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LANTHANIDE CONTRACTION IN CHELATES OF ETHYLENEDIAMINETETRAACETIC ACID BASED ON CRYSTALLOGRAPHIC DATA: A SHORT REVIEW.

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The lanthanide (Ln) series has been attracted so much attention not only for its physical properties but also for its applications in organic synthesis and biomedical engineering. In the lanthanide chemistry, lanthanide contraction is a crucial concept meaning the gradual decrease in ionic radii as the atomic number of the Ln series increases. As a prominent chelator, ethylenediaminetetraacetic acid (EDTA) has been well-known to give stable complexes with various metals including Ln ions, resulted in forming (EDTA−4H)$^{4-}$ anion by deprotonation; over 100 kinds of Ln-EDTA complexes have hitherto been synthesized and structurally characterized using X-ray crystallography. While the lanthanide contraction phenomenon has been extensively studied in certain complexes of Ln, systematization on the Ln-EDTA remains inadequate though the chelates of EDTA are commonly used. Thus, this study presents a comprehensive analysis based on the data from the Cambridge Crystallographic Data Centre (CCDC). In mononuclear EDTA complexes X[Ln(EDTA−4H)(H_2O)$_m$]·$n$$H_2O$ (X^+ = NH_4^+ and its analogues) systematic lanthanide contraction depending on their coordination number are presented except for a few cases. However, in the case of non-mononuclear complexes or coordination polymers, the compositions become more complicated, and a greater variation in atomic bond length occurs, which is unusual for the lanthanide contraction studies in previous research. These varieties are considered to be influenced by different types of counter-cations, inorganic anions, solvent molecules and bridging O atoms from another EDTA anions. This suggests the flexibility and versatility of EDTA as a ligand. Such findings in the Ln-EDTA complexes could potentially provide us further development of a novel function in the future.

Keywords: coordination compound, f-block, rare-earth element, polyaminocarboxylic acid.

INTRODUCTION. Lanthanides (Ln) have been the extensive subject aimed at elucidating their characteristics, namely electronic, magnetic, and optical properties, besides other aspects such as applications in the catalysts of organic syntheses and the agents in biomedical engineering [1–3]. In lanthanide chemistry, a key concept called 'lanthanide contraction' refers to the gradual decrease in ionic radii as the atomic number of the lanthanide series increases [4–6]. The cases of lanthanide contraction were first studied in simple binary compounds [7]. Subsequently, renewed interest led to further studies of several families of coordination compounds in the solid state, and it was found that lanthanide contraction reduces the coordination numbers for some complexes having rigid ligands [8–10]. Moreover, such knowledge of the lanthanide contraction in the well-characterized complexes has led to the development of a novel phenomenon, for example, 'switching photochromism' in coordination polymers [11]. Nevertheless, the series whose lanthanide contraction clarified doesn't cover all the existing complexes with various ligands.

As one of the most prominent chelators, ethylenediaminetetraacetic acid (EDTA; see Figure 1) is of great interest not only in chemical analysis, but also in the advancement of materials science. One example of its potential applications involves gas storage and separation in metal-organic frameworks (MOFs) [12]. This is due to its ability to form stable complexes with practically all metal ions, including trivalent lanthanides, where EDTA molecules are deprotonated to form a tetravalent anion; i.e., $(EDTA-4H)^{4-}$ [13–16].

So far, over one hundred EDTA complexes of lanthanide have been synthesized and characterized using X-ray crystallography [17]. Earlier studies have suggested evidence of the lanthanide contraction in a series of Ln-EDTA complexes with coordinated water molecules [18–25]. However, despite the existence of more than one hundred various types of Ln-EDTA complexes with reported crystal structures [17], systematic demonstration of the distances between centered Ln ions and coordinated atoms, depending on the coordination numbers, is yet to be presented.

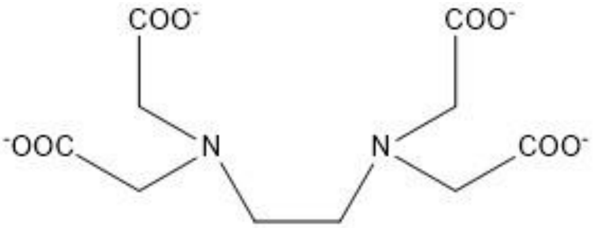

Fig. 1. A chemical structure of $(EDTA-4H)^{4-}$ representing the tetravalent anion where four hydrogen atoms are deprotonated from EDTA molecule.

As to the Ln-EDTA complexes, a systematic comprehension of the lanthanide contraction could be expected to provide us some additional insights into lanthanide chemistry, influenced by counter-cations, crystal solvents, crystal packing effects, and so on. Therefore, I report herein a comprehensive investigation into the lanthanide contraction of the complexes of Ln-EDTA based on the crystal data that is free available from the Cambridge Crystallographic Data Centre (CCDC).

EXPERIMENT AND DISCUSSION OF THE RESULTS. A total of 111 kinds of Ln-EDTA complexes were identified and summarized along with their respective coordination numbers (CN), excluding promethium (Pm), which was not examined due to its radioactivity as usual, and thulium (Tm), the second-least abundant of the lanthanides. Therefore, in the present article, I only deal with each EDTA complex of Ln; La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu, as per my previous work [26]. Some cif files deposited on CCDC couldn't be opened (3D Structure Unavailable) by the crystal viewer software Mercury.

Complexes could be classified into two categories in general terms: mononuclear complexes and non-mononuclear ones (= metal coordination polymers). In the latter, EDTA anions act as a bridging ligand between centered Ln cations. A typical mononuclear Ln-EDTA complex with three coordinated water molecules [27] were shown in Figure 2. Monomeric complexes with formulae X[Ln(EDTA−4H)$(H_2O)_m$]·nH_2O, where X^+ = NH_4^+, MA^+ (= $CH_3NH_3^+$), $N_2H_5^+$, and Gu^+ (= $C(NH_2)_3^+$), with Ln = Ce−Nd, Sm−Er were hit by search in the CCDC; Gu_2[Ln(EDTA−4H)$(H_2O)_2$]ClO_4·$6H_2O$ (Ln = Er, Yb, and Lu) are also included. Hereafter, some abbreviations, 'NH_4-Er' are used for NH_4[Ln(EDTA−4H)$(H_2O)_2$]·$5H_2O$, for example, in which EDTA anion and water molecules are omitted. Bond parameters for these isostructural compounds X[Ln(EDTA−4H)$(H_2O)_m$]·nH_2O are listed in Table 1-5; d(Ln-N), d(Ln-O_{Ac}), and d(Ln-O_w) are mean bond distances between centered Ln atoms and corresponding coordinated atoms; N = nitrogen atoms in the ethylenediamine moiety of EDTA anions, O_{Ac} and O_w = oxygen atoms in -COO^- and H_2O, respectively.

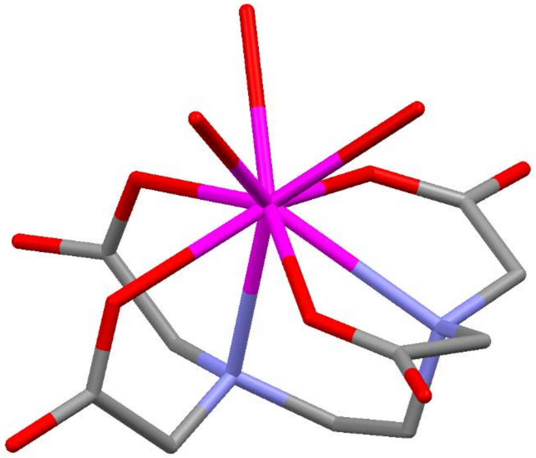

Fig. 2. An example of Ln-EDTA complexes with three coordinated water molecules: [Eu(EDTA−4H)$(H_2O)_3$]$^-$ moiety is demonstrated in the crystal of NH_4[Eu(EDTA−4H)$(H_2O)_3$]·$5H_2O$ [27]; where Eu (red purple), O (red), N (blue), and C (gray). H atoms, NH_4^+ (counter cation), and crystalline water molecules uncoordinated to Eu^{3+} are omitted.

Table 1.

Average atomic bond lengths in the crystals of NH_4[Ln(EDTA−4H)$(H_2O)_m$]·$5H_2O$ (*m* = 3 except for the cases of *m* = 2 in both Er). The Eu and Ho have CN = 9, whereas the Er has CN = 8.

NH_4-Ln	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{63}$Eu	2.696	2.490	2.420	[27]
$_{67}$Ho	2.644	2.422	2.365	[28]
$_{68}$Er(1)	2.558	2.319	2.270	[29]
$_{68}$Er(2)	2.543	2.316	2.278	[30]

Table 2.

Average atomic bond lengths in the crystals of MA[Gd(EDTA−4H)(H_2O)$_3$]·4H_2O (MA = CH_3NH_3; CN = 9).

MA-Ln	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{64}$Gd	2.678	2.492	2.412	[31]

Table 3.

Average atomic bond lengths in the crystals of N_2H_5[Ln(EDTA−4H)(H_2O)$_3$]·*n*H_2O (*n* = 5 except for the cases of Ce has *n* = 4, and Eu has *n* = 3; all have CN = 9).

N_2H_5-Ln	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{58}$Ce	2.731	2.554	2.471	[32]
$_{59}$Pr	2.713	2.537	2.454	[33]
$_{60}$Nd	2.702	2.523	2.440	[33]
$_{62}$Sm	2.679	2.489	2.415	[33]
$_{63}$Eu	2.692	2.498	2.419	[32]
$_{64}$Gd	2.663	2.463	2.395	[34]
$_{65}$Tb	2.654	2.452	2.385	[34]
$_{66}$Dy	2.676	2.448	2.371	[35]

Table 4

Average atomic bond lengths in the crystals of Gu[Ln(EDTA−4H)(H_2O)$_3$] (Gu = C(NH_2)$_3$; all have CN = 9).

Gu-Ln	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{60}$Nd	2.551	2.506	2.521	[36]
$_{63}$Eu	2.696	2.661	2.675	[37]
$_{64}$Gd	2.447	2.400	2.415	[25]

Table 5.

Average atomic bond lengths in the crystals of Gu_2[Ln(EDTA−4H)(H_2O)$_2$]ClO_4·6H_2O (Gu = C(N-H_2)$_3$; all have CN = 8).

Gu_2-Ln-ClO_4	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{68}$Er	2.591	2.344	2.275	[38]
$_{70}$Yb	2.577	2.322	2.254	[39]
$_{71}$Lu	2.568	2.316	2.245	[25]

The atomic numbers vs. mean bond distances (Å) of mononuclear Ln-EDTA complexes are demonstrated in Figure 3. The lanthanide contraction phenomenon is obtained; mean bond distances are gradually reduced (Ce–Lu). The complexes of CN = 8 (Er–Lu) have even shorter ion radii than those of CN = 9 (Ce–Ho), possibly explained by reducing the steric repulsion between the ligands around the coordination sphere.

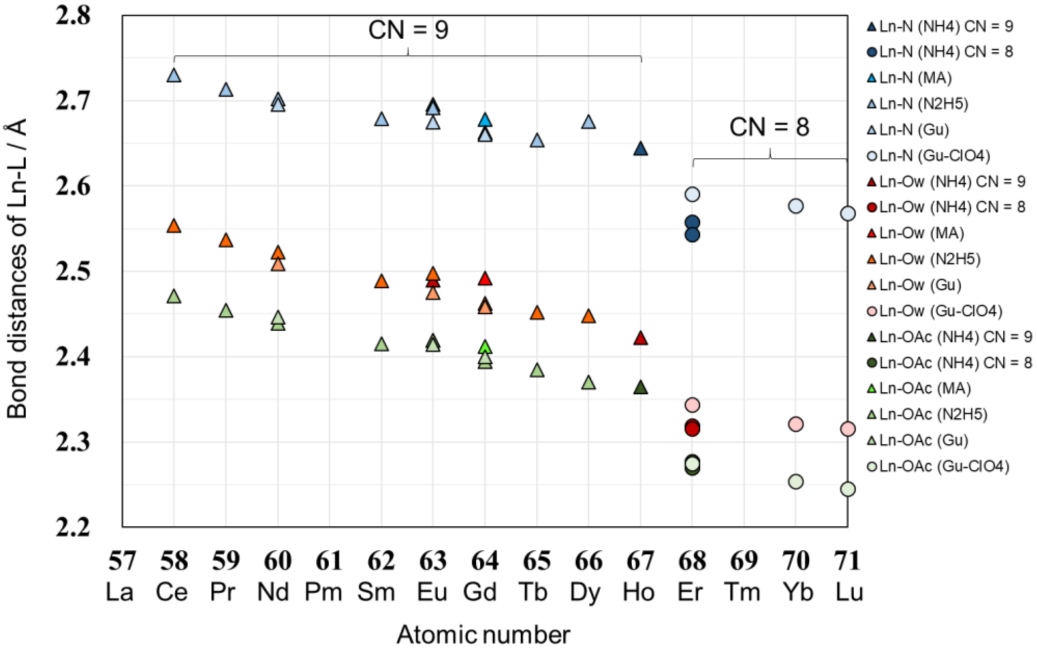

Fig. 3. Mean atomic bond distances (Å) of *d*(Ln-N), *d*(Ln-O_{Ac}), and *d*(Ln-O_w) vs. atomic numbers of mononuclear complexes of $X[Ln(EDTA-4H)(H_2O)_m]\cdot nH_2O$, where $X^+ = NH_4^+$, MA^+ (= $CH_3NH_3^+$), $N_2H_5^+$, and Gu^+ (= $C(NH_2)_3^+$), in addition to $Gu_2[Ln(EDTA-4H)(H_2O)_2]ClO_4\cdot 6H_2O$. From Ce to Ho, the complexes have 9-coordinate geometry (denoted as triangles), whereas from Er to Lu, CN = 8 (circules).

Consequently, the mean bond distances of the complexes of $M[Ln(EDTA-4H)(H_2O)_m]\cdot nH_2O$, where M = Na, K, and Cs, are shown in Table 6-8. As mentioned above, the abbreviation such as Na-La means $Na[Ln(EDTA-4H)(H_2O)_3]\cdot 5H_2O$. These complexes $M[Ln(EDTA-4H)(H_2O)_m]\cdot nH_2O$ are still thought to be mononuclear, because there are no bridged Ln ions present. Alkali metal ions, however, are bridged to Ln ions via oxygen atoms (Figure 4). All the Na-Ln complexes have CN = 9. Among the K-Ln complexes, only one K-Yb complex has 8-coordinate, and others have CN = 9. Cs-Sm and Cs-Gd have 9-coordinate geometry; on the contrary, Cs-Dy, Cs-Ho, and Cs-Yb have CN = 8. The mean bond lengths vs. atomic numbers of the Ln series (La–Yb, except for Pm and Tm) with Na, K, and Cs are shown in Figure 5.

Table 6.

Average atomic bond lengths in the crystals of Na[Ln(EDTA–4H)(H_2O)$_m$]·$n$$H_2O$ (m = 3, n = 5, except for the case of n = 3.25 in Dy(3).

Na-Ln	Bond length / Å			Ref.
	d(Ln-N)	d(Ln-O_w)	d(Ln-O_{Ac})	
$_{57}$La	2.768	2.589	2.493	[24]
$_{58}$Ce	2.709	2.571	2.491	[40]
$_{59}$Pr	2.714	2.536	2.458	[19]
$_{60}$Nd(1)	2.700	2.535	2.451	[24]
$_{60}$Nd(2)	2.696	2.521	2.454	[36]
$_{62}$Sm(1)	2.673	2.499	2.423	[24]
$_{62}$Sm(2)	2.667	2.494	2.421	[41]
$_{62}$Sm(3)	2.614	2.466	2.381	[42]
$_{63}$Eu(1)	2.675	2.495	2.411	[24]
$_{63}$Eu(2)	2.665	2.480	2.410	[43]
$_{64}$Gd(1)	2.651	2.472	2.399	[19]
$_{64}$Gd(2)	2.653	2.469	2.400	[44]
$_{65}$Tb	2.643	2.448	2.377	[43]
$_{66}$Dy(1)	2.627	2.464	2.392	[18]
$_{66}$Dy(2)	2.640	2.456	2.377	[43]
$_{66}$Dy(3)	2.649	2.461	2.381	[45]
$_{67}$Ho(1)	2.633	2.453	2.363	[22]
$_{67}$Ho(2)	2.654	2.457	2.395	[46]
$_{68}$Er	2.618	2.428	2.351	[47]

Table 7.

Average atomic bond lengths in the crystals of K[Ln(EDTA–4H)(H_2O)$_m$]·$n$$H_2O$ (m = 3, n = 5, except for the cases of m = 2 in Yb; n = 3.5 in Eu).

K-Ln	Bond length / Å			Ref.
	d(Ln-N)	d(Ln-O_w)	d(Ln-O_{Ac})	
$_{60}$Nd	2.712	2.539	2.436	[23]
$_{62}$Sm	2.692	2.503	2.412	[48]
$_{63}$Eu	2.677	2.500	2.402	[49]
$_{64}$Gd(1)	2.677	2.483	2.399	[50]

Table 7.

$_{64}$Gd(2)	2.719	2.553	2.464	[51]
$_{65}$Tb	2.655	2.470	2.390	[52]
$_{67}$Ho	2.617	2.446	2.367	[47]
$_{70}$Yb	2.519	2.343	2.272	[53]

Table 8.

Average atomic bond lengths in the crystals of Cs[Ln(EDTA−4H)(H_2O)$_m$]·5H_2O (*m* = 3, except for the cases of *m* = 2 in both Er).

Cs-Ln	Bond length / Å			Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})	
$_{62}$Sm	2.671	2.466	2.423	[47]
$_{64}$Gd	2.654	2.434	2.400	[47]
$_{66}$Dy	2.574	2.392	2.318	[47]
$_{67}$Ho	2.584	2.378	2.314	[47]
$_{70}$Yb	2.532	2.369	2.262	[18]

Table 9.

Average atomic bond lengths in the crystals of [Ln(EDTA−3H)(H_2O)$_m$]·*n*H_2O, except for the case of H-Ce = [Cr(OH)$_6$Mo$_6$O$_{18}$][Ce$_3$(EDTA−3H)$_2$(H_2O)$_9$]·13H_2O (CN = 10). From La to Sm: *m* = 1, *n* = 0 (La & Ce, CN = 10; Nd & Sm, CN = 9); Gd to Dy(1): *m* = 0, *n* = 3; Dy(2) to Er; *m* = 0, *n* = 2 (CN = 8).

H-Ln	Bond length / Å				Ref.
	d(Ln-N)	*d*(Ln-O_w)	*d*(Ln-O_{Ac})		
			inter	intra	
$_{57}$La	2.849	2.655	2.726	2.524	[55]
$_{58}$Ce	2.789	2.564	2.700	2.504	[56]
$_{60}$Nd	2.776	2.552	2.453	2.452	[57]
$_{62}$Sm	2.773	2.548	2.453	2.454	[58]
$_{64}$Gd	2.626	-	2.354	2.353	[59]
$_{66}$Dy(1)	2.626	-	2.355	2.354	[61]
$_{66}$Dy(2)	2.604	-	2.328	2.325	[60]
$_{67}$Ho	2.592	-	2.323	2.311	[62]
$_{68}$Er	2.577	-	2.306	2.299	[63]

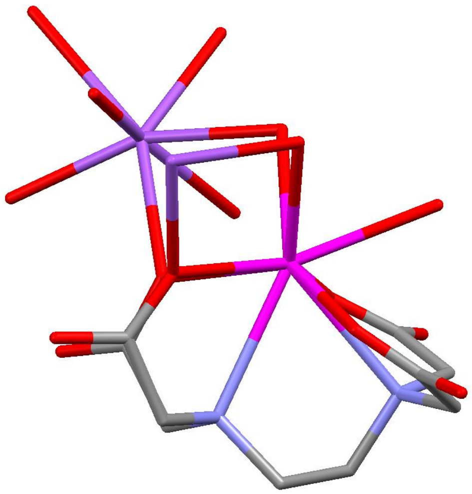

Fig. 4. The crystal structures of mononuclear Na[La(EDTA−4H)$(H_2O)_3$]·$5H_2O$ [24], where La (red purple), Na (purple), O (red), N (blue), and C (gray). H atoms are not shown.

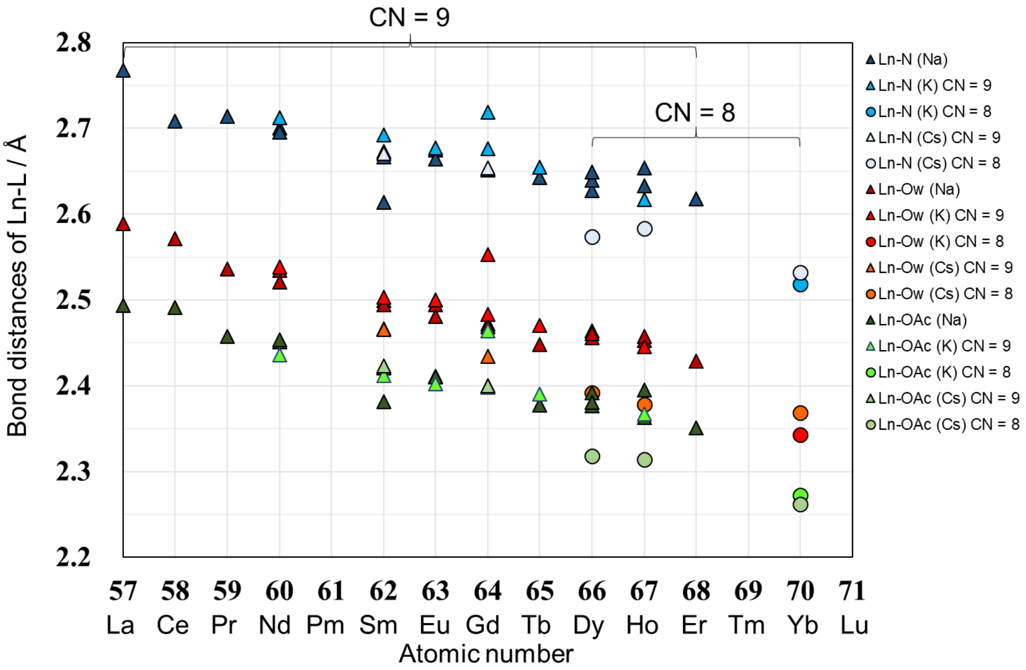

Fig. 5. Mean atomic bond distances (Å) of *d*(Ln-N), *d*($Ln\text{-}O_w$), and *d*($Ln\text{-}O_{Ac}$) vs. atomic numbers of mononuclear complexes of M[Ln(EDTA−4H)$(H_2O)_m$]·nH_2O, where M^+ = Na^+, K^+, and Cs^+. Although K-Yb, Cs-Dy, Cs-Ho, and Cs-Yb have CN = 8, the remaining complexes have CN = 9.

The complex of Na-Sm(3) has slightly shorter bond distances than that of Na-Sm(1) and Na-Sm(2). For example, does the amount of crystalline water molecules differ? Wang et al. (2010) reported an X-ray crystallography with its approximately consistent elemental analysis [42]; hence, a possibility of the different composition would be incorrect. Conversely, as to the case of the K-Gd(2) complex, the bond distances are irregularly longer compared with others. By Yang et al. (2002), X-ray crystallography was the only method for its characterization (both elemental analysis and IR spectroscopy weren't reported) [51]. It's difficult to say what the deviation would mean, but by contrast, it should be wondered if the composition is really accurate in the case of K-Gd(2).

Between Dy and Er, complexes having CN = 8 and 9 are overlapping. The complexes of Cs-Dy and Cs-Ho have CN = 8, whereas Na-Dy, Na-Ho, Na-Er, and K-Ho have CN = 9. Compared with 9-coordinate, 8-coordinate have significantly shorter distances. These facts seem to indicate that the geometry around the Ln atoms is influenced by the size and electrostatic properties of the counter-cations according to Sakagami et al. (1999) [47]. However, these findings of the cases of the complexes having alkali metal ions (M^+) are in contrast to those described for the cases of X^+ (NH_4^+ and its analogues such as MA^+, $N_2H_5^+$, and Gu^+) as counter ions, because in Er, both NH_4-Er and Gu_2-Er-ClO_4 in spite of having the same 8-coordinate geometry. By manifestation of these two things, as counter-cations, alkali metals could have strong perturbation through coordination bonding to the coordination sphere around the Ln ions than the cases having NH_4^+ and its analogues, not having coordination bonding to the Ln ions by themselves. The mean bond distances are reduced from La to Yb.

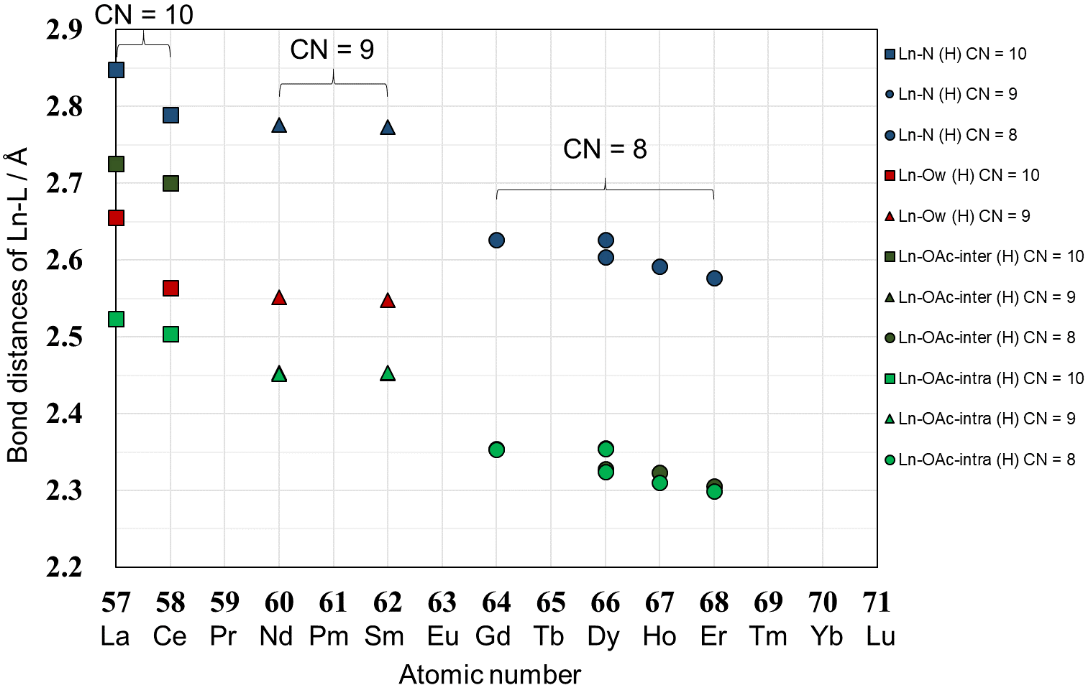

Fig. 6. Mean atomic bond distances (Å) of *d*(Ln-N), *d*(Ln-O_w), *d*(Ln-$O_{Ac\text{-}intra}$), and *d*(Ln-$O_{Ac\text{-}intra}$) vs. atomic numbers of mononuclear complexes of $[Ln(EDTA-3H)(H_2O)_m]\cdot nH_2O$, except for the case of H-Ce = $[Cr(OH)_6Mo_6O_{18}][Ce_3(EDTA-3H)_2(H_2O)_9]\cdot 13H_2O$ (CN = 10).

Janicki & Mondry (2014) have summarized the monomeric $[Ln(EDTA-4H)(H_2O)_n]^-$ (n = 2, 3, 4) having counter-cations of H^+, Na^+, K^+, Cs^+, NH_4^+, and Gu^+, where the one having H^+ was $H[La(EDTA-4H)(H_2O)_4]$ [38]. But actually, it is more appropriate to denote the complex $H[La(EDTA-4H)]$ as $[La(EDTA-3H)]$, since H^+ is on one carboxylate group by Lind et al. (1965) [54]. Another problem by Janicki & Mondry (2014) is that the other Ln complexes having $(EDTA-3H)^{3-}$ and water molecules as ligands weren't discussed [38]. While another $[Ln(EDTA-3H)]$ series with crystal structures had been reported; not as monomeric complexes but as ones having bridged Ln ions by oxygen atoms described in Table 9 and Figure 6. Some $[Ln(EDTA-3H)]$ are denoted as $H_3O[Ln(EDTA-4H)]$ in the original articles [61-63]. Since it should be the $-COO^-$ more basic than water molecules to receive H^+, all compounds are unified as a category within a series of $[Ln(EDTA-3H)]$ herein.

In the early study based upon the crystal structure of the H-La complex, its coordination number had been reported to be CN = 10 [38]. On the other hand, the recent study by Xiong et al. (2007) reported the CN as 9 [55]. In the present study, the two La^{3+} are considered to have both CN = 10, including two coordinated intermolecular $-COO^-$ groups. The bond lengths of two $La\text{-}O_{\text{Ac-inter}}$ is 2.475 Å and 2.974 Å, respectively; the longer one being considered non-bonding because it is too long [55].

Among the H-Ln series, a question of the presence or absence of coordinated water molecules is of interest. In the case of the light rare earths (LRE) from La to Sm, the complexes exhibit coordinated water molecules, whereas the heavy rare earths (HRE) from Gd to Er do not. As these series of complexes lack counter-cations such as M^+ or X^+ (NH_4^+ and its analogues), the intermolecular distances between each H-Ln complex are shortened, resulting in the replacement of bridging $-COO^-$ groups instead of water molecules. This phenomenon is particularly evident in the complexes of HRE. Furthermore, the transition to CN = 8 is occurring from Gd that is earlier than in previously discussed monomeric complexes. This distinction would suggest that the H-Ln complexes should be differentiated from other monomeric one having alkali metal ions, ammonium ions and its analogues as counter-cations.

Hereafter, the remaining complexes of Ln-EDTA with coordinated water molecules are discussed whose bond lengths are listed in Table 10. For the cases where Ln ions lacking coordination with water molecules are also incorporated, only the bond lengths of Ln ions with coordination bonds are demonstrated. The complexes have somewhat complicated chemical formulae as follow:

La(1): $[La_5Cl_2(EDTA-4H)_3(H_2O)_{18}]_nCl_n\cdot 8nH_2O$;
La(2): $[La_2(SO_4)(EDTA-4H)(H_2O)_3]_n$;
La(3): $K_2(NH_4)_8[La(EDTA-4H)(H_2O)_2]_2[La(cit-3H)(EDTA-4H)]_2\cdot 22H_2O$
(cit = citric acid);
La(4): $(H_2en)[La(EDTA-4H)(H_2O)]_2\cdot 10H_2O$;
La(5): $[\{(CH_3)_2N\}_2C1_3H_8I]_2[\{La(EDTA-4H)(H_2O)_2\}_2]\cdot 4H_2O$;
La(6): $(NH_4)_5[La_3(CO_3)(EDTA-4H)_3(H_2O)_3]\cdot 12H_2O$;
La(7): $K_5[La_3(CO_3)(EDTA-4H)_3(H_2O)_3]\cdot 13.5H_2O$;

Ce: $K_5[Ce_3(CO_3)(EDTA-4H)_3(H_2O)_3]\cdot13.5H_2O$;
Pr: $H_2(PhNHNH_2)_3[Pr_2(EDTA-4H)_2(H_2O)_4]\cdot5H_2O$;
Nd: $[Nd_2\{o\text{-}C_6H_4(COO)_2\}(EDTA-4H)(H_2O)_2]\cdot1.5H_2O$;
Eu(1): $Na[Eu_8(EDTA-4H)_6(H_2O)_{22}]ClO_4\cdot28H_2O$;
Eu(2): $Na[Eu_9(EDTA-4H)_6(H_2O)_{27}](ClO_4)_4\cdot26H_2O$;
Gd(1): $Na[Gd_8(EDTA-4H)_6(H_2O)_{22}]ClO_4\cdot28H_2O$;
Gd(2): $Na[Gd_9(EDTA-4H)_6(H_2O)_{27}](ClO_4)_4\cdot26H_2O$.

Table 10.

Average atomic bond lengths in the crystal compounds of the Ln-EDTA complexes that have coordinated water molecules. La(1) to La(5), Pr, and Nd have CN = 10; whereas the remaining complexes have CN = 9.

H_2O-Ln	Bond length / Å				Ref.
	d(Ln-N)	*d*($Ln\text{-}O_w$)	*d*(Ln-O)		
			inter	intra	
$_{57}$La(1)	2.821	2.568	–	2.566	[64]
$_{57}$La(2)	2.785	2.532	2.609	2.612	[64]
$_{57}$La(3)	2.806	2.650	2.637	2.531	[48]
$_{57}$La(4)	2.852	2.561	2.643	2.529	[65]
$_{57}$La(5)	2.833	2.587	2.589	2.539	[66]
$_{57}$La(6)	2.780	2.529	–	2.535	[67]
$_{57}$La(7)	2.763	2.529	–	2.534	[67]
$_{58}$Ce	2.736	2.534	–	2.507	[67]
$_{59}$Pr	2.796	2.524	2.672	2.475	[68]
$_{60}$Nd	2.765	2.504	2.615	2.466	[69]
$_{63}$Eu(1)	2.682	2.497	2.417	2.406	[70]
$_{63}$Eu(2)	2.680	2.495	2.416	2.409	[70]
$_{64}$Gd(1)	2.675	2.477	2.401	2.396	[70]
$_{64}$Gd(2)	2.668	2.483	2.428	2.416	[70]

As displayed in Figure 7, these complexes with coordinated water molecules have CN = 10 (La–Nd), and CN = 9 (La–Gd). There is a large overlap between CN = 10 and 9 compared with the previous shown Ln-EDTA complexes. The cases of that the proportion of non-major components except for the lanthanide-centered EDTA moieties within each complex is relatively large, it is probable that the coordination numbers are strongly influenced.

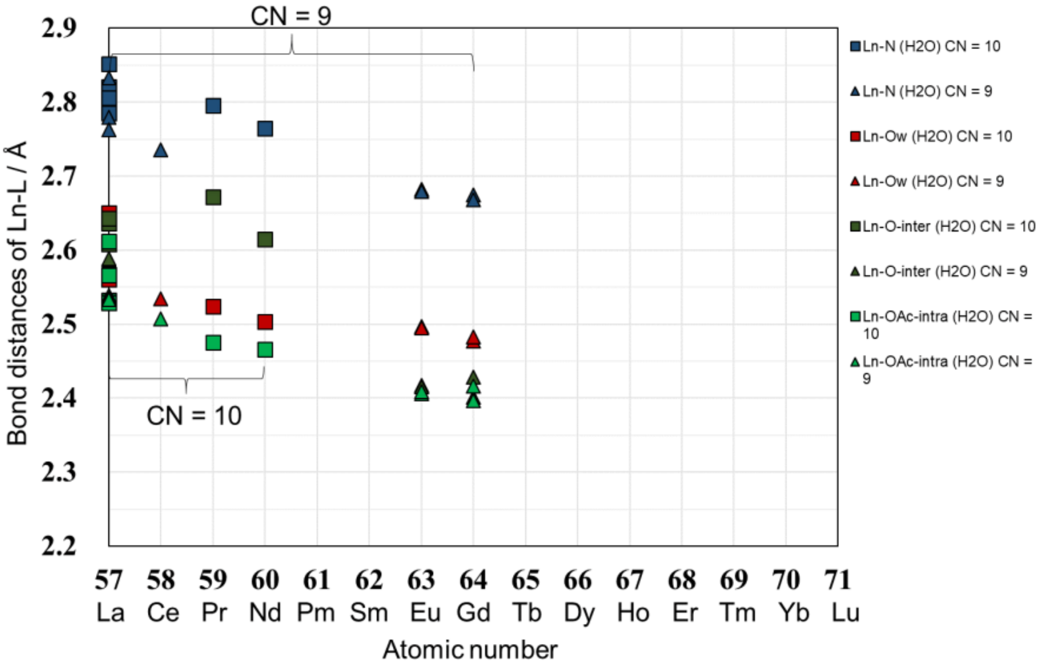

Fig. 7. Mean atomic bond distances (Å) of *d*(Ln-N), *d*(Ln-O_w), *d*(Ln-$O_{Ac\text{-}intra}$), and *d*(Ln-$O_{\text{-}intra}$) vs. atomic numbers of the complicated remaining complexes of Ln-EDTA with coordinated water molecules. It should be noted that the O atoms in *d*(Ln-$O_{\text{-}intra}$) are not necessarily belonging to the -COO^- in adjacent EDTA moieties.

Now that the last remaining series of Ln-EDTA complexes which do not have any coordinated water molecules are outlined as shown in Table 11 and 12. Here, bond parameters of the series without coordinated water molecules from Ln-EDTA complexes, which are depicted in Table 10, are also presented. As aforementioned, former studies indicated the lanthanide contraction of EDTA complexes using only some Ln-EDTA complexes with coordinated water molecules [18-25]. This means that a thorough examination of the lanthanide contraction in EDTA complexes, lacking coordinated water molecules, is yet to be carried out. Each bond distance is plotted against atomic number for the complexes without coordinated water molecules in Figure 8. The chemical formulae for the variety of each compound are not provided here, however, in some complexes, hydroxide, nitrate, carbonate, peroxide, phosphite, oxalate, malonate, and citrate ions are coordinated in place of water molecules or the O atoms of the -COO^- from the neighboring EDTA anions. In particular, the difference in bond length surpasses any previous series, with some bond lengths even practically resembling those of Er complexes with CN = 8, despite the Ce complex having CN = 10; it is due to that Ce(4)–Ce(6) have tetravalence; Ce(IV) [75]. Another characteristic of this series is the difference in the range of coordination numbers. The Ln-EDTA complexes with coordinated water molecules have a CN = 10, which ranges from La to Nd (also overlapping with CN = 9). Conversely, up to Eu, the CN in the Ln-EDTA complexes without coordinated water molecules increases to 10. This suggests that the coordination number of Ln-EDTA complexes can be significantly tunable while retaining the EDTA anions as the primary ligands.

Table 11.

Average atomic bond lengths in the crystal compounds of the remaining LRE-EDTA complexes that have no coordinated water molecules; only Sm(1)-EDTA complexes has CN = 9, whereas others have CN = 10.

LRE-EDTA	Bond length / Å			
	d(Ln-N)	*d*(Ln-O)		Ref.
		inter	intra	
$_{57}$La(1)	2.813	2.563	2.588	[71]
$_{57}$La(2)	2.785	2.563	2.611	[71]
$_{57}$La(3)	2.802	2.562	2.609	[71]
$_{57}$La(4)	2.746	2.515	2.657	[64]
$_{57}$La(5)	2.808	2.568	2.596	[48]
$_{57}$La(6)	2.803	2.566	2.601	[48]
$_{57}$La(7)	2.822	2.566	2.650	[72]
$_{57}$La(8)	2.830	2.573	2.630	[72]
$_{57}$La(9)	2.771	2.559	2.625	[73]
$_{57}$La(10)	2.803	2.568	2.593	[73]
$_{57}$La(11)	2.767	2.556	2.613	[67]
$_{57}$La(12)	2.768	2.541	2.626	[67]
$_{57}$La(13)	2.785	2.572	2.581	[67]
$_{58}$Ce(1)	2.720	2.418	2.342	[74]
$_{58}$Ce(2)	2.795	2.543	2.568	[71]
$_{58}$Ce(3)	2.782	2.543	2.595	[71]
$_{58}$Ce(4)	2.562	2.494	2.317	[75]
$_{58}$Ce(5)	2.590	2.484	2.316	[75]
$_{58}$Ce(6)	2.712	2.408	2.331	[75]
$_{58}$Ce(7)	2.763	2.535	2.597	[73]
$_{58}$Ce(8)	2.788	2.548	2.578	[73]
$_{58}$Ce(9)	2.764	2.553	2.566	[67]
$_{58}$Ce(10)	2.757	2.523	2.618	[67]
$_{62}$Sm(1)	2.442	2.660	2.432	[48]
$_{62}$Sm(2)	2.771	2.491	2.482	[76]

Table 12.
Average atomic bond lengths in the crystal compounds of the remaining HRE-EDTA complexes that have no coordinated water molecules; Eu(3’) have CN = 3, Eu(3), Gd(2), and Gd(4’) have CN = 9, others have CN = 8.

HRE-EDTA	Bond length / Å			
	d(Ln-N)	*d*(Ln-O)		Ref.
		inter	intra	
$_{63}$Eu(1)	2.748	2.597	2.611	[77]
$_{63}$Eu(2)	2.793	2.556	2.569	[78]
$_{63}$Eu(3)	2.755	2.467	2.388	[70]
$_{63}$Eu(3’)	2.771	2.481	2.501	[70]
$_{64}$Gd(1)	2.617	2.407	2.308	[79]
$_{64}$Gd(2)	2.657	2.396	2.421	[79]
$_{64}$Gd(3)	2.610	2.393	2.319	[79]
$_{64}$Gd(4)	2.758	2.483	2.595	[79]
$_{64}$Gd(4’)	2.796	2.434	2.559	[79]
$_{68}$Er(1)	2.513	2.291	2.343	[80]
$_{68}$Er(2)	2.574	7.432	2.329	[81]
$_{70}$Yb(1)	2.553	2.282	2.306	[82]
$_{70}$Yb(2)	2.539	2.274	2.303	[82]
$_{70}$Yb(3)	2.533	2.272	2.299	[82]
$_{70}$Yb(4)	2.541	2.276	2.294	[82]

It is primarily the Ln-O bond lengths that exhibit the most variation, whereas the Ln-N bond lengths display comparatively little variation between them. Evidently, factors beyond the coordinating EDTA anion, such as distinctions in crystal packing due to the kind of coordinating other anions and non-coordinating moieties, occasionally have an impact on the atomic bond lengths. This would be because, in contrast to other rigid ligands, EDTA anions are flexible. Nonetheless, it is undeniable that the overall trend towards the lanthanide contraction is obvious even in this series. From La to Yb, the average atomic bond lengths are decreasing.

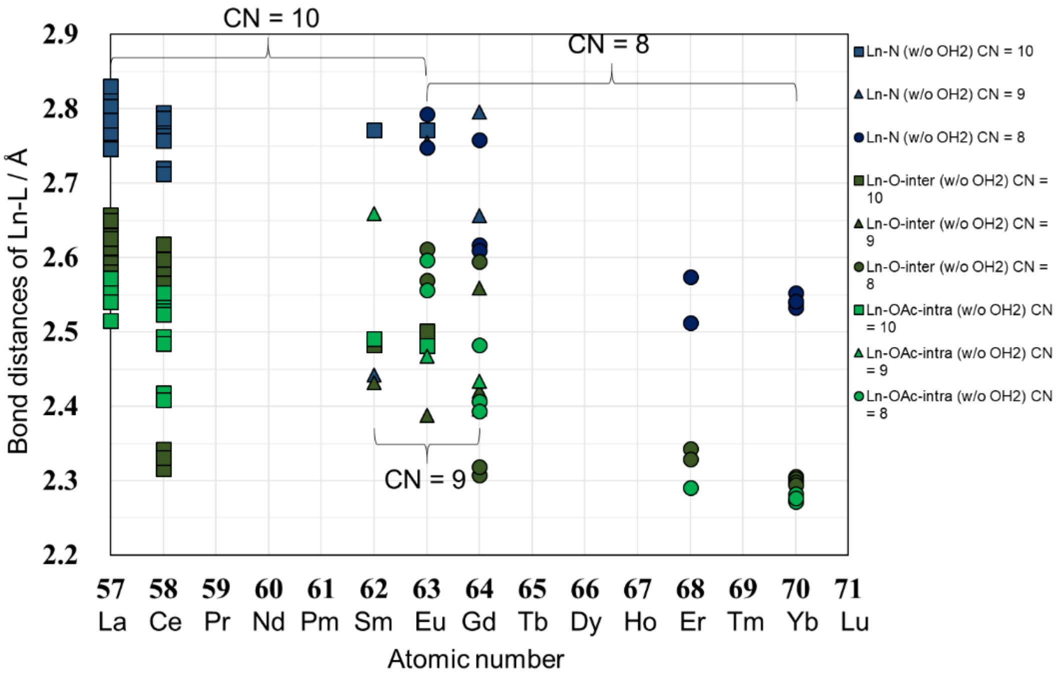

Fig. 8. Mean atomic bond distances (Å) of *d*(Ln-N), *d*(Ln-O$_{\text{-inter}}$), and *d*(Ln-O$_{\text{Ac-intra}}$) vs. atomic numbers of the remaining complexes of Ln-EDTA without coordinated water molecules. It should be noted that the O atoms in *d*(Ln-O$_{\text{-intra}}$) are not necessarily belonging to -COO⁻ in the neighbouring EDTA moieties.

CONCLUSIONS. In order to achieve a comprehensive understanding on the lanthanide contraction among the complexes of Ln-EDTA already reported individually, I searched and analyzed data on 111 kinds of crystal structures obtained from the CCDC. The finding indicates clear lanthanide contraction in the series of mononuclear Ln-EDTA complexes with coordinated water molecules having ammonium ions, its analogues, and alkali metals as counter-cations. However, there is a tendency for greater variation in the average atomic bond lengths as the Ln-EDTA complexes became non-mononuclear or coordination polymers. This phenomenon is influenced by various types of counter-cations, including bridging another Ln ions coordinated to the O atoms of -COO⁻ in neighboring EDTA anions, as well as factors beyond the coordination sphere. Such variation is uncommon in the studies of the lanthanide contraction of the complexes having rigid ligands previously reported. It is suggested that the EDTA anions have a versatility as ligands, which could provide a flexibility in the CN and atomic bond lengths in the lanthanide contraction. This manuscript is a revised version of my preprint (doi: 10.51094/jxiv.560).

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КОНТРАКЦІЯ ЛАНТАНІДУ В ХЕЛАТАХ ЕТИЛЕНДІАМІНТЕТРАОЦТОВОЇ КИСЛОТИ НА ОСНОВІ КРИСТАЛОГРАФІЧНИХ ДАНИХ: КОРОТКИЙ ОГЛЯД

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Хоча явище скорочення лантаноїдів було вже широко вивчено, систематизація етилендіамінтетраацетату лантаноїду (Ln-EDTA) залишається недостатньою, хоча зазвичай використовують хелати EDTA. Таким чином, це дослідження являє собою комплексний аналіз на основі даних Кембриджського центру кристалографічних даних (CCDC). У моноядерних комплексах EDTA з координованими молекулами води представлено систематичне скорочення лантаноїдів залежно від їхнього координаційного числа. Однак у немоноядерних комплексах або координаційних полімерах спостерігаємо більшу варіацію довжини атомного зв'язку, що є рідкістю для досліджень скорочення лантаноїдів у попередніх дослідженнях. Це свідчить про гнучкість і універсальність EDTA як ліганду.

Ключові слова: координаційна сполука, f-блок, рідкоземельний елемент, поліамінокарбонова кислота.

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