エチレンジアミン四酢酸錯体に関する結晶構造研究の補遺

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Addendum of crystal structural study on ethylenediaminetetraacetate complexes

by

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Ethylenediaminetetraacetic acid (EDTA) is a multidentate ligand well-known for its ability to form chelates with nearly all metal ions. Its extensive studies in coordination chemistry using specifically XRD measurements have resulted in their structural variability. Here, as an addendum, I present additional findings on some unique structures of EDTA salts and chelates, including their metal types and coordination numbers, obtained through meticulous investigation at the Cambridge Crystallographic Data Centre (CCDC). It was revealed that the existing research has uncovered some reports that have accumulated without being cited properly with each other. Although it was reviewed up until the 1980s, a comprehensive systematization is still required. Thus, following endeavor will lead to new knowledge.

Key words: *Aminopolycarboxylic acid*, *CCDC*, *Coordination number*, *EDTA Chelate*.

１．はじめに

代表的なキレート剤として知られているエチレンジアミン四酢酸（EDTA）から生じる 4 価の陰イオン $\{CH_2N(CH_2COO)_2\}_2{}^{4-}$内の窒素原子がプロトン化される場合，EDTA は非キレート性の塩として存在する（野口 2023a）[1]．こうした塩に加え，EDTA のアルカリ金属およびアルカリ土類金属キレートの既報の結晶構造データをまとめ（野口 2022a,b）[2,3]，分子内原子間距離や配位構造を系統的に示した（Noguchi 2022）[4]．このように，以前に結晶構造が報告されている金属-EDTA 錯体のデータを分析しては，随時，報告してきたが，これまでの調査では網羅しきれていなかったものがあるため，ここで補遺として取りまとめておく．

２．結果と考察

ケンブリッジ結晶学データセンター（CCDC）に登録されている EDTA 錯体のデータを入念に検索し，未確認だった EDTA の塩，主要族元素金属および第一系列遷移金属までの EDTA キレートをまとめた（表 1）．

EDTA の非キレート性の塩については最近になって確認するに至ったが，$Sr_2(EDTA{-}2H)_2(H_2O)_4{\cdot}2H_2O$ および $Ba(EDTA{-}2H)(H_2O)_3{\cdot}H_2O$ の結晶構造データが Uliel et al.（2021）[5]に紐づけられて CCDC に登録されていた．加えて，図 1 に示す $Ag_2(EDTA{-}2H)$も登録されていたのを追加的に見い出した（Wimmer et al. 2021）[6].

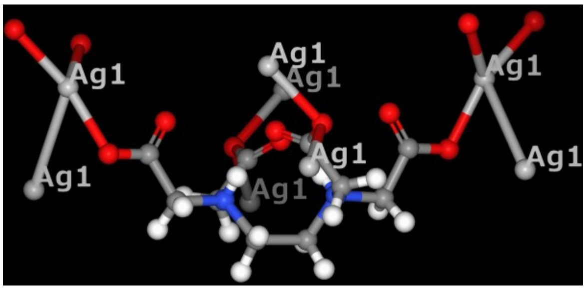

図 1 $Ag_2(EDTA{-}2H)$の結晶構造[6].

金属イオンとして銀イオンのみを有する EDTA 塩として，同じく一価のアルカリ金属イオンの EDTA 塩との構造比較が求められるとともに，銀イオンの化合物にその存在が知られている Ag-Ag 親銀性相互作用（Schmidbaur & Schier 2015）[7]が EDTA 部分の構造にどう関与しているか明らかとなることが期待される．

アルカリ土類金属-EDTA キレートの結晶構造とそ

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表 1 データが CCDC に登録されていることを新たに確認した EDTA 錯体の化学式，配位数（CN）および参考文献（主要族金属・第一系列遷移金属-EDTA）

(1) 非キレート性塩	CN	Ref		CN	Ref
$\mathrm{Sr_2(EDTA-2H)_2(H_2O)_4 \cdot 2H_2O}$	8	[5]	$\mathrm{Ag_2(EDTA-2H)}$	4	[6]
$\mathrm{Ba(EDTA-2H)(H_2O)_3 \cdot H_2O}$	9	[5]			
(2) アルカリ土類金属キレート					
$\mathrm{\{C(NH_2)_3\}_4[Ca(EDTA-4H)]_2 \cdot 8H_2O}$	8	[9]			
(3) 土類金属キレート					
$\mathrm{[Al(EDTA-3H)(H_2O)]}$	6	[11]	$\mathrm{Na(H_2O)[In(EDTA-4H)(H_2O)] \cdot H_2O}$	7	[13]
$\mathrm{(H_2en)[In(EDTA-4H)(H_2O)]_2 \cdot 4H_2O}$	7	[12]	$\mathrm{K[In(EDTA-4H)(H_2O)] \cdot 10/3H_2O}$	7	[14]
(4) 14 族半金属キレート					
$\mathrm{[\{Sn(CH_3)_2\}_2(EDTA-4H)(H_2O)_2] \cdot H_2O}$	6×2	[16,17]			
(5) 第一系列遷移金属キレート					
$\mathrm{(NH_4)_2[Ti(EDTA-4H)(O_2)] \cdot 2H_2O}$	7	[18]	$\mathrm{[Co(sarmp)(NH_3)_3][Co(EDTA-4H)] \cdot H_2O}$ sarmp = sarcosinato-*N*-propionate	6	[38]
$\mathrm{NH_4[Ti(EDTA-3H)(O_2)] \cdot 2H_2O}$	7	[18]			
$\mathrm{[Sr(H_2O)_7][Ti(EDTA-4H)(O_2)] \cdot H_2O}$	7	[19]	$\mathrm{[Co(ebp)][Co(EDTA-4H)] \cdot 5H_2O}$ ebp = diamino-3,3,8,8-tetramethyl-4,7-dithia-1,10-decanedioate	6	[39,40]
$\mathrm{K[VO(EDTA-3H)] \cdot 3H_2O}$	6	[20]			
$\mathrm{[VO(phen)_2][VO(EDTA-4H)] \cdot 11H_2O}$	6	[21]			
$\mathrm{[Mg(H_2O)_6][Mn(EDTA-4H)(H_2O)] \cdot 2H_2O}$	7	[22]	$\mathrm{[Co(mida)(dien)][Co(EDTA-4H)] \cdot 2H_2O}$ mida = *N*-methyliminodiacetate dien = 3-azapentane-1,5-diamine	6	[41]
$\mathrm{Na_2[Mn(EDTA-4H)(H_2O)] \cdot 5H_2O}$	7	[22]			
$\mathrm{Rb_2[Mn(EDTA-4H)(H_2O)] \cdot 3H_2O}$	7	[22]			
$\mathrm{[Mn(H_2O)_4][Mn(EDTA-4H)(H_2O)] \cdot 4H_2O}$	7	[22]	$\mathrm{[Co(EDTA-2H)(dmg)] \cdot H_2O}$ dmg = dimethylglyoximate	6	[42]
$\mathrm{(NH_2NH_3)_3[Mn(EDTA-4H)(H_2O)]NO_3 \cdot H_2O}$	7	[23]			
$\mathrm{C(NH_2)_3[Mn_2(EDTA-4H)_2] \cdot 6H_2O}$	7	[24]	$\mathrm{[Co(EDTA-3H)(NH_3)]}$	6	[43]
$\mathrm{Na_4[Mn(EDTA-4H)(H_2O)](ClO_4)_2 \cdot 6H_2O}$	7	[25]	$\mathrm{Na[Ba_6(H_2O)_{25}][Co(EDTA-4H)]_4(ClO_4)_9 \cdot 5H_2O}$	6	[44]
$\mathrm{La_2(H_2O)_8[Mn(EDTA-4H)(H_2O)_3]_3 \cdot 12H_2O}$	7	[26]	$\mathrm{NaBa_2[Co(EDTA-4H)]_2(ClO_4)_3 \cdot 9H_2O}$	6	[45]
$\mathrm{Ba[Fe(EDTA-4H)(H_2O)]_2 \cdot 4H_2O}$	7	[27]	$\mathrm{Na[Co(EDTA-3H)] \cdot H_2O}$	6	[46]
$\mathrm{NH_2NH_3[Fe(EDTA-4H)(H_2O)]}$	7	[28]	$\mathrm{[Pt(NH_3)_4][Co(EDTA-3H)]_2 \cdot 2H_2O}$	6	[47]
$\mathrm{\{NH(CH_2CH_2OH)_3\}_6H_{10}[(SiMo_{12}O_{40}) \subset Mo_{24}\{Fe(EDTA-4H)\}_{12}O_{72}] \cdot 129H_2O}$	7	[29]	$\mathrm{Mn(H_2O)_4[Ni(EDTA-4H)] \cdot 2H_2O}$	6	[48]
			$\mathrm{Na[Ni(EDTA-3H)] \cdot 3H_2O}$	6	[49]
$\mathrm{\{NH(CH_2CH_2OH)_3\}_7K_2H_9[(P_2W_{18}O_{62}) \subset Mo_{24}\{Fe(EDTA-4H)\}_{12}O_{72}] \cdot 116H_2O}$	7	[29]	$\mathrm{[Ni(EDTA-3H)(NH_2NH_3)] \cdot 2H_2O}$	6	[50]
			$\mathrm{Mn(H_2O)_4[Cu(EDTA-4H)] \cdot 2H_2O}$	6	[48]
$\mathrm{NH_4[Fe(EDTA-4H)(H_2O)] \cdot 3H_2O}$	7	[30,31]	$\mathrm{[Cu(EDTA-2H)] \cdot CO(NH_2)_2 \cdot H_2O}$	6	[51]
$\mathrm{Na_{15}[(PMo_{12}O_{40}) \subset Mo_{24}\{Fe(EDTA-4H)\}_{12}O_{72}] \cdot 90H_2O}$	7	[32]	$\mathrm{\{Cu(EDTA-4H)\}_2(bpy)Cu(OH)\text{-}Cu(H_2O)(OH)\{Cu(bpy)_3\}_2 \cdot 2H_2O}$ bpy = 4,4'-bipyridine	6	[52]
$\mathrm{Na_{16}[(Mo_{12}O_{36}(HPO_3)_2(H_2O)_6) \subset Mo_{24}\{Fe(EDTA-4H)\}_{12}O_{72}] \cdot 85H_2O}$	7	[32]	$\mathrm{[Cu_2(EDTA-4H)(3\text{-}PyOH)_2]}$ Py = pyridine	5	[53]
$\mathrm{Na_{18}[(P_2W_{18}O_{62}) \subset Mo_{24}\{Fe(EDTA-4H)\}_{12}O_{72}] \cdot 100H_2O}$	7	[32]	$\mathrm{Er(H_2O)_4\{Cu_2(H_2O)_2\}\{Cu(EDTA-4H)\text{-}(H_2O)\}_2] \cdot 3ClO_4 \cdot 5H_2O}$	6	[54]
$\mathrm{Li(H_2O)_3[Fe(EDTA-4H)]}$	6	[33]			
$\mathrm{[Fe(EDTA-3H)(H_2O)] \cdot 3/2H_2O}$	7	[34]	$\mathrm{[Cu(EDTA-2H)(H4abim)] \cdot 3/2H_2O}$ H4abim = 4-azabenzimidazole	6	[55]
$\mathrm{\{NH(CH_2CH_2OH)_3\}_{14}Na_{10}K_8H_8[(NaP_5W_{30}O_{110})_2 \subset Mo_{22}\{Fe(EDTA-4H)\}_8O_{68}(H_2O)_2] \cdot 50H_2O}$	7	[35]	$\mathrm{K[Cu(EDTA-3H)]}$	6	[56]
$\mathrm{[Co(ntb)Cl][Co(EDTA-4H)] \cdot 3H_2O}$ ntb = *N*,*N*,*N*-tris(2-benzimidazolylmethyl)amine	6	[36]	$\mathrm{[Cu_2(EDTA-4H)(Him)_2] \cdot 2H_2O}$ Him = imidazole	5	[57]
$\mathrm{Gd_2(H_2O)_8[Co(EDTA-4H)]_3 \cdot 9.5H_2O}$	7	[37]	$\mathrm{[Zn(EDTA-2H)(H_2O)] \cdot 2H_2O}$	7	[58]

の配位数および配位座数を以前にまとめた（野口 2022b; 2023b）[3,8]．{$C(NH_2)_3$}$_4$[Ca(EDTA−4H)]$_2$·8H_2Oの結晶構造（Flörke & Meier 2016）[9]が CCDC に登録されているのを最近になって追加的に確認した（図 2）．

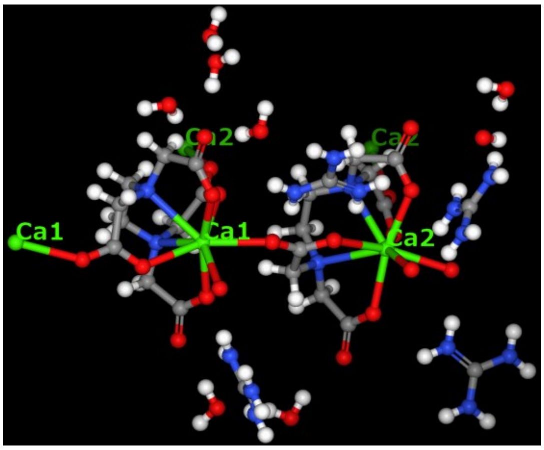

図 2 {$C(NH_2)_3$}$_4$[Ca(EDTA-4H)]$_2$·8H_2O の結晶構造[9].

土類金属-EDTA キレートの結晶構造とその配位数および配位座数も以前にまとめていた（野口 2022c）[10]．エチレンジアミン四酢酸一水素イオンと水がアルミニウムイオンに配位した[Al(EDTA−3H)(H_2O)]の結晶構造（Ilyukhin & Petrosyants 2001）[11]が新たに確認された．インジウム-EDTA 錯体は 6 種類をまとめていたが，今回新たに(H_2en)[In(EDTA−4H)(H_2O)]$_2$·4H_2O [12]，Na(H_2O)[In(EDTA−4H)(H_2O)]·H_2O [13]および K[In(EDTA−4H)(H_2O)]·10/3H_2O [14]の 3 種類を追加で確認した．

14 族半金属元素-EDTA の結晶構造もまとめたが（野口 2023c）[15]，その後，EDTA アニオンが配位した有機スズ(IV)錯体[{$Sn(CH_3)_2$}$_2$(EDTA−4H)(H_2O)$_2$]·H_2O の結晶構造（Aizawa et al. 1996）[16]（のちに Marsh et al.（2002）が空間群を訂正している[17]）（図 3）が報告されていたのを最近になって追加的に確認した．他の Sn(IV)-EDTA はいずれも単核錯体であるため，EDTA 架橋による二核錯体の例として，構造的に興味深い．

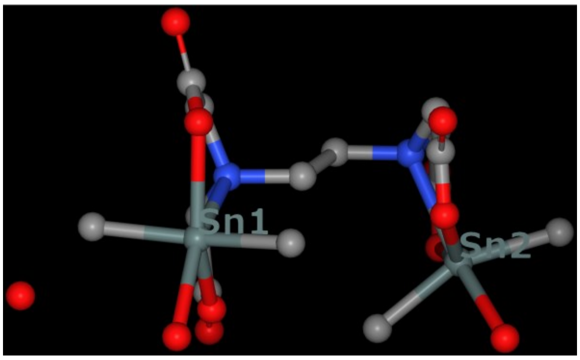

図 3 [$(SnMe_2)_2$(EDTA−4H)$(H_2O)_2$]·H_2O の結晶構造[17].

なお，高周期 15 族元素であるアンチモンやビスマスの EDTA キレートについては，以前の報告（野口 2023b）[8]で扱われなかった組成を有する結晶のデータは，新たには確認されなかった．

ここまで，先述した非キレート性の EDTA 銀塩を除き，主要族金属-EDTA キレートの結晶構造を扱った．次は，遷移金属-EDTA キレートの結晶構造の追加事例を見ていこう．中心金属がチタン，バナジウム，マンガン，鉄，コバルト，ニッケル，銅，亜鉛の各種 EDTA キレートが，新たに確認された．大雑把には，チタンからマンガンまでの第一系列前期遷移金属の EDTA キレートでは，EDTA アニオンに加えて水分子や陰イオン由来の原子がさらに配位した配位数 7 の錯体が比較的多い．もっとも，V-EDTA の場合，4 価であるバナジウムの配位数は 6 である．4 価のバナジウムではイオン半径が 2 価や 3 価のものに比べて小さくなり，配位数が低下するのだろう．

一方，鉄から銅の第一系列後期遷移金属の EDTA キレートでは，配位数 6 が多い傾向がみられる．原子番号の増大に伴って中心金属イオンの半径がわずかではあるが小さくなることが，配位数の低下に寄与している一つの要因として推測される．また，Zn-EDTA 錯体のうち，配位構造や対カチオンの異なる結晶構造 10 種類（配位数 5 が一種類，配位数 6 が七種類，配位数 7 が二種類）は既に報告していたが（野口 2023d）[59]，その後，結晶構造が CCDC へ登録された配位数 7 のキレートが新たに確認された（Semenov et al. 2023）[58]．配位数 5 および 6 の Cu^{2+}のイオン半径は 0.65 Å から 0.73 Å なのに対し，同じ配位数の場合の Zn^{2+}のイオン半径は 0.68 Å から 0.74 Å と Cu^{2+}より少し大きいとされており（Shannon 1976）[60]，この些細な違いが異なる配位数をもつ傾向に反映されていると考えられる．

最後に，紙幅の都合によりここでは詳述できないが，第二･三系列遷移金属 EDTA キレートも簡潔に示す（表 2）．この系列では，以前にもまとめたように（野口 2023e）[93]，配位数 6 の二核錯体を形成しているものが特にモリブデン錯体で散見されるほか，配位数が 6 を超えるものについては，第七の配位子をさまざまにすることで，多様な構造体が合成されてきたことが明らかである．EDTA キレートの結晶構造全体を網羅した総説は，Porai-Koshits & Polynova（1985）[94]を最後に久しく見当たらない．こうした多様な配位構造を引き続き調査･整理すれば，新たな知見を導けるだろう．

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表 2 CCDC へのデータ登録を新たに確認した EDTA 錯体の化学式，配位数（CN）および参考文献（表 1 の続き）

(6) 第二系列遷移金属キレート	CN	Ref		CN	Ref
$\{C(NH_2)_3\}_3[YF_2(EDTA-4H)]\cdot H_2O$	8	[61,62]	$[Ru(EDTA-3H)(Htrz)]\cdot 4H_2O$	6	[78]
$\{C(NH_2)_3\}_2[ZrF_2(EDTA-4H)]\cdot 3/2H_2O$	8	[63]	Htrz = 1H-1,2,4-triazole		
$\{C(NH_2)_3\}_2[Zr(EDTA-4H)(CO_3)]\cdot 4H_2O$	8×2	[64]	$[\{Ru(EDTA-3H)\}_2(NC_4H_4N)]\cdot 8H_2O$	6×2	[79]
$Na_3[Zr(EDTA-4H)(H_2O)_2]_2[Cr(OH)_6Mo_6O_{18}]\cdot 10H_2O$	8	[65]	$[\{Ru(EDTA-3H)\}_2(bpy)]\cdot 2H_2O$	6×2	[80]
$(NH_4)_2\{(CH_3)_4N\}_6[Zr_2(EDTA-2H)(\alpha\text{-}HSiW_{11}O_{39})_2]\cdot 26H_2O$	8×2	[66]	$[Ru(EDTA-2H)(2,5\text{-}Pydc)]\cdot 3H_2O$	6	[81]
syn-$K_2[Mo_2O_4S(EDTA-4H)]\cdot H_2O$	6×2	[67]	2,5-Pydc = 5-carboxypyridine-2-carboxylate		
syn-$Na_2[Mo_2O_2S_2(EDTA-4H)]\cdot 2H_2O$	6×2	[68]	$[Ru(EDTA-3H)(4\text{-}ptz)]\cdot 4H_2O$	6	[81]
syn-$Na_2[Mo_2O_2S_2(EDTA-4H)]\cdot 3H_2O$	6×2	[68]	4-ptz = 5-(4-pyridyl)tetrazole		
syn-$Na_2[Mo_2O_4(EDTA-4H)]\cdot 3H_2O$	6×2	[68]	$[PdBr_2(EDTA)]\cdot 5H_2O$	6	[82]
syn-$Na_2[Mo_2O_4(EDTA-4H)]\cdot 4H_2O$	6×2	[68]	$Mg[Cd(EDTA-4H)]\cdot 9H_2O$	(7)	[83]
syn-$Ba[Mo_2O_4(EDTA-4H)]\cdot 6H_2O$	6×2	[68]	$[Cd(EDTA-2H)(Hdatrz)_2]$	6	[84]
syn-$Ca_3[Mo_4S_4(EDTA-4H)_2]\cdot 26H_2O$	6×4	[69,70]	Hdatrz = 3,5-diamino-1,2,4-triazole		
syn-$Na_2[Mo_4S_4(EDTA-4H)_2]\cdot 6H_2O$	6×4	[70,71]	$[Eu(H_2O)_4]_2[Cd(EDTA-4H)(H_2O)]_3\cdot 14H_2O$	7	[85]
syn-$Mg_2[Mo_4S_4(EDTA-4H)_2]\cdot 20H_2O$	6×4	[70,71]	$[Sm(H_2O)_4]_2[Cd(EDTA-4H)(H_2O)]_3\cdot 14H_2O$	7	[85]
syn-$Na_{5/2}H_{1/2}[Mo_4Se_4(EDTA-4H)]\cdot 10H_2O$	6×4	[72]	$H_2dap[Cd(EDTA-3H)(H_2O)]\cdot H_2O$	7	[86]
syn-$[Fe(H_2O)_6][Mo_2O_4(EDTA-4H)]\cdot 5H_2O$	7×2	[73]	$H_2dap = H_2(N3,N7)\text{-}2,6\text{-diaminopurinium}$		
syn-$(NH_4)_2[Mo_2O_2S_2(EDTA-4H)]\cdot 3.5H_2O$	6×2	[74]	$[Cd(Him)(H_2O)_2][Cd(EDTA-4H)(Him)]\cdot H_2O$	7	[87]
syn-$[Ni(H_2O)_6][Mo_2O_2S_2(EDTA-4H)]\cdot 2H_2O$	6×2	[75]	$[Cd(H9heade)(H_2O)][Cd(EDTA-4H)(H_2O)]\cdot 2H_2O$	7	[87]
$[RuCl_2(EDTA-H)]\cdot 4H_2O$	6	[76]	H9heade = 9-(2-hydroxyethyl)adeninium		
$Na(H_3O)[RuCl_2(EDTA-2H)]_2\cdot 8H_2O$	6	[77]			
(7) 第三系列遷移金属キレート					
syn-$Ba[W_2O_2(\mu\text{-}O)(\mu\text{-}S)(EDTA-4H)]\cdot 6.5H_2O$	7×2	[88]	$Na_3[HgCl(EDTA-4H)]\cdot 6H_2O$	7	[91]
anti-$K_2(NH_4)_2[W_2O_6(EDTA-4H)]\cdot 4H_2O$	6×2	[89]	$[Hg_2(EDTA\text{-}2H)_2\{(C_7H_6N_2)_2C_4H_8\}]\cdot 2CH_3OH$	6	[92]
$[PtCl_2(EDTA)]\cdot 5H_2O$	4	[90]			

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