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希土類-エチレンジアミン四酢酸（REE-EDTA）の結晶状態における配位数：ミニ・レビュー

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Coordination numbers for rare-earths ethylenediaminetetra-acetate (REE-EDTA) in crystalline state: a mini-review

by

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The crystal structures of rare earth elements ethylenediaminetetraacetate (REE-EDTA), including potential applications towards biomedical engineering in MRI, have been briefly reviewed by some researchers. However, there is no systematization of almost all of REE-EDTA complexes; therefore, in the present study, a total of 114 kinds of REE-EDTA (except Sc, Pm, and Tm) were searched in the Cambridge Crystallographic Data Centre (CCDC) and their coordination numbers (C.N.) are summarized. The largest number of registered REE-EDTA is La-EDTA for 22 kinds, followed by 15 Gd-EDTA. The C.N. of each complex ranged from 10 to 9 for light REE (La–Sm) and 10 to 8 for heavy REE (Y and Eu–Lu), suggesting that a decreasing in the C.N. of lanthanoid (Ln)-EDTA is considered to be due to ‘lanthanoid contraction’. The C.N. of Tb-EDTA deviated slightly from the overall decreasing C.N. in Ln-EDTA complexes would be because of a lack of a sufficient number of the studied samples.

Key words: *Aminopolycarboxylate*, *Chelate*, *Complex ion*, *Lanthanide*.

１．はじめに

ポリアミノポリカルボン酸（PAPC）のランタノイド（Ln）錯体は数十年にわたり研究され（Zalupski et al. 2021）[1]，医療用の核磁気共鳴画像法（MRI）における診断用プローブとしての応用が期待されている（Zapolotsky et al. 2022）[2]．診断薬としての改良は錯体の構造的知見に基づくべきであるとして，Wang et al.（2010）は PAPC が配位した希土類元素（REE）錯体の結晶構造を総説した[3]．その中で，PAPC のうち最もよく知られるエチレンジアミン四酢酸（EDTA：図 1）がキレート配位した REE 錯体に関し，15 報の研究論文に基づき 19 種類の結晶構造が扱われた．さらに，「Carboxylates of rare earth elements（希土類元素のカルボン酸塩）」と題された総説が Janicki et al.（2017）によってのちに公刊され，多数のカルボン酸 REE 錯体が取り上げられたものの，REE-EDTA 錯体の結晶構造（配位数）への言及は 16 報の研究論文に基づいた特徴的なものを簡単に紹介するのみと，限定的な扱いにとどめられた[4]．なお筆者の文献調査によると，本稿執筆時点でケンブリッジ結晶学データセンター（CCDC）には 100 種類あまりの REE-EDTA 錯体の結晶構造データが登録されていることを確認している．しかしながら，これらを網羅して配位構造を解説した総説は，管見の限りでは存在しない．

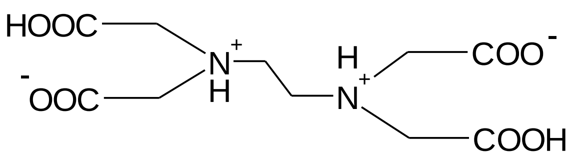

図 1　エチレンジアミン四酢酸（EDTA）の双性イオン．

例えば，エルビウム（Er）の EDTA 錯体には，エルビウムイオン Er^{3+}に対し EDTA アニオン（$[EDTA\text{-}4H]^{4-}$）と二つの水分子が配位した$[Er(EDTA\text{-}4H)(H_2O)_2]^-$に加え，さらにもう一つ水分子が配位した錯イオン（$[Er(EDTA\text{-}4H)(H_2O)_3]^-$）をそれぞれ含んだ異なる結晶

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構造が報告されており，これらは水溶液中で化学平衡の状態で存在する（Cotton et al. 2022）[5]．したがって，REE-EDTA 錯体の構造への理解をより深めるためには，些細なものも含めて，できるだけ多くの結晶構造データを紐解く必要があるのではないだろうか．

そこで Sc，Pm，Tm を除く REE-EDTA 錯体の結晶構造データを CCDC（https://www.ccdc.cam.ac.uk/）から取得し，配位構造（配位数）を手短にまとめ，報告する．ここで，REE は周期表第 3 族のスカンジウム（Sc），イットリウム（Y）および Ln を含む元素の総称で，便宜上，ランタン（La）からサマリウム（Sm）までの軽希土類（LREE）と，ユウロピウム（Eu）からルテチウム（Lu）までの元素に Y を加えた重希土類（HREE）に分類されるのが普通である（Wall 2021）[6]（図 2）．

Y	La	Ce	Pr	Nd	Pm	Sm	Eu
Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

図 2 Sc を除く希土類元素（REE）を軽希土類（LREE）（太線内）と重希土類（HREE）に分類したもの[6]．

２．結果と考察

CCDC に結晶構造データが登録された REE-EDTA 錯体を検索し，化学式，配位数（C.N）および引用文献を表 1 に報告年代順でまとめた（EDTA アニオンは全て六座配位であった）．なお，プロメチウム（Pm）には安定同位体が存在せず，登録データはなかった．また，ツリウム（Tm）の EDTA 錯体の結晶（$K[Tm(EDTA\text{-}4H)]\cdot nH_2O$）の合成はかつて報告されているものの，「The Thulium crystals obtained were of very poor quality , so the study of the Thulium compound was not pursued after the initial photography.（得られたツリウム結晶は非常に品質が悪く，最初の撮影以降はツリウム化合物の研究は行われなかった．）」とある（Mullins 1983）[81]．

ここで，例えば La-EDTA の配位数の報告に着目してみよう．1965 年には配位数 10 および 9 の二つの錯体の X 線回折結果が相次いで報告された．配位数 10 の La-EDTA 錯体では La^{3+}にエチレンジアミン四酢酸一水素イオン（$[EDTA\text{-}3H]^{3-}$）が六座配位するとともに，さらに四つの水分子が配位しているとされた．一方，配位数 9 の錯体では，La^{3+}にエチレンジアミン四酢酸イ

表 1 結晶構造データが CCDC に登録されている REE-EDTA 錯体の化学式，配位数（C.N）および参考文献（一部，結晶構造データが CCDC には登録されていないものも含む）．cit＝クエン酸，mal＝リンゴ酸

(1) ランタン（La）	C.N	Ref		C.N	Ref
$[La(EDTA\text{-}3H)(H_2O)_4]\cdot 3H_2O$	10	[7]	$[La_2(EDTA\text{-}4H)(SO_4)(H_2O)_3]$	10	[14]
$K[La(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[8]	$K_4(NH_4)_4[La(EDTA\text{-}4H)(cit\text{-}3H)]_2\cdot 17H_2O$	10	[15]
$[\{(CH_3)_2N\}_2C_{13}H_8I]_2[\{La(EDTA\text{-}4H)\text{-}(H_2O)_2\}_2]\cdot 4H_2O$	9	[9]	$K_2(NH_4)_8[La(EDTA\text{-}4H)(H_2O)_2]_2\text{-}[La(EDTA\text{-}4H)(cit\text{-}3H)]_2\cdot 22H_2O$	10	[15]
$Na[La(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[10]	$Na_{12}[La(EDTA\text{-}4H)(HPO_3)]_4\cdot 8NaCl\cdot 4H_2O$	10	[16]
$Na_{10}[La_4(EDTA\text{-}4H)_4(OH)_4](ClO_4)_2\cdot 27H_2O$	9	[11]	$Na_{12}[La(EDTA\text{-}4H)(CO_3)]_4\cdot 8NaCl\cdot 4H_2O$	10	[16]
$[\{La(EDTA\text{-}3H)(H_2O)\}_2]$	9	[12]	$H_2en[La(EDTA\text{-}4H)(H_2O)]_2\cdot 10H_2O$	10	[17]
$(NH_4)_8[La(EDTA\text{-}4H)(cit\text{-}3H)]_2\cdot 9H_2O$	10	[13]	$K_8[La_2(EDTA\text{-}4H)_2(cit\text{-}3H)(CO_3)]Cl\cdot 10.5H_2O$	10	[18]
$K_8[La(EDTA\text{-}4H)(cit\text{-}3H)]_2\cdot 16H_2O$	10	[13]	$K_6[La_2(EDTA\text{-}4H)_2(mal\text{-}2H)(CO_3)]\cdot 12.5H_2O$	10	[18]
$K_6[La(EDTA\text{-}4H)(mal\text{-}2H)]_2\cdot 14H_2O$	10	[13]	$(NH_4)_5[La_3(EDTA\text{-}4H)_3(CO_3)(H_2O)_3]\cdot 12H_2O$	10	[19]
$[La_5(EDTA\text{-}4H)_3Cl_2(H_2O)_{18}]Cl\cdot 8H_2O$	10	[14]	$K_5[La_3(EDTA\text{-}4H)_3(CO_3)(H_2O)_3]\cdot 13.5H_2O$	10	[19]
$[La_2(EDTA\text{-}4H)(NO_3)_2(H_2O)_5]\cdot 3H_2O$	10	[14]	$Na_8[La_2(EDTA\text{-}4H)_2(CO_3)_3]\cdot 17.5H_2O$	10	[19]
(2) セリウム（Ce）					
$K_2Na_2[Ce(EDTA\text{-}4H)(O_2)]_2\cdot 13H_2O$	10	[20]	$Rb_4[Ce(EDTA\text{-}4H)(O_2)]_2\cdot 14H_2O$	10	[24]
$Na[Ce(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[21]	$K[Co(NH_3)_6][Ce(EDTA\text{-}4H)(O_2)]_2\cdot 7H_2O$	10	[24]
$[Ce_3(EDTA\text{-}3H)_2(H_2O)_9][Cr(OH)_6(Mo_6\text{-}O_{18})]\cdot 13H_2O$	10	[22]	$K_8[(EDTA\text{-}4H)_2(cit\text{-}3H)(CO_3)]Cl\cdot 10.5H_2O$	10	[18]
$N_2H_5[Ce(EDTA\text{-}4H)(H_2O)_3]\cdot 4H_2O$	9	[23]	$K_6[Ce_2(EDTA\text{-}4H)_2(mal\text{-}2H)(CO_3)]\cdot 12.5H_2O$	10	[18]
$(NH_4)_8[Ce(EDTA\text{-}4H)(cit\text{-}3H)]_2\cdot 9H_2O$	10	[13]	$Na_8[Ce_2(EDTA\text{-}4H)_2(CO_3)_3]\cdot 17.5H_2O$	10	[19]
$K_6[Ce(EDTA\text{-}4H)(mal\text{-}2H)]_2\cdot 14H_2O$	10	[13]	$K_5[Ce_3(EDTA\text{-}4H)_3(CO_3)(H_2O)_3]\cdot 13.5H_2O$	10	[19]
$K_4[Ce(EDTA\text{-}4H)(O_2)]_2\cdot 14H_2O$	10	[24]			
(3) プラセオジム（Pr）					
$Na[Pr(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[25]	$N_2H_5[Pr(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[27]

$C(NH_2)_3[Pr(EDTA\text{-}4H)(H_2O)_3]$	9	[26]	$H_2(PhNHNH_2)[Pr_2(EDTA\text{-}4H)_2(H_2O)_4]\cdot 3.5H_2O$	10	[28]
(4) ネオジム（Nd）					
$C(NH_2)_3[Nd(EDTA\text{-}4H)(H_2O)_3]$	9	[29-30]	$[Nd(EDTA\text{-}3H)(H_2O)]$	9	[32]
$K[Nd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[31]	$[Nd_2\{C_6H_4(COO)_2\}(EDTA\text{-}4H)(H_2O)_2]\cdot 1.5H_2O$	10	[33]
$Na[Nd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[10,30]	$N_2H_5[Nd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[27]
$Na_8\{[Na(H_2O)]_4[Nd_{12}(EDTA\text{-}4H)_8(OH)_{16}]\}\cdot 13H_2O$	9	[11]			
(5) サマリウム（Sm）					
$Na[Sm(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[25,34-6]	$N_2H_5[Sm(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[27]
$Cs[Sm(EDTA\text{-}4H)(H_2O)_3]\cdot 4H_2O$	9	[37]	$K_4[Sm(EDTA\text{-}4H)(cit\text{-}3H)]\cdot 10H_2O$	9	[15]
$[Sm(EDTA\text{-}3H)(H_2O)]$	9	[38]	$[Sm_{33}(EDTA\text{-}4H)_{12}(OAc)_2(CO_3)_4(OH)_{40}\text{-}(H_2O)_{38}]\cdot OAc\cdot 50H_2O$	10	[40]
$K[Sm(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[15,39]			
(6) イットリウム（Y）					
$\{C(NH_2)_3\}_3[Y(EDTA\text{-}4H)F_2]\cdot H_2O$	8	[26,41]	$Na[Y(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[44-45]
$NH_4[Y(EDTA\text{-}4H)(H_2O)_3]\cdot 3H_2O$	9	[42-43]			
(7) ユウロピウム（Eu）					
$C(NH_2)_3[Eu(EDTA\text{-}4H)(H_2O)_3]$	9	[26,46]	$K[Eu(EDTA\text{-}4H)(H_2O)_3]\cdot 3.5H_2O$	9	[50]
$C(NH_2)_3[Eu(EDTA\text{-}4H)F_2]\cdot H_2O$	8	[26]	$\{C(NH_2)_3\}_2[Eu(EDTA\text{-}4H)]\cdot 4H_2O$	8	[51]
$\{C(NH_2)_3\}_4[Eu(EDTA\text{-}4H)F(H_2O)]_2\cdot 2H_2O$	9	[26,47]	$N_2H_5[Eu(EDTA\text{-}4H)(H_2O)_3]\cdot 4H_2O$	9	[23]
$Na[Eu(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[10,45]	$[NaEu_8(EDTA\text{-}4H)_6(H_2O)_{22}]\cdot ClO_4\cdot 28H_2O$	9	[52]
$Na_3[Eu(EDTA\text{-}4H)]Cl\cdot 7H_2O$	8	[48]	$[NaEu_9(EDTA\text{-}4H)_6(H_2O)_{27}]\cdot (ClO_4)_4\cdot 26H_2O$	9	[52]
$NH_4[Eu(EDTA\text{-}4H)(H_2O)_3]\cdot H_2O$	9	[49]	$[Eu_{33}(EDTA\text{-}4H)_{12}(OAc)_2(CO_3)_4(OH)_{40}\text{-}(H_2O)_{38}]\cdot OAc\cdot 70H_2O$	10	[40]
(8) ガドリニウム（Gd）					
$Na[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[25,53]	$K_3[Gd(EDTA\text{-}4H)(HPO_3)]\cdot 7H_2O$	8	[56]
$\{C(NH_2)_3\}_3[Gd(EDTA\text{-}4H)F_2]\cdot H_2O$	8	[26]	$(NH_4)_2Na[Gd(EDTA\text{-}4H)(cit\text{-}2H)]\cdot 4H_2O$	9	[56]
$Cs[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 4H_2O$	9	[37]	$Na_6[Gd_2(EDTA)_2(HPO_3)_2]\cdot 2.5NaCl\cdot 21H_2O$	8	[56]
$K[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[54-5]	$C(NH_2)_3[Gd(EDTA\text{-}4H)(H_2O)_3]$	9	[60]
$NH_4[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[43]	$[NaGd_8(EDTA\text{-}4H)_6(H_2O)_{22}]\cdot ClO_4\cdot 28H_2O$	9	[52]
$[Gd(EDTA\text{-}3H)]\cdot 3H_2O$	8	[56]	$[NaGd_9(EDTA\text{-}4H)_6(H_2O)_{27}]\cdot (ClO_4)_4\cdot 26H_2O$	9	[52]
$N_2H_5[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[57]	$[Gd_{32}(EDTA\text{-}4H)_{12}(OAc)_2(C_2O_4)(CO_3)_2\text{-}(OH)_{40}(H_2O)_{36}]\cdot 70H_2O$	10	[40]
$CH_3NH_3[Gd(EDTA\text{-}4H)(H_2O)_3]\cdot 4H_2O$	9	[58]			
(9) テルビウム（Tb）					
$Na[Tb(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[45,61]	$N_2H_5[Tb(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[57]
$K[Tb(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[62]			
(10) ジスプロシウム（Dy）					
$Na[Dy(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[63-64]	$N_2H_5[Dy(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[67]
$Cs[Dy(EDTA\text{-}4H)(H_2O)_2]\cdot 3H_2O$	8	[36]	$[Dy(EDTA\text{-}3H)]\cdot 3H_2O$	8	[68]
$H_3O[Dy(EDTA\text{-}4H)]\cdot H_2O$	8	[65]	$Na[Dy(EDTA\text{-}4H)(H_2O)_2]\cdot 3H_2O$	9	[45]
$Na[Dy(EDTA\text{-}4H)(H_2O)_3]\cdot 3.25H_2O$	9	[66]			
(11) ホルミウム（Ho）					
$Na[Ho(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[64,69]	$NH_4[Ho(EDTA\text{-}4H)(H_2O)_3]\cdot 1.5H_2O$	9	[70]
$K[Ho(EDTA\text{-}4H)(H_2O)_3]\cdot 3H_2O$	9	[36]	$H_3O[Ho(EDTA\text{-}4H)]\cdot H_2O$	8	[71]
$Cs[Ho(EDTA\text{-}4H)(H_2O)_2]\cdot 3H_2O$	8	[36]			
(12) エルビウム（Er）					

$NH_4[Er(EDTA\text{-}4H)(H_2O)_2]\cdot 3H_2O$	8	[72-3]	$Na_4[Er_2(EDTA\text{-}4H)_2(C_2O_4)]\cdot 8H_2O$	8	[75]
$\{C(NH_2)_3\}_2[Er(EDTA\text{-}4H)F_2]\cdot H_2O$	8	[26]	$\{C(NH_2)_3\}_2[Er(EDTA\text{-}4H)(H_2O)_2]ClO_4\cdot 6H_2O$	8	[76]
$H_3O[Er(EDTA\text{-}4H)]\cdot H_2O$	8	[74]	$\{C(NH_2)_3\}_3[Er(EDTA\text{-}4H)(CO_3)]\cdot H_2O$	8	[77]
$Na[Er(EDTA\text{-}4H)(H_2O)_3]\cdot 5H_2O$	9	[36]			
(13) イッテルビウム（Yb）					
$Cs[Yb(EDTA\text{-}4H)(H_2O)_2]\cdot 3H_2O$	8	[63]	$K_3[Yb(EDTA\text{-}4H)(CO_3)]\cdot 6H_2O$	8	[80]
$K[Yb(EDTA\text{-}4H)(H_2O)_2]\cdot 5H_2O$	8	[78]	$Rb_3[Yb(EDTA\text{-}4H)(CO_3)]\cdot 6H_2O$	8	[80]
$\{C(NH_2)_3\}_2[Yb(EDTA\text{-}4H)(H_2O)_2]ClO_4\cdot 6H_2O$	8	[79]	$Cs_3[Yb(EDTA\text{-}4H)(CO_3)]\cdot 6H_2O$	8	[80]
$K_3[Yb(EDTA\text{-}4H)(CO_3)]\cdot 2H_2O$	8	[80]			
(14) ルテチウム（Lu）					
$\{C(NH_2)_3\}_3[Lu(EDTA\text{-}4H)F_2]\cdot H_2O$	8	[26]	$\{C(NH_2)_3\}_2[Lu(EDTA\text{-}4H)(H_2O)_2]ClO_4\cdot 6H_2O$	8	[60]

オン（$[EDTA\text{-}4H]^{4-}$）が六座配位し，加えて三つの水分子が配位しているとされた（Lind et al. 1965; Hoard et al. 1965）[7-8]．それまでは一般にランタノイド錯体も六配位であると考えられてきたが（Cotton 2017）[82]，これらの報告は，ランタノイド錯体が高配位数で存在することが確立されるためのブレークスルーであった（Cotton 2005）[83]。そしてその 42 年後の 2007 年までに配位数 9 の La-EDTA 錯体が 4 種類報告され（Chen et al. 1989; Nakamura et al. 1995; Wang et al. 2000; Xiong et al. 2007）[9-12]，その時点までは配位数 9 の方が優勢であった．しかし，その後は配位数 10 の La-EDTA 錯体が再び報告されるようになり（Chen et al. 2012; Guo et al. 2015; Chen et al. 2018; Wang et al. 2019, 2021; Shi et al. 2022; Lin et al. 2022）[13-19]，これまでのところ, 全体としては配位数 9 の錯体よりも配位数 10 の錯体の方が多いことが伺える．つまり，ある特定の種類の REE-EDTA 錯体における平均的な配位数を知りたい場合には，できる限り多くのデータを参照したほうがより確からしい考察ができるようになるといえよう．

そこで, 表 1 に基づいて各 REE-EDTA 錯イオンの平均配位数を求めたところ，軽希土類（La–Sm）では La = Ce = 9.8, Pr = 9.3, Nd = Sm = 9.1（各錯体の配位数は 10 または 9)，重希土類（Y および Eu–Lu）では Y = 8.7, Eu = Gd = 8.8, Tb = 9.0, Dy = Ho = 8.6, Er = 8.1, Yb = Lu = 8.0（各錯体の配位数は，10，9 または 8）となった．

ランタノイド化学において「ランタノイド収縮」は重要な概念である．原子番号が大きくなるにつれてランタノイドのイオン半径は徐々に小さくなり，Lu^{3+}はLa^{3+}より約 16%小さい．このランタノイド収縮はさまざまな形で現れるが，そのうちの一つとして，単純な二元系化合物における固体状態での配位数の減少が挙げられる（Cotton 2017）[82]．今回の調査から，カウンターカチオンやその他の配位子が異なる錯体どうしでの配位数の比較であるにもかかわらず，ランタノイド収縮による平均配位数の減少傾向が REE-EDTA 錯体においてもおおむね成立していることが示唆された．

ただ，Tb-EDTA の平均配位数は，今回の得られた一連の傾向からはやや外れている．また，Y^{3+}のイオン半径は Er^{3+}に最も近いにもかかわらず（Wall 2021）[6]，平均配位数では Eu から Ho の EDTA 錯体のものに近い結果となった．これらは，La や Gd のような他の REE に比べ，各サンプル数が必ずしも十分ではなく，配位数が特定のものにのみ偏った錯体ばかりがたまたま報告されているために, 有意な値ではないかもしれない．

３．まとめ

医工学的応用が期待される希土類元素-エチレンジアミン四酢酸錯体（REE-EDTA）の結晶構造に基づき，野口（2023）[84]を上回る 114 種類の各 EDTA 錯体の配位数をまとめた．各配位数は，軽希土類（LREE-EDTA）で 10 または 9，重希土類（HREE-EDTA）では 10 から 8 となり, Pm と Tm を除く Ln-EDTA において，「ランタノイド収縮」によると考えられる配位数の減少傾向がおおむね成り立っているのが明らかとなった．

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