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Lanthanide complexes of aminopolycarboxylates reveal deuteration of aminoacetate carbons in alkaline aqueous media†

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Hydrogen isotope exchange at aminoacetate carbons is facilitated in lanthanide aminopolycarboxylate complexes in NaOD D_2O solution. Ionic radius-dependent yields revealed that Lu^{3+} is the choice. NMR and Raman spectroscopy evidence yields insights into selectivity, while theoretical calculations help in understanding the mechanism.

Since its discovery in 1931,[1] deuterium has become increasingly important for numerous research applications, not only in the form of deuterated solvents used in various spectroscopies,[2] but also as an isotopic label in *in situ* and *in vivo* reaction mechanistic studies or pharmacokinetic studies.[3] Since the strength of the C–D bond slows metabolism, D-containing drugs reveal longer biological half-lives, requiring lower pharmaceutical doses.[4] Spin-labeling has revolutionized NMR spectroscopy of proteins. In particular, deuteration enhances the signal-to-noise ratio by suppressing spin diffusion and improves resolution by narrowing the line widths upon reducing dipolar interactions and relaxation rates of ^{13}C and ^{15}N spins, thereby facilitating the determination of 3D structures.[5] Given the significant interest in deuterated compounds, it is essential to develop straightforward methods for their syntheses.

To introduce deuterium into the target molecule, several strategies have been pursued.[6] One way is to start from deuterated compounds as building blocks, for instance ethylene-d_4 glycol, acetic acid-d_3, or aniline-d_5, to build up the target molecule.[7–9] Alternative approaches facilitate transition metal catalysts, frustrated ion pairs, or radicals.[10–17] Electro- and photo-catalytical deuteration has also been described.[18,19] Per-deuterated complex biomolecules can be obtained by microorganisms growing in deuterated media.[20] Deuterium sources are diverse: for instance, hexafluoro-2-propanol-d_1, ^{t}BuOD, or DBpin as well as gaseous D_2 were reported.[13,15,18,21] Utilizing D_2O as both a deuterium source and solvent, deuteration can be an environmentally friendly and cost-effective process.[11–13,16–18,22] NaOD/D_2O mixtures have been used to deuterate various substrates. For instance, using an iridium bipyridonate complex as a catalyst deuterates secondary alcohols (at 100 °C).[23] Additionally, several metal catalyst-free reactions are reported, *e.g.*, deuteration of dimethyl sulfoxide and benzyl methyl sulfoxide,[24] porphobilinogen derivatives,[25] nucleobases in nucleotides (in DMSO mixtures at 60 °C),[26] N-heterocyclic oxides (at 100 °C under N_2 atmosphere),[27] pyridine (at around 200 °C),[28] as well as methyl moieties in dimethyl-2,2′-bipyridines (>10 bar, >160 °C, microwave-assisted).[29]

In this work, we report on the *in situ* deuteration occurring at the aminoacetate methylene carbons in aminopolycarboxylate complexes of lanthanides under alkaline conditions, using D_2O/OD^- as the deuterium source and reagent. Typically, Lewis acid- as well as base-catalyzed H–D exchange reactions occur at elevated temperatures of around 100 °C.[30] In the present study, the Ln^{3+}-augmented deuteration reaction proceeds already at room temperature. Although the reaction is slow at room temperature, requiring approximately 6–8 weeks, the H–D exchange is virtually complete, making this approach very mild and thus suitable for temperature-sensitive ligands. Of course, elevated temperatures help to accelerate the reaction. Aminoacetate groups in aminopolycarboxylic acids possess an increased C–H acidity due to multiple electron-withdrawing groups nearby. Treating only the ligand with a NaOD solution is insufficient to abstract the methylene hydrogens. However, upon formation of the lanthanide complexes, the polarity of the aminoacetate methylene groups' C–H bond increases. This augments C–H-bond activation to facilitate substitution of H by D. Selecting La^{3+}, Lu^{3+}, and Sm^{3+} as representatives of largest, smallest, and intermediate ionic radius, respectively, in a parallel approach, the yield of deuterated product was strongly dependent on the Lewis acidity of the Ln^{3+}, rendering Lu^{3+} the most effective among the metal ions tested.

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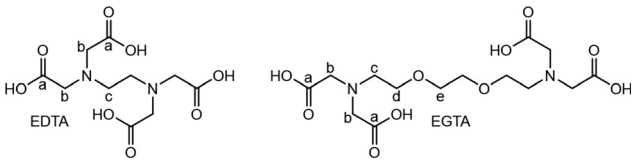

Fig. 1 Structures of the substrates (ligands) EDTA and EGTA, along with atomic labelling for further assignment. The site of interest, *i.e.*, the aminoacetate methylene groups, is denoted by b.

Working in the field of (aqueous) Ln and actinide (An) chemistry, understanding their complexation behavior and environmental fate, including *in vivo* effects and decorporation, multidentate chelators are of importance not only as benchmarking model substances but also as a means to address these complex issues. Therefore, different aminopolycarboxylates were used to complex Ln^{3+}, revealing deuteration at the methylene carbons of the aminoacetate. These comprise nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), ethylene glycol-bis(β-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA), and diethylenetriaminepentaacetic acid (DTPA). The presented results focus on EDTA and EGTA (Fig. 1). Further details on experimental procedures, as well as additional spectra of all ligands, including NTA and DTPA, are provided in the ESI.† C–H bond activation is the prerequisite for H–D exchange, which can be facilitated by metal ions, here Ln^{3+}. In the absence of Ln^{3+}, *i.e.*, treating only the substrates at pD 13–14 for several weeks, has no effect. The D content in the final product can be easily determined by high-resolution mass spectrometry or ^{1}H, ^{2}H, or ^{13}C NMR spectroscopy, exploiting nuclear properties for direct observation or indirectly *via* characteristic spin coupling patterns.[8–10,18,31]

Decreasing the Ln's ionic radius, *i.e.*, increasing its Lewis acidity, translates into higher yields of (faster conversion into) selectively deuterated compounds.

The results demonstrate a stepwise replacement of aminoacetate methylene carbon-bound protons by deuterons, facilitated by Ln^{3+}-augmented bond polarization. This work highlights the potential of Ln^{3+}-mediated H–D exchange for targeted, low-temperature isotopic substitution, advancing the deuteration of compounds with high selectivity at low cost.

To achieve this, we prepared solutions of the corresponding Ln-ligand complexes in D_2O/NaOD at a pD value of approximately 12.5. These solutions were shaken at room temperature for up to 8 weeks. Afterwards, the reaction was quenched using DCl to adjust the pD to ~7, and the mixture was further processed with HCl/H_2O. Upon adjusting pH to around 1.5, the metal–ligand complexes dissociate concomitantly protonating the ligand. Prevailing in their charge-neutral zwitterions forming in strongly acidic medium,[32] the ligands reach their minimum solubility and crystallize. As such, they can be easily separated from the supernatant mother liquor and obtained in high purity. The Ln salts can be recovered and reused. For further details on the experimental procedure, see ESI.† Depending on the Ln^{3+} used, different degrees of deuteration (yields) were achieved, as shown in Fig. 2, using EGTA as an example.

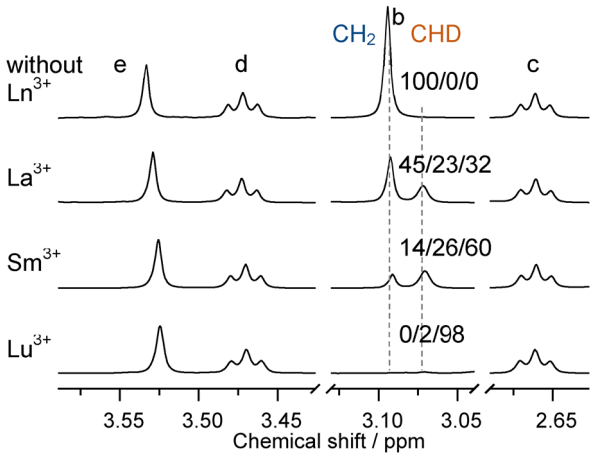

Fig. 2 Post-reaction ^{1}H NMR spectra of EGTA treated with D_2O/NaOD at pD 12.5 without and in the presence of different Ln^{3+} for 8 weeks. Signal assignment is according to Fig. 1. Numbers represent percentages of CH_2/CHD/CD_2 groups in the molecule obtained from signal integrals. Note that CD_2 groups are not visible in the ^{1}H NMR.

Apparently, with decreasing Ln^{3+} ionic radius, the corresponding aminopolycarboxylate complexes become better substrates, easing the H–D exchange. Evidently, the more substantial Lewis acidity increases C–H bond polarization (*i.e.*, corresponding to increased C–H acidity), facilitating, H^+ abstraction by a base. The base, in this study, deuteroxide ions (OD^-), remove a hydrogen from the most acidic site at a pD of around 12.5 (with all carboxyl and amino groups deprotonated), being a C–H-acidic site, presumably resulting in the formation of a short-lived carbanion. Since the reaction occurs in heavy water, upon nucleophilic attack, the carbanion efficiently abstracts a deuteron (D^+) from a D_2O molecule, yielding a CHD group (Fig. 3). Further reaction then successively replaces the remaining aminoacetate methylene H by D, eventually yielding CD_2.

The ^{13}C NMR spectrum of EGTA obtained from Lu^{3+}-augmented deuteration evidences the virtually complete substitution of the aminoacetate groups' protons by deuterons (see Fig. 4A). While all signals associated with ^{1}H-bearing carbons (and of course the quaternary carboxyl carbons) are singlets due to ^{1}H-decoupling (at 600 MHz), the aminoacetate carbon gives rise to a quintet (M = 5). The multiplicity M is calculated by $2 \times N \times I + 1$, where I is the spin quantum number (I = 1 for ^{2}H) and N is the number of coupled nuclei. Correspondingly, the number of deuterons (N) equals 2, proving that

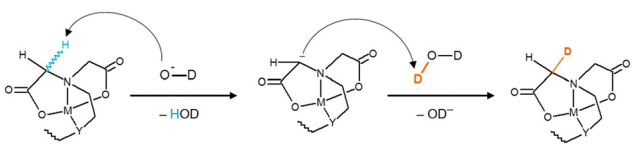

Fig. 3 Proposed reaction mechanism of the deuteration of the aminoacetate groups in D_2O with NaOD. For better visualization, the molecule is simplified. M and Y denote a trivalent lanthanide ion and *N* or *O* donor atoms in EDTA or EGTA, respectively.

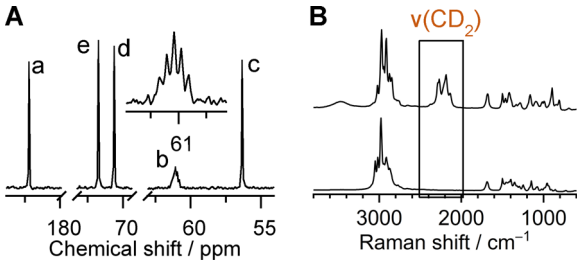

Fig. 4 (A) Inverse-gated ^{1}H-decoupled ^{13}C NMR spectrum of EGTA-d_8. (B) Raman spectra of EGTA-d_8 (top) and EGTA-d_0 (bottom).

deuterium binds exclusively to the aminoacetate carbon, whose one-bond coupling ($^{1}J_{CD}$) of 22 Hz (compared to the aminoacetates' $^{1}J_{CH}$ of 145 Hz) is not removed since ^{2}H is not decoupled as it correspondingly resonates at 92 MHz (at 14.1 T). Raman spectroscopy provides further evidence for the effective deuteration of the aminopolycarboxylates. Normally, the 2500–2000 cm^{-1} spectral region is void of signals except for X≡Y triple bonds (X,Y being C or N) or cumulative double bonds, as well as thiol groups. Therefore, the Raman spectrum of EGTA-d_0 shows no signals in this particular region, but the regular CH stretching vibrations around 2900 cm^{-1} (Fig. 4B). In contrast, owing to the doubled isotopic mass of D compared to that of H, the vibrational frequency shifts to approximately 2250 cm^{-1}, making the stretching vibrational mode, $\nu(CD_2)$, a unique and valuable analytical marker, as is the NMR signal of the deuterium nucleus.

Since ^{2}H has a very low natural abundance (0.016%), spectra of isotopically labeled compounds are often more transparent and easier to interpret by reducing the number of (background) signals. Fig. 5 depicts ^{2}H NMR spectra of aminoacetate-deuterated EDTA and EGTA in the presence of Lu^{3+}, depending on pH present as free ligand (acidic solution) and/or as Lu^{3+} complex. In the free ligand, the four aminoacetate residues are equivalent; thus, the signals appear as singlets. In the Lu^{3+} complexes, however, the molecular symmetry is reduced, rendering the four aminoacetate residues pairwise equivalent.[33] This results in two distinct resonances for each pair of equivalent methylene groups, *i.e.*, four signals overall. Further spectroscopic examination is discussed in the ESI.†

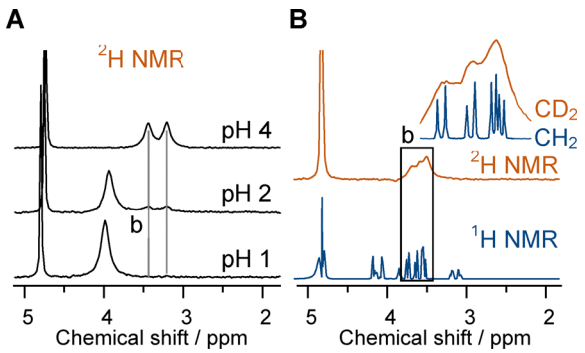

Fig. 5 (A) pH-Dependent ^{2}H NMR spectra of EDTA-d_7 in presence of Lu^{3+}. (B) ^{1}H NMR spectrum of Lu(EGTA-d_0) in D_2O (blue, bottom) and ^{2}H NMR spectrum of Lu(EGTA-d_8) in H_2O (orange, top). The respective aminoacetate signals are denoted by b.

Coupled cluster calculations corroborate experimental findings. Gibbs free energy, G, of species with protonated and deprotonated aminoacetate C–H bond in free EDTA and EGTA, as well as in their respective La^{3+} and Lu^{3+} complexes, were calculated (Table 1). In general, H^{+} abstraction from the aminoacetate carbon, *i.e.*, formation of the carbanion, is much lower in energy for the respective Ln^{3+} complexes than for the free ligand. In the Ln^{3+} complexes, the electron-withdrawing effects on the C–H bond and thus its polarization are reinforced, causing sufficient bond activation to facilitate the above-discussed H–D exchange (*cf.* Fig. 3).

Regarding our primary interest in Ln and An coordination chemistry, studying Ln^{3+} and An^{3+} exploits their outstanding luminescence properties. However, excited-state quenching, involving vibrational energy transfer, is a significant cause of non-radiative deactivation.[34] With a ligand at hand that is virtually quantitatively deuterated in its aminoacetate methylene groups, we performed exemplary experiments to study its impact on luminescence quenching behavior. Details are presented in the ESI.† Briefly, we can show that aminoacetate methylene groups (CH_2, more than CD_2) as moieties enclosed between the coordinating carboxyl and amino groups contribute to vibrational energy transfer quenching. This demonstrates that the deuteration approach presented here can help mitigate such effects, thereby advancing studies of a ligand's fundamental luminescence behavior.

In summary, this study presents a straightforward, mild, and cost-effective method for the selective deuteration of aminoacetate methylene carbons in aminopolycarboxylic acids under aqueous alkaline conditions, utilizing Ln^{3+} ions for C–H bond activation. Among the Ln^{3+} ions, Lu^{3+} was shown to be the choice owing to its strong Lewis acidity caused by the smallest ionic radius of all Ln. Multinuclear NMR as well as Raman spectroscopies unambiguously prove the yield and selectivity of the H–D exchange reaction. In addition, quantum chemical calculations support the hypothesized mechanism of a carbanionic intermediate, and TRLFS results contribute to the growing body of evidence elucidating the role of ligand vibrational dynamics on luminescence quenching phenomena. Presented

Table 1 Coupled cluster calculated energy differences between species with protonated and deprotonated aminoacetate methylene C–H bond in free EDTA and EGTA, as well as in their respective La^{3+} and Lu^{3+} complexes

Species[a]	G protonated (Hartree)	G deprotonated (Hartree)	ΔG (kJ mol^{-1})
EDTA	−1098.943	−1098.382	249
EDTA + La	−9815.489	−9814.974	175
EDTA + Lu	−15 879.038	−15 878.525	188
EGTA	−1406.182	−1405.628	239
EGTA + La	−9970.306	−9969.631	174
EGTA + Lu	−15 957.148	−15 956.636	161

[a] Protonated and deprotonated species refer to the tetraanionic ligand L^{4-} and its corresponding carbanion L_{-H}^{5-}, as well as the Ln^{3+} complex $[LnL]^{-}$ and its carbanion $[LnL_{-H}]^{2-}$, respectively.

results open up new opportunities for the synthesis of functionally deuterated compounds, which hold promise for applications ranging from molecular spectroscopy to biomedical research. It is therefore conceivable to selectively label the aminoacetate carbons with tritium, ^{3}H, using T_2O/NaOT as the isotope source.

The results presented here form the basis for a follow-up study[35] that leverages the synthesis method and access to meaningful analyses. Beyond numerous conceivable examples (molecules), the described deuteration reaction can be applied to and their subsequent usage; we utilize these compounds in the context of *in vitro* speciation studies. That is, radionuclide sequestration is studied in artificial body fluids of the digestive system. The deuterated aminopolycarboxylates are valuable probes that enable the examination of chemically active substances in complex mixtures with a strongly interfering (biomolecular) ^{1}H signal background, accessible by ^{2}H NMR.

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Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting this article have been included as part of the ESI.†

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