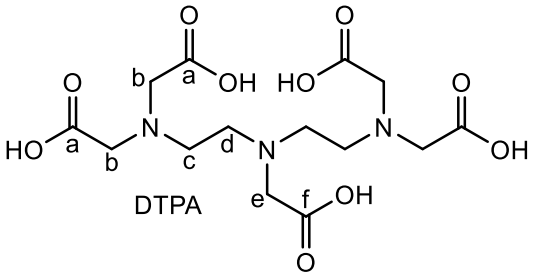


Figure S10. Generic structure of aminopolycarboxylate ligand DTPA along with atomic labeling for further assignment. Sites b and e refer to the aminoacetate methylene groups.

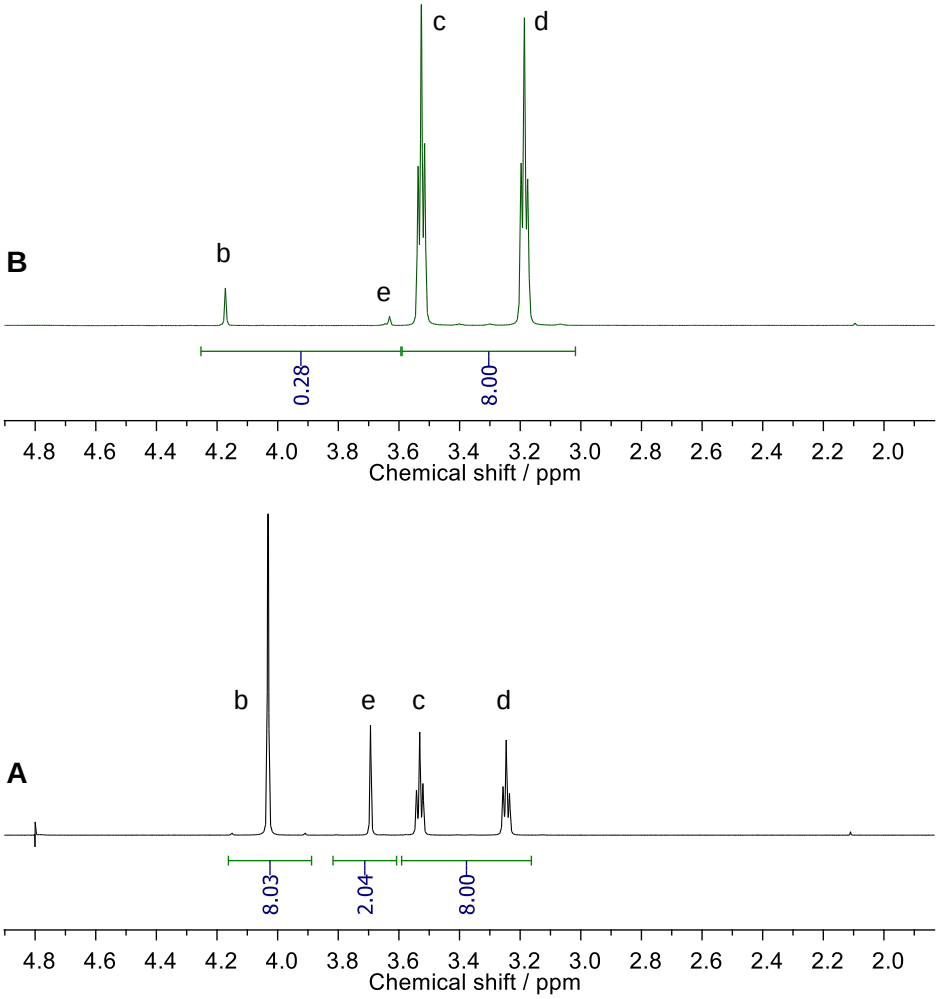


Figure S11. ^{1}H NMR spectrum of non-deuterated DTPA (A) and after deuteration of DTPA's aminoacetate methylene groups (b and e). A remainder of 0.28 H instead of 10 corresponds to a deuteration degree of >97% in these sites. Note the slightly different pD values (around 2) of the D_2O solutions.

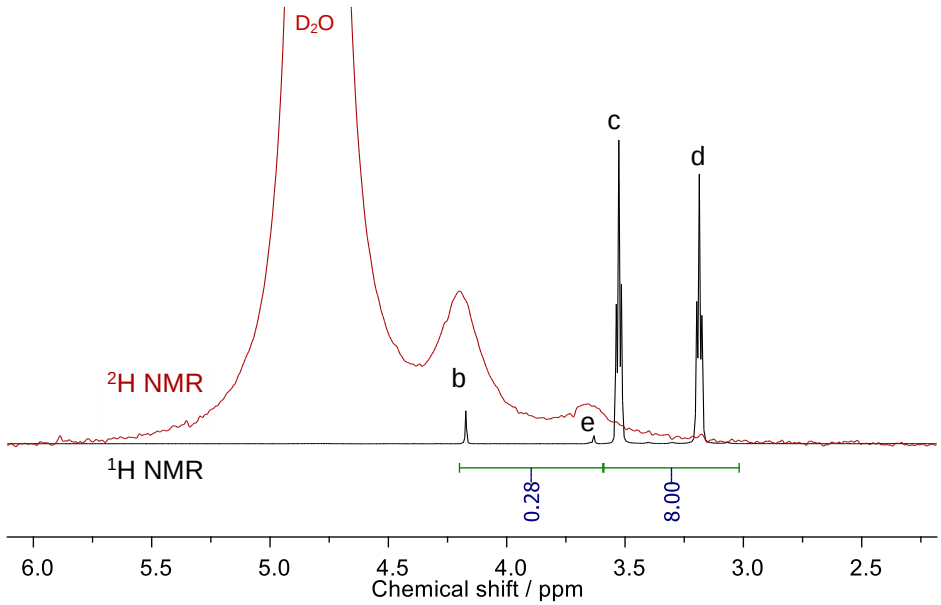


Figure S12. NMR spectra of deuterated DTPA in D_2O solution (pD ~2) along with signal assignment. The ^1H spectrum in black was acquired applying solvent signal suppression and shows signal integrals. The ^2H spectrum in red reveals only 2 DTPA signals, which are associated with the aminoacetate CD_2 groups.

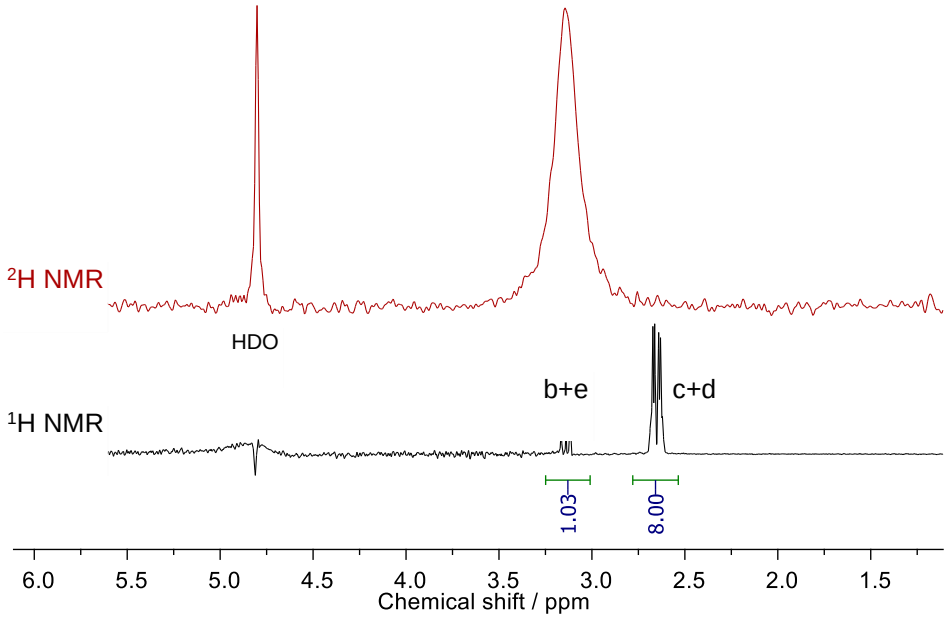


Figure S13. NMR spectra of deuterated DTPA in H_2O solution (pH = 11.4) along with signal assignment. The ^1H spectrum in black was acquired applying solvent signal suppression and shows signal integrals. The ^2H spectrum in red reveals only one DTPA-associated feature of two overlapping signals (barely distinct in the much better resolved ^1H spectrum), which are associated with the aminoacetate CD_2 groups.

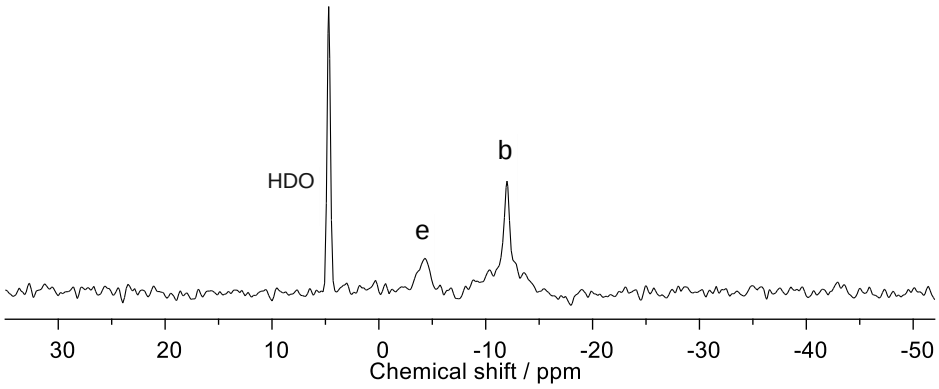


Figure S14. ^{2}H NMR spectrum of a solution 10 mM in each DTPA-d_{10} and Eu(III) in H_2O at pH = 6.5, proving the detectability of the ^{2}H signals associated with the aminoacetate CD_2 groups in $[Eu(DTPA\text{-}d_{10})]^{2-}$. The signals are shifted upfield to δ_H −4.3 and −12.0 ppm owing to pseudocontact hyperfine interaction between the ^{2}H nuclei and the paramagnetic Eu(III)'s six 4*f* electrons.

NTA

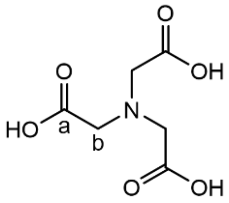


Figure S15. Generic structure of aminopolycarboxylate ligand NTA along with atomic labeling for further assignment. Sites b refer to the aminoacetate methylene groups.

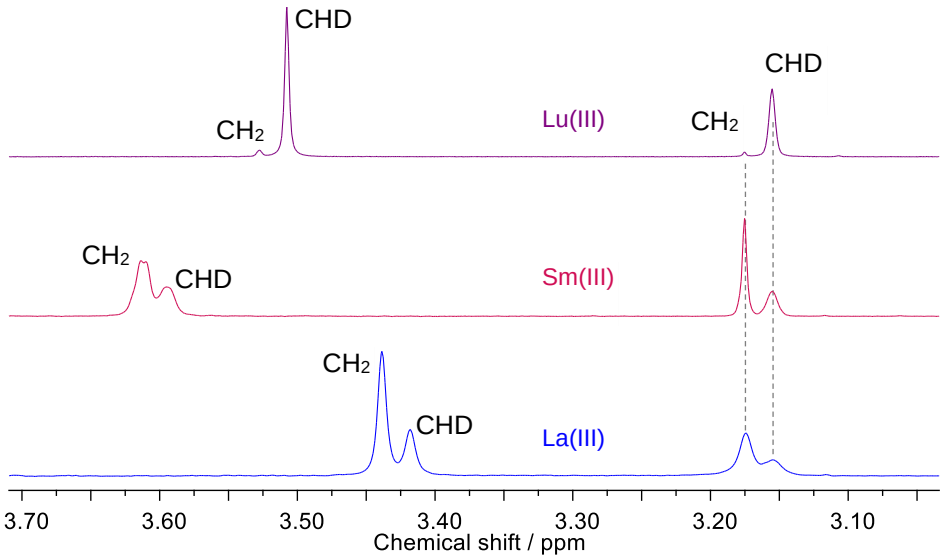


Figure S16. ^{1}H NMR spectra of NTA after treatment with D_2O/NaOD at pD 12.5 in presence of different Ln(III). Initially prepared with a given Ln(III):NTA molar ratio of 1:2, due to hydrolysis at pD 12.5 some of the Ln(III) is removed from the solution eventually shifting the equilibrium to a threefold excess in NTA. That is, two NTA equivalents are Ln(III) bound (with δ_H depending on the metal ion) and one equivalent unbound in solution (δ_H 3.175 and 3.155 ppm, corresponding to signals associated with CH_2 and CHD, and an isotopic shift of −0.02 ppm). Considering the two number of hydrogens contributing to the signals of the CH_2 and CHD groups, the ratio of CH_2:CHD groups amounts to 33:67, 35:65, and 2:98 in case of La(III), Sm(III), and Lu(III), respectively. The broadening of the lines (apart from Sm(III)'s small paramagnetic effects), most prominent for the La(III) solution, is caused by ligand exchange between free and bound ligand (see EXSY spectra below), interestingly without provoking quantitative precipitation upon hydrolysis, indicating an associative ligand substitution mechanism.

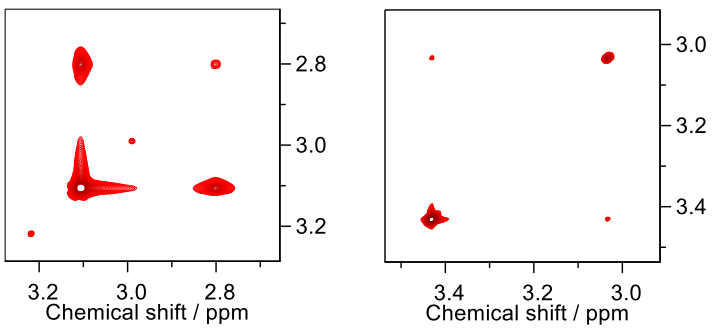


Figure S17. H,H-EXSY spectra (phase-sensitive NOESY, t_{mix} = 300 ms) NMR spectra obtained at 4 °C of pD 12.5 D_2O solutions of 1:3 Ln(III):NTA molar ratio, with that of La(III) shown left, and that of Lu(III) shown right. The smaller exchange rate of NTA bound to Lu(III) may contribute to the higher yield of H–D substitution.

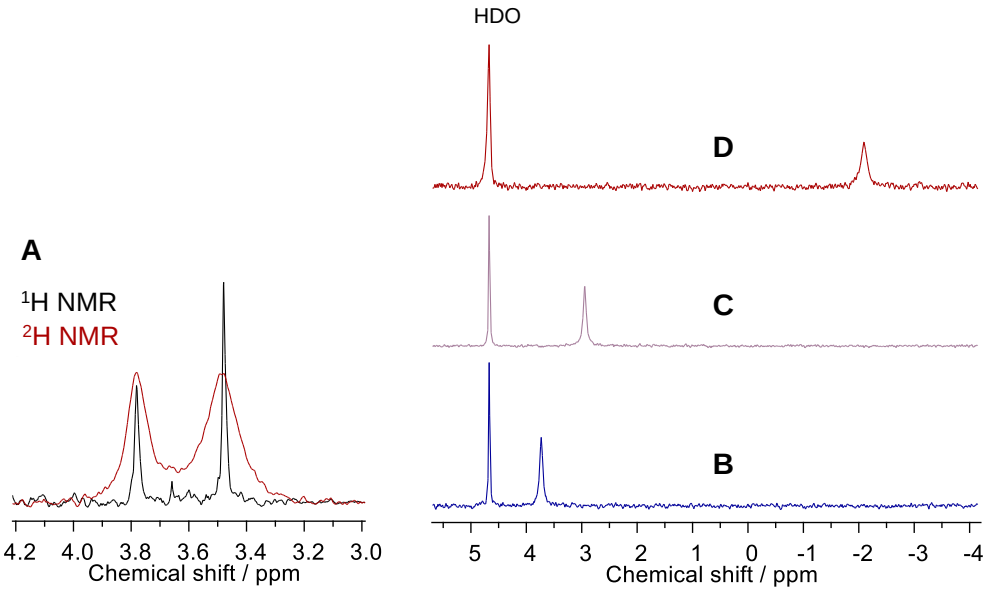


Figure S18. An aliquot of the reaction mixture of NTA and Lu(III) was acidified with DCl, lyophilized, and re-dissolved in Milli-Q H_2O (resulting pH 3), and subjected to ^{1}H and ^{2}H NMR with spectra depicted in (A) showing signals of free and Lu(III)-bound NTA, the latter of which giving rise to the downfield resonance. The ^{1}H NMR signals refer only to CHD groups (cf. Figure S16). Taking also into account the poor signal-to-noise ratio, conversion of NTA is almost complete. Signals of the ^{2}H NMR spectrum are due to CHD and CD_2 groups. The ligand is thus be assumed to be NTA-d_5. After its crystallization at pH ~1, the crystals were re-dissolved in H_2O and 2H NMR soectra were recorded at pH 2 (B) and pH 10 (C). (D) depicts the ^{2}H NMR spectrum associated with $[Eu(NTA\text{-}d_5)_2]^{3-}$ (at pH 10) with the upfield shift caused by pseudocontact hyperfine interaction between the ^{2}H nuclei and the paramagnetic Eu(III)'s six 4*f* electrons.

XYZ files of calculated structures

EDTA

C	-0.2542698	1.6225575	0.1901477
C	0.0523695	0.7603772	1.4002936
N	-1.4516363	2.4367817	0.3413892
H	0.6193150	2.2627216	-0.0391148
H	-0.3856876	0.9657272	-0.6711965
H	-0.8811212	0.3120246	1.7439804
H	0.4120809	1.4001375	2.2290023
N	1.0086971	-0.3040049	1.1316150
C	1.1414764	-1.1199759	2.3213395
C	2.2993137	0.2018601	0.7104962
C	-1.3506940	3.3749890	1.4407380
C	-1.7003287	3.1320877	-0.9049896
H	0.1397001	-1.3512900	2.6966773
H	1.6462481	-0.5774551	3.1419737
C	1.8548269	-2.4715176	2.1723201
O	2.0153737	-3.0897674	3.2549677
O	2.2013769	-2.8673245	1.0416247
H	3.0447312	-0.5702361	0.9140705
H	2.5932750	1.0899139	1.2960537
C	2.5021836	0.5305930	-0.7752528
O	1.7536629	0.0198815	-1.6305250
O	3.4916155	1.2724598	-1.0109433
H	-2.0570984	4.1870361	1.2544243
H	-0.3469846	3.8312253	1.4887947
C	-1.7118606	2.8853259	2.8501289
O	-1.2843217	3.6201131	3.7786963
O	-2.4261894	1.8741571	2.9908707
H	-1.6148039	2.4132694	-1.7259704
H	-0.9360407	3.9048488	-1.1083860
C	-3.0714330	3.8018570	-1.0763105
O	-3.9489400	3.6480279	-0.2037721
O	-3.1917068	4.4609986	-2.1399933

EDTA carbanion

C	-0.3072801	1.6154615	0.1945233
C	0.0132510	0.7524849	1.4025868
N	-1.4831034	2.4465854	0.3402133
H	0.5789297	2.2434665	-0.0415024
H	-0.4518144	0.9712008	-0.6747382
H	-0.9112138	0.2875221	1.7507249
H	0.3667572	1.3947915	2.2323371
N	0.9883399	-0.2985513	1.1382919
C	1.1585368	-1.0854373	2.3415426
C	2.2585599	0.2290683	0.6849783
C	-1.3943593	3.3323830	1.4844640
C	-1.6996314	3.1793438	-0.8921474
H	0.1678408	-1.3411107	2.7314320
H	1.6517048	-0.5101254	3.1472833
C	1.9144432	-2.4157760	2.2153102
O	2.1348380	-2.9891553	3.3126843
O	2.2339142	-2.8421367	1.0878096
H	3.0326608	-0.5063291	0.9181316
H	2.5254934	1.1538311	1.2239403
C	2.4391828	0.4902954	-0.8165885
O	1.7281738	-0.1185133	-1.6387078
O	3.3796935	1.2788485	-1.0993111
H	-2.1586887	4.1012377	1.3367527
H	-0.4161187	3.8497483	1.5213513
C	-1.6896641	2.7849860	2.8874470
O	-1.1505187	3.4166720	3.8363844
O	-2.4843907	1.8306008	3.0212676
H	-0.8006732	3.6982256	-1.2624145
C	-2.9155223	3.8837661	-1.1065817
O	-3.9618365	3.6366826	-0.3968348
O	-2.9695648	4.7740729	-2.0515102

EGTA

C	-1.6663080	3.9906337	0.2440403
C	3.1595956	-0.5254562	1.2846910
N	-2.7995803	4.8786984	0.4197272
N	3.7852964	-1.8118754	1.5445049
C	2.9750463	-2.6926323	2.3537158
C	5.1393967	-1.7085830	2.0421580
C	-2.5502476	6.2023674	-0.1149223
C	-3.9677505	4.2830014	-0.1977177
H	2.7262659	-2.2834608	3.3460313
H	3.5557909	-3.6005418	2.5513172
C	1.6603041	-3.1778547	1.7196453
O	0.8433429	-3.6811876	2.5296081
O	1.5076359	-3.0817747	0.4848786
H	5.5217682	-2.7247705	2.1940457
H	5.2121023	-1.2156920	3.0241735
C	6.1533166	-1.0267067	1.1088760
O	7.1872358	-0.5970568	1.6761977
O	5.9161991	-0.9871374	-0.1163110
H	-3.5155958	6.6764007	-0.3036980
H	-2.0261945	6.1530160	-1.0848829
C	-1.8032062	7.2067117	0.7736767
O	-1.7290081	7.0075344	2.0012221
O	-1.3570663	8.2096656	0.1586011
H	-4.0474063	3.2441304	0.1386865
H	-3.8769564	4.2351174	-1.2977793
C	-5.3257558	4.9286111	0.1159705
O	-5.4031042	5.7953235	1.0088539
O	-6.2779905	4.4852362	-0.5734421
C	-0.4142910	4.4158610	0.9802377
H	-1.4118305	3.8674279	-0.8266382
H	-1.9455175	3.0011496	0.6177823
H	-0.6380622	4.6116732	2.0348645
H	0.0051271	5.3385271	0.5587703
O	0.5188752	3.3635129	0.8493807
C	3.0774435	0.4182625	2.4859204
H	2.1452234	-0.7120307	0.9258429
H	3.7112814	-0.0476364	0.4730817
H	2.6964192	-0.1140481	3.3597782
O	2.1838791	1.4961819	2.2780098
H	4.0695988	0.8123332	2.7442418
C	1.7629256	3.6741349	1.4294636
C	2.6607721	2.4708786	1.3779189
H	1.6293136	3.9866129	2.4745909
H	2.2411282	4.5031585	0.8888545
H	3.6787248	2.7777598	1.6563258
H	2.6936129	2.0838634	0.3521858

EGTA carbanion

C	0.0533713	2.9978150	-0.6702680
C	-0.2740768	-3.3997429	0.0389673
N	-0.3204855	4.3572063	-0.3658075
N	-0.5698571	-4.8151843	-0.1072217
C	-1.3472268	-5.3662287	0.9803798
C	0.5909557	-5.6224159	-0.4082158
C	0.8135173	5.2615117	-0.3990821
C	-1.3625046	4.7789974	-1.2840413
H	-0.8431557	-5.3136220	1.9583589
H	-1.4893098	-6.4351032	0.7852801
C	-2.7638870	-4.7987652	1.1677803
O	-3.2987128	-5.0835598	2.2676847
O	-3.2912047	-4.1522245	0.2395767
H	0.2761160	-6.6712836	-0.4326731
H	1.3777376	-5.5730057	0.3615686
C	1.2713727	-5.3722096	-1.7643114
O	2.3901170	-5.9281818	-1.8931140
O	0.6830244	-4.6944555	-2.6312227
H	0.3970592	6.2732589	-0.3732878
H	1.3740953	5.1655415	-1.3487974
C	1.8279106	5.2370144	0.7521162
O	1.4429700	4.9274985	1.8995702
O	2.9939408	5.6097973	0.4527415
H	-1.0961729	4.6311243	-2.3436168
C	-2.0884227	5.9781050	-1.0323707
O	-2.0996150	6.5143188	0.1373590
O	-2.7661845	6.5145979	-1.9998589
C	1.0428410	2.3509002	0.2782267
H	0.4681295	2.9134635	-1.6990398
H	-0.8618013	2.3980982	-0.6612410
H	0.7488925	2.5225363	1.3196096
H	2.0526480	2.7640043	0.1526061
O	1.0592082	0.9648806	-0.0119723
C	0.5444680	-3.0083060	1.2694900
H	-1.2209666	-2.8573073	0.0745842
H	0.2490985	-3.0827235	-0.8643457
H	-0.0036190	-3.2431085	2.1843218
O	0.7880105	-1.6137135	1.3113030
H	1.4968844	-3.5523817	1.3071738
C	2.0723828	0.2822271	0.6846627
C	1.8877378	-1.2009438	0.5313227
H	2.0453918	0.5406049	1.7526055
H	3.0613697	0.5656565	0.2972411
H	2.8008587	-1.7109642	0.8685179
H	1.7396894	-1.4424731	-0.5286244

$[La(EDTA)(H_2O)_3]^-$

C	4.2256112	2.5833988	7.6590300
C	2.7925704	2.0889085	7.8446482
H	2.8083082	1.1709755	8.4415074
H	2.3124937	2.8506470	8.4629550
C	0.6215344	2.3051327	6.7971115
H	0.5809520	3.2071428	7.4125379
H	0.0496539	1.5315274	7.3220115
C	-0.0950040	2.6624315	5.4955490
C	2.0793393	0.5429853	6.1135234
H	1.3759995	0.4598012	5.2808826
H	1.7308370	-0.1496444	6.8918212
C	3.4592178	0.1158939	5.6649980
H	4.1834159	0.3175972	6.4544170
H	3.4629266	-0.9703902	5.5142660
C	5.3576846	0.8309671	4.3466241
H	5.7478433	-0.1344974	4.0081010
H	5.7644161	1.0244420	5.3422694
C	5.9313731	1.9480632	3.4735059
C	3.3068126	0.1897707	3.2561317
H	2.3232869	-0.2093824	3.5170231
H	3.9147400	-0.6559587	2.9193380
C	3.0392778	1.1270633	2.0779766
N	2.0206235	1.9257702	6.6123425
N	3.8963097	0.8149262	4.4452560
O	4.5027803	3.1434918	6.5502405
O	4.9981449	2.4612997	8.6108355
O	-1.3278547	2.6298630	5.4900529
O	0.6412503	3.0276370	4.5259432
O	5.2915098	3.0434285	3.4674735
O	7.0038018	1.7378196	2.8982335
O	2.6739333	2.3081621	2.3699507
O	3.1183531	0.6615260	0.9386458
O	4.7446766	5.4681330	5.0659763
O	1.9596350	5.3830777	5.8946469
O	2.6462382	5.0881061	2.5391583
La	3.0817543	3.4233588	4.5375708
H	5.4507965	5.4636630	4.4121279
H	1.0318703	5.6237251	5.8325284
H	5.1323373	5.0473493	5.8460022
H	2.4752063	4.4767092	1.8124887
H	2.0046399	5.7969056	2.4483428
H	2.4338835	6.2075328	6.0346548

$[La(EDTA)(H_2O)_3]^-$ carbanion

C	4.1708750	2.6710486	7.7691542
C	2.7468032	2.1393126	7.8951661
H	2.7519003	1.2417400	8.5227277
H	2.2142540	2.9104906	8.4574041
C	0.6306429	2.2357931	6.7316733
H	0.5198358	3.1599484	7.3049382
H	0.0651304	1.4592327	7.2601276
C	-0.0315476	2.5075526	5.3810025
C	2.2019023	0.5205347	6.1765957
H	1.4315017	0.3329970	5.4269013
H	1.9960843	-0.1640959	7.0112825
C	3.5667202	0.2008545	5.5992216
H	4.3546498	0.5040594	6.2895194
H	3.6488950	-0.8901884	5.4879598
C	5.2451128	0.8377411	3.9739300
H	5.6802770	-0.1517419	3.8421862
C	5.9790729	1.9696654	3.6404910
C	3.0388812	0.2854147	3.2437645
H	2.0083024	0.1094914	3.5747073
H	3.4521867	-0.6814311	2.9358839
C	2.9181059	1.1989560	2.0305377
N	2.0508926	1.9131953	6.6294854
N	3.8401361	0.8725783	4.3194238
O	4.4610867	3.2745148	6.6926352
O	4.9210827	2.5338408	8.7416208
O	-1.2603719	2.3933253	5.3114664
O	0.7312348	2.8840552	4.4400688
O	5.3850756	3.1638880	3.7106704
O	7.1998278	1.9205753	3.2728077
O	2.8441502	2.4432440	2.2760244
O	2.8288380	0.6884061	0.9071104
O	5.0920319	5.3945497	4.9463056
O	1.9623223	5.4252439	5.8478866
O	2.6021752	5.0801831	2.5411727
La	3.1695638	3.4394951	4.5669240
H	5.5629406	4.6630104	4.4726624
H	1.0338193	5.6424184	5.7331283
H	5.2620347	5.1990836	5.8744174
H	2.5063356	4.3436882	1.9171975
H	1.8154473	5.6214584	2.4414333
H	2.3905510	6.2508106	6.0888145

$[Lu(EDTA)(H_2O)_2]^-$

Lu	3.7197867	7.4072850	9.2146215
O	2.8235382	9.3409710	8.5059920
O	2.8802074	11.0997299	7.1410927
O	4.9301402	8.1084760	10.9472539
O	6.3963375	9.5059706	11.8713429
O	3.9060887	6.8376793	7.0709907
O	4.8594680	5.6881723	5.4202828
O	3.5798513	5.3069606	9.9845809
O	4.5613288	3.5794428	10.9919282
O	2.2421709	7.8106070	11.0535517
O	1.4510482	6.8439678	8.6165518
N	5.4874005	9.0037638	8.4233726
N	5.8549714	6.1381391	8.8628711
C	6.6518348	8.2645027	7.9173321
H	7.5300486	8.9169085	7.8452531
H	6.4240144	7.9293154	6.9051614
C	6.9830872	7.0732552	8.7899914
H	7.8802476	6.5789485	8.3982240
H	7.2183970	7.3996645	9.8028209
C	5.9581111	5.2317936	10.0033116
H	6.2762312	5.8042448	10.8778854
H	6.6874715	4.4320632	9.8419404
C	4.5985967	4.6309071	10.3555562
C	5.7023373	5.3807730	7.6160078
H	5.2503679	4.4124091	7.8443613
H	6.6705838	5.1763207	7.1498237
C	4.7666962	6.0232310	6.6002515
C	4.8683864	9.8233525	7.3837803
H	4.8537721	9.2534868	6.4522757
H	5.4179362	10.7513860	7.1988619
C	3.4089672	10.1402630	7.6998008
C	5.8374860	9.8268897	9.5847671
H	5.1176958	10.6461664	9.6622044
H	6.8278152	10.2788114	9.4750217
C	5.7444522	9.0919705	10.9156755
H	2.5159211	8.4468937	11.7188144
H	1.3052082	7.9521954	10.8973335
H	1.0895704	7.4783628	7.9900291
H	1.3019664	5.9782194	8.2260920

$[Lu(EDTA)(H_2O)_2]^-$ carbanion

Lu	3.7335901	7.3494350	9.1729712
O	2.7739342	9.2878805	8.5379111
O	2.9369076	11.2558668	7.5136080
O	4.7724042	8.0568595	10.9637362
O	5.8849745	9.7204529	11.9839215
O	3.8982368	6.6880675	7.0277022
O	4.8472086	5.4705189	5.4236587
O	3.6020443	5.2710519	10.0298176
O	4.6188069	3.5886501	11.0771576
O	2.2234321	7.8693387	11.0705651
O	1.4855975	6.7481779	8.4427087
N	5.4608072	8.9306627	8.4404959
N	5.8642996	6.0793235	8.8378591
C	6.6027634	8.2087451	7.8545589
H	7.4697971	8.8733549	7.7522769
H	6.3358825	7.8669453	6.8511277
C	6.9711923	7.0392403	8.7358607
H	7.8815559	6.5516226	8.3653347
H	7.1710397	7.4238101	9.7368430
C	5.9813593	5.2225246	10.0126587
H	6.2897186	5.8406772	10.8590494
H	6.7217614	4.4260827	9.8848931
C	4.6339218	4.6202100	10.4041586
C	5.7220104	5.2796783	7.6198607
H	5.2970808	4.3065742	7.8798188
H	6.6916193	5.0854586	7.1509304
C	4.7648590	5.8634451	6.5878182
C	4.8281721	9.8069130	7.4616004
H	4.7368611	9.2814374	6.5039351
H	5.4109803	10.7182097	7.2900745
C	3.4110659	10.1770944	7.8767563
C	5.8212105	9.6624176	9.6349766
H	6.4972682	10.5044980	9.5037367
C	5.5171683	9.1752950	10.8972888
H	3.0853893	8.1512452	11.4555805
H	1.7321504	8.6794248	10.9073060
H	1.0124090	7.5703338	8.2770886
H	1.5914495	6.3478762	7.5729238

$[La(EGTA)(H_2O)]^-$

La	3.8636252	3.9272244	9.9881088
O	5.8995246	3.3263961	11.2148036
O	7.4322416	4.1169240	12.6273984
O	5.0067368	3.7508876	7.7549066
O	6.7830069	3.9538619	6.4241796
O	3.3336603	6.4658506	9.3674189
O	1.3733435	4.6726941	10.3474522
O	3.8201800	5.4247116	11.9655818
O	3.7386753	5.8509376	14.1504527
O	3.1648490	1.5743905	9.9617217
O	2.6957181	-0.3790294	10.9241102
O	2.3375187	3.5608652	7.7878708
H	1.9173299	2.6961367	7.7942840
H	3.0846131	3.4815568	7.1782234
N	6.0719511	5.4710552	9.5875963
N	2.7191347	2.9364207	12.2919425
C	6.7024727	5.5634978	10.8992672
H	6.1384597	6.2590494	11.5225303
H	7.7328374	5.9325660	10.8353187
C	6.6940406	4.2255575	11.6476824
C	6.9501490	4.7794946	8.6474342
H	7.4548862	3.9645933	9.1724349
H	7.7271269	5.4445026	8.2545570
C	6.1970269	4.1243666	7.4939733
C	5.6784937	6.7706612	9.0304756
H	5.5003248	6.6311899	7.9619028
H	6.4885916	7.5046569	9.1304105
C	4.4269799	7.3409647	9.6441161
H	4.5178694	7.4569998	10.7279489
H	4.2265821	8.3214066	9.2009722
C	2.1110956	6.9444351	9.9216294
H	1.8187779	7.8750093	9.4240523
H	2.2546170	7.1384658	10.9888805
C	1.0500706	5.9008766	9.6988006
H	0.0839124	6.2704985	10.0504946
H	0.9721578	5.6670963	8.6365091
C	0.8807946	4.5279023	11.6748415
H	-0.2108770	4.6003101	11.6631688
H	1.2695652	5.3237730	12.3149396
C	1.2713166	3.1548589	12.1633602
H	0.7705920	2.9689235	13.1230357
H	0.8849408	2.4268372	11.4467773
C	3.2787775	3.6383711	13.4430345
H	4.2291698	3.1666939	13.7044187
H	2.6289275	3.5715845	14.3229743
C	3.6264351	5.1011187	13.1767013
C	2.9918988	1.5031770	12.3401935
H	2.3302318	0.9748312	13.0357434
H	4.0171439	1.3564832	12.6898620
C	2.9247573	0.8306206	10.9688441

$[La(EGTA)(H_2O)]^-$ carbanion

La	3.8565451	3.9304497	10.0643416
O	5.9728003	3.3661913	11.2123461
O	7.5811558	4.1513698	12.5414776
O	4.9496118	3.7872357	7.7724906
O	6.6924819	3.9785332	6.3962118
O	3.3486953	6.5073819	9.3890676
O	1.3479324	4.7575985	10.3384238
O	3.8172526	5.4017199	12.0644014
O	3.7230388	5.6546266	14.2743730
O	3.2786594	1.6336859	9.8820260
O	3.0325187	-0.4058134	10.7886396
O	2.2659447	3.1299864	7.9399283
H	2.3755843	2.2953353	8.4407385
H	2.9911794	3.1285303	7.3031721
N	6.0817851	5.5084927	9.5745267
N	2.5611837	2.9138275	12.2238290
C	6.7450700	5.6044324	10.8674713
H	6.1812405	6.2824429	11.5113446
H	7.7653880	5.9981324	10.7812623
C	6.7850663	4.2631550	11.6052864
C	6.9242264	4.8095705	8.6104009
H	7.4412203	3.9932506	9.1210928
H	7.6929082	5.4676337	8.1888570
C	6.1312811	4.1540699	7.4818472
C	5.6838054	6.8102190	9.0328325
H	5.4832564	6.6806220	7.9670138
H	6.4971143	7.5428741	9.1227565
C	4.4439483	7.3724466	9.6748279
H	4.5479570	7.4633836	10.7607244
H	4.2420533	8.3647824	9.2586394
C	2.1221318	7.0070958	9.9070297
H	1.8566590	7.9412552	9.4003699
H	2.2357793	7.2020505	10.9784863
C	1.0607649	5.9713377	9.6578834
H	0.0821206	6.3546464	9.9587223
H	1.0264417	5.7227457	8.5952842
C	0.8401179	4.6645107	11.6664949
H	-0.2434742	4.8212273	11.6470484
H	1.2874983	5.4356256	12.2989171
C	1.1326172	3.2665134	12.1543141
H	0.6499681	3.1253913	13.1325598
H	0.6725817	2.5681223	11.4548832
C	3.2008047	3.5146075	13.3891660
H	4.1390170	2.9788182	13.5543185
H	2.5948626	3.3960042	14.2971786
C	3.5940216	4.9836382	13.2435274
C	2.7533794	1.4820842	12.1603116
H	2.3856962	0.8960438	13.0015380
C	3.0132375	0.8579056	10.9450560

[Lu(EGTA)]$^{-}$

Lu	2.7284610	6.1348844	1.2586139
C	5.7279305	6.9333246	1.3953116
C	3.8274017	4.0583912	-0.8184934
C	5.0479124	4.2046478	0.0839395
H	5.6158586	3.2696008	0.0984519
H	5.6767709	4.9533511	-0.4047989
C	0.5036327	7.9161710	2.8161597
H	-0.0519327	8.8211749	3.0922407
H	0.6614904	7.3368212	3.7280210
C	2.7320752	8.6244009	3.3492602
H	2.2819415	9.3232238	4.0616393
H	3.6123628	9.1079665	2.9201588
C	4.4298731	3.5515989	2.3430227
H	4.4041500	3.9495284	3.3572318
H	5.1999640	2.7727188	2.2932691
C	1.5771419	8.6991035	-0.1781332
C	0.7810004	3.5789405	1.9285537
H	0.5238546	2.7046389	2.5324150
H	0.6626341	3.3330260	0.8679738
C	3.2457140	7.3931000	4.0899941
C	3.0845569	2.9425229	2.0431816
H	3.0303176	2.5170705	1.0359006
H	2.8712903	2.1459193	2.7611902
C	5.8045303	5.5161539	1.9601807
H	6.7991666	5.0981689	1.7789911
H	5.6750631	5.6159444	3.0400294
C	-0.0867563	4.7387889	2.3157767
H	-1.1321172	4.5267104	2.0803204
H	0.0103542	4.9465393	3.3854935
C	1.7363674	9.2807095	1.2227572
H	2.6729344	9.8411949	1.1994593
H	0.9356015	10.0021885	1.4123362
C	-0.3205465	7.0889098	1.8605547
H	-1.2956391	6.8699826	2.2982015
H	-0.4844455	7.5972632	0.9110843
N	4.7357586	4.6670580	1.4392075
N	1.8225935	8.2615884	2.2660665
O	3.1666212	6.2889816	3.4560656
O	3.7276827	7.5393797	5.2119476
O	1.8825532	7.4698174	-0.3165084
O	1.2078676	9.4477077	-1.0826623
O	2.8216136	4.7801129	-0.5121883
O	3.9015083	3.3149381	-1.7955549
O	4.5834863	7.3007567	0.9560978
O	6.7328504	7.6382103	1.4299007
O	2.1195144	3.9777419	2.1805611
O	0.3610054	5.8650468	1.5616686

[Lu(EGTA)]$^{-}$ carbanion

Lu	2.7632784	6.2118756	1.2255361
C	5.8354155	6.8538660	1.3738312
C	3.8061996	4.0261513	-0.8076652
C	5.0395622	4.1584744	0.0811811
H	5.5919960	3.2130571	0.0912154
H	5.6745265	4.8941450	-0.4197972
C	0.5096437	7.8895787	2.8614226
H	-0.0464519	8.7843826	3.1724544
H	0.6816350	7.2777904	3.7532960
C	2.7372365	8.6457177	3.3183847
H	2.3023399	9.3510336	4.0374447
H	3.5861522	9.1427818	2.8433395
C	4.4237793	3.5337003	2.3448434
H	4.4052659	3.9413355	3.3555743
H	5.1786558	2.7380358	2.3034973
C	1.7523897	8.8025616	-0.1110972
C	0.7854729	3.5986621	1.9332614
H	0.5183520	2.7241357	2.5341004
H	0.6747768	3.3523602	0.8712599
C	3.2972826	7.4384421	4.0628269
C	3.0681821	2.9476239	2.0531080
H	3.0043676	2.5206520	1.0464325
H	2.8497003	2.1512010	2.7713225
C	5.8528255	5.4413292	1.9498730
H	6.8316325	4.9818674	1.7775740
H	5.7217017	5.5576831	3.0280202
C	-0.0812626	4.7614408	2.3093487
H	-1.1285555	4.5443965	2.0819174
H	0.0167774	4.9747550	3.3787453
C	1.6760473	9.2333269	1.2086740
H	1.3102342	10.2245343	1.4676170
C	-0.3078221	7.1048852	1.8699358
H	-1.3055851	6.8866170	2.2557530
H	-0.3942242	7.6639000	0.9383853
N	4.7535440	4.6331359	1.4349557
N	1.8033981	8.2656755	2.2676223
O	3.2464978	6.3291687	3.4371551
O	3.7932428	7.6007818	5.1814806
O	2.0375122	7.5160113	-0.3214126
O	1.5721720	9.5611661	-1.1198116
O	2.8152127	4.7619322	-0.5020824
O	3.8637655	3.2694511	-1.7796436
O	4.7128621	7.2644525	0.9320518
O	6.8754097	7.5136948	1.4015056
O	2.1200724	3.9924305	2.1960101
O	0.3611830	5.8772603	1.5469931

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