

後期第一系列遷移金属-EDTA キレート の比較構造解析

野口大介*

Comparative structural analysis of late first-row transition metal-EDTA chelates

by

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Based on the data available in Cambridge Crystallographic Data Centre (CCDC), the crystal structures of late first-row transition metal-complexes chelated by ethylenediaminetetraacetic acid (EDTA) are overviewed. Herein, it is summarized that the crystal structures of 17 of Fe^{III}-EDTA, 6 of Fe^{II}-EDTA, 21 of Co^{III}-EDTA, 14 of Co^{II}-EDTA, 13 of Ni-EDTA, 22 of Cu-EDTA, and 7 of Zn-EDTA complexes (total 100 kinds) have coordination numbers (CN) ranging from 5 to 7, most have CN = 6 (70/100), and the denticities of these chelates are tetra-, penta-, and hexadentate. In analytical chemistry, typically learned complexes of hexadentate and CN = 6 are found to be only 33 cases (ca. 33%), not major species in the late first-row transition metal-EDTA complexes, following up on the former review.

Key words: D-block, Denticity, Sexidentate ligand, Transition elements, X-ray crystallography.

1. はじめに

エチレンジアミン四酢酸 (EDTA) はキレート滴定法などに用いられる代表的な六座配位子の一つである (図 1)。例えば, キレート滴定法を説明した 1950 年代の『Journal of Chemical Education』掲載の Martell (1952) [1]によると, Ca-EDTA レートや Zn-EDTA キレートは, EDTA アニオンが六座配位子として各金属イオンにキレートした典型的な六配位・八面体構造で示されている。また, Johnston et al. (1958) [2]や斎藤 (1957)[3]においても, 二価の陽イオンの EDTA キレートが同様の構造で表記されている。このように, 分析化学では, 金属-EDTA キレートの構造が基本的に六配位・八面体構造として半世紀以上前から学ばれてきた。

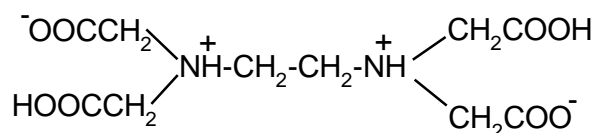


図 1 エチレンジアミン四酢酸 (EDTA) の双性イオン。

ただし, 金属-EDTA 錯体の構造が X 線結晶構造解析によって決定されたのは 1959 年であったため (斎藤 1967) [4], 1950 年代に示されていた EDTA キレートの立体構造は, それら自体の直接的な X 線結晶構造解析によるものでないことが明白である。その後 1960 年代になると, (当時の) 最新の研究結果を踏まえ, 『EDTA 錯体の立体化学は, これまで考えられていたような簡単なものではないことがしだいに明らかにされつつある』, 『EDTA が五座配位子となって, 一配位座を他の配位子に譲るか, または EDTA は六座配位のままで中心金属の配位数が増加して 7~10 にまでなる』と説明されるようになった (新村 1965) [5]。しかしその一方で, Chang (2010) [6]のように, キレート滴定の解説において, 依然として典型的な六配位・八面体構造のみで説明する状況が, 今日に至るまで続いている。

筆者はこれまでに既報の結晶構造解析研究に基づき, 主要族元素の金属-EDTA 錯体の配位数と配位座数を一覧にした (野口 2023) [7]。引き続き, 本稿では後期第一系列遷移金属-EDTA 錯体の配位数と配位座数を調査したため, その結果を報告する。

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2. 結果と考察

表 1 に Fe^{III}-EDTA, Fe^{II}-EDTA, Co^{III}-EDTA, Co^{II}-EDTA, Ni-EDTA, Cu-EDTA, Zn-EDTA について結晶構造データ (cif ファイル) がケンブリッジ結晶学データセンター (CCDC) に登録され, 正常に開くことができたものの化学式, 配位数, 配位座数および文献をまとめた. cif ファイルが正常に開けなかったものとして, 例えば [Mn(H₂O)₄Ni(EDTA-4H)]·2H₂O (Solans et al. 1983) [52] などがあり, そうしたものは適宜省いた.

Stezowski & Hoard (1984) [99] はかつて, 46 種類の重金属-EDTA キレート結晶の結晶構造データをまとめた. そのうち後期第一系列遷移金属-EDTA 錯体は 21 種類であった. だが今回の調査では, 17 種類の Fe^{III}-EDTA, 6 種類の Fe^{II}-EDTA, 21 種類の Co^{III}-EDTA, 14 種類の Co^{II}-EDTA, 13 種類の Ni-EDTA, 22 種類の Cu-EDTA そして 7 種類の Zn-EDTA の計 100 種類となる結晶構造を確認できた. 配位数 6 の錯体が 70 種類と全体のおよそ 70% を占め, 残りは配位数 5 や 7 であった. これ

表 1 第一系列後期遷移金属-EDTA キレートの化学式, 配位数, 配位座数, 文献

(1) Fe ^{III} -EDTA 錯体							
化学式	配位数	配位座数	文献	化学式	配位数	配位座数	文献
Rb[Fe(EDTA-4H)(H ₂ O)]·H ₂ O	7	6	[8]	(C ₂ H ₅) ₄ N[Fe(EDTA-4H)(H ₂ O)]·2H ₂ O	7	6	[17]
Li[Fe(EDTA-4H)(H ₂ O)]·2H ₂ O	7	6	[8,9]	(CH ₂ NH ₃) ₂ [Fe(EDTA-4H)(H ₂ O)] ₂ ·6H ₂ O	7	6	
[Fe(EDTA-3H)(H ₂ O)]	6	5	[10,11]	[Cu(en) ₂][Fe(EDTA-4H)] ₂ ·2H ₂ O	6	5	[18]
Li[Fe(EDTA-4H)]·3H ₂ O	6	6	[12]	[Ni(H ₂ O) ₆][FeCl(EDTA-3H)] ₂ ·4H ₂ O	6	5	[19]
H ₂ N=C(NH ₂) ₂ [Fe(EDTA-4H)(H ₂ O)]·2H ₂ O	7	6	[13]	K[Fe(EDTA-3H)(Cl)]·H ₂ O	6	5	[20]
Na[Fe(EDTA-4H)(H ₂ O)]·2H ₂ O	7	6	[14-16]	K[Fe(EDTA-4H)(H ₂ O)]·1.5H ₂ O	7	6	
Ag[Fe(EDTA-4H)(H ₂ O)]·2H ₂ O	7	6		SrFe(EDTA-4H)Cl·5H ₂ O	7	6	[21]
K[Fe(EDTA-4H)(H ₂ O)]·H ₂ O	7	6	[15]	Na ₁₅ [(H ₆ FeMo ₆ O ₂₄) ₂ Cl ₂ Mo ₂₄ -Fe ₁₂ (EDTA-4H) ₁₂ O ₇₂]·80H ₂ O	7	6	[22]
Tl[Fe(EDTA-4H)(H ₂ O)]·H ₂ O	7	6					
(2) Fe ^{II} -EDTA 錯体							
Na ₂ [Fe(EDTA-4H)(H ₂ O)]·2NaClO ₄ ·6H ₂ O	7	6	[23]	(NH ₄) ₂ [Fe(EDTA-4H)(H ₂ O)]·3H ₂ O	7	6	[26]
[Fe(H ₂ O) ₄][Fe(EDTA-3H)(H ₂ O)] ₂ ·4H ₂ O	7	6	[24,25]	Fe(H ₂ O) ₂ [Fe(NO)(EDTA-3H)] ₂	7	6	[27]
[Fe(EDTA-2H)(H ₂ O)]·2H ₂ O	7	6	[24]	Cs ₂ [Fe(EDTA-4H)(H ₂ O) ₃]·H ₂ O	7	6	[28]
(3) Co ^{III} -EDTA 錯体							
acac=acetylacetonate, Py=pyridine, sarmp= sarcosinate- <i>N</i> -propionato acac=acetylacetonate							
NH ₄ Co(EDTA-4H)]·2H ₂ O	6	6	[29]	[Mg(H ₂ O) ₆][Co(EDTA-4H)] ₂ ·4H ₂ O	6	6	[40]
[Co(sarmp)(NH ₃) ₃]-[Co(EDTA-4H)(H ₂ O)]	6	6	[30]	[Ca(H ₂ O) ₇][Co(EDTA-4H)] ₂	6	6	
[Co(EDTA-2H)(en)]ClO ₄ ·3H ₂ O	6	4	[31]	[Co(EDTA-3H)]·2H ₂ O	7	6	[41]
[Co(EDTA-3H)H ₂ O]·3H ₂ O	6	5	[32]	K ₄ [Co(H ₂ O) ₆][Co(C ₁₀ H ₁₂ N ₂ O ₈) ₂][β-Mo ₈ O ₂₆]·6H ₂ O	6	6	[42]
[Co(EDTA-2H)(en)]Cl·3H ₂ O	6	4	[33]	H ₃ O[Co(EDTA-3H)CN]·H ₂ O	6	5	[43]
Co ₂ (EDTA-4H)·2H ₂ O	6	5	[34]	Sr[Co(EDTA-4H)] ₂ ·9H ₂ O	6	6	[44]
[Co(EDTA-2H)(acac)]·H ₂ O	6	4	[35]	Ba[Co(EDTA-4H)] ₂ ·8H ₂ O	6	6	
Ba[Co(EDTA-4H)(SCN)]	6	5	[36]	[Co(EDTA-3H)]·2H ₂ O	6	5	[45]
[Co(en) ₃][Co(EDTA-4H)] ₂ ·Cl·10H ₂ O	6	6	[37,43]	K[Co(EDTA-4H)]·2H ₂ O	6	6	[46]
[Co(EDTA-3H)Py]·2H ₂ O	6	5	[38]	[Co(sep)][Co(EDTA-4H)]Cl ₂ ·2H ₂ O	6	6	[47]
Ca[Co(EDTA-3H)(CN)] ₂ ·6H ₂ O	6	5	[39]	sep = 1,3,6,8,10,13,16,19- octaazabicyclo[6.6.6]icosane			
(4) Co ^{II} -EDTA 錯体							
Ca[Co(EDTA-4H)(H ₂ O)]·4H ₂ O	6	5	[48,49]	Sr[Co(EDTA-3H)(H ₂ O)] ₂ ·4H ₂ O	6	5	[56]

[Co(H ₂ O) ₄ Co(EDTA-4H)]·2H ₂ O	6	6	[50]	Sr[Co(EDTA-4H)(H ₂ O)]·4H ₂ O	6	5	[57]
[Co(EDTA-2H)(H ₂ O)]·2H ₂ O	7	6	[51]	[Na ₆ (Co(EDTA-4H)) ₂ (H ₂ O) ₁₃]·(H ₂ SiW ₁₂ O ₄₀)·xH ₂ O	6	6	[58]
[Mn(H ₂ O) ₄ Co(EDTA-4H)]·2H ₂ O	6	6	[52]	[Co(EDTA-4H)(H ₂ O)] ₂ ·(SiW ₁₂ O ₄₀)·15H ₂ O	6	5	[59]
[Co(H ₂ O) ₆][Co(EDTA-3H)(H ₂ O)] ₂ ·2H ₂ O	6	5	[53]	Na _{2n} [Co(EDTA-4H)] _n ·4nH ₂ O	6	5	[50]
Gd ₂ Co ₃ (EDTA-4H) ₃ (H ₂ O) ₁₁ ·12H ₂ O	7	6	[54]	[Sr(H ₂ O) ₈][Co(EDTA-4H)] ₂ ·H ₂ O	6	6	[60]
Ce ₂ Co ₃ (EDTA-4H) ₃ (H ₂ O) ₁₁ ·12H ₂ O	7	6	[55]				
Ca[Co(EDTA-3H)(H ₂ O)] ₂ ·4H ₂ O	6	5	[56]				
(5) Ni-EDTA 錯体							
[Ni(EDTA-2H)(H ₂ O)]	6	5	[61,62]	[Ni(en) ₃][Ni(EDTA-4H)]·4H ₂ O	6	6	[69]
[Ni(H ₂ O) ₆][Ni(EDTA-3H)(H ₂ O)] ₂ ·2H ₂ O	6	5	[63]	Ni ₂ (EDTA-4H)(H ₂ O) ₄ ·2H ₂ O	6	6	[70]
[Cu(en) ₂][Ni(EDTA-4H)]·2H ₂ O	6	6	[64]	Li[Ni(EDTA-3H)]·2H ₂ O	6	5	[71]
[Cu(en) ₂][Ni(EDTA-4H)]·4H ₂ O	6	6	[65]	[Zn(H ₂ O) ₄ Ni(EDTA-4H)]·2H ₂ O	6	6	[72]
Li[Ni(EDTA-3H)(H ₂ O)]·H ₂ O	6	5	[66]	Ca[Ni(EDTA-3H)(H ₂ O)] ₂ ·4H ₂ O	6	5	[73]
Ni ₂ (en)(EDTA-4H)·4H ₂ O	6	6	[67]	{(PW ₁₂ O ₄₀)·[Na ₂ Ni(EDTA-2H)(H ₂ O)(EDTA)(H ₂ O)] ₂ ·2H ₂ O·H ₃ O} _n	6	6	[74]
Ca[Ni(EDTA-4H)]·4H ₂ O	6	6	[68]				
(6) Cu-EDTA 錯体							
[Cu(EDTA-2H)(H ₂ O)]	6	5	[75]	(AdeH ₂)[Cu(EDTA-3H)(H ₂ O)]·2H ₂ O	6	5	[85]
K ₂ [Cu(EDTA-4H)]·3H ₂ O	6	6	[76]	[Cu(EDTA-2H)]	6	5	[86]
[Cu ₂ (EDTA-4H)(H ₂ O)] ₂ ·2H ₂ O	5×2	(6)	[77]	[Cu ₂ (EDTA-4H)(Py) ₂ (H ₂ O)] ₂ ·2H ₂ O	5×2	(6)	[87]
[Mn(H ₂ O) ₄ Cu(EDTA-4H)]·2H ₂ O	6	6	[52]	[Cu(Im) ₆]{Cu(Im) ₄ [Cu(EDTA-4H)(Im)] ₂ }·6H ₂ O	5×2	(6)	[88]
Ca[Cu(EDTA-4H)]·4H ₂ O	6	5	[68,78]	Na ₄ (OH)[Cu ₂ (EDTA-4H)PW ₁₂ O ₄₀]·17H ₂ O	5×2	(6)	
Cu ₂ (en) ₂ (EDTA-4H)·6H ₂ O	6	6	[79]	Na ₄ [Cu ₂ (EDTA-4H)SiW ₁₂ O ₄₀]·19H ₂ O	5×2	(6)	[89]
[Zn(H ₂ O) ₄ Cu(EDTA-4H)]·2H ₂ O	6	6	[72,80]	[N ₂ H ₅ Cu(EDTA-3H)]·H ₂ O	6	5	
SrCu(EDTA-4H)·4H ₂ O	6	5	[81]	Gd(H ₂ O) ₄ {Cu ₂ (H ₂ O) ₂ } ₂ {Cu(EDTA-4H)(H ₂ O) ₂ } ₂ ·3ClO ₄ ·5H ₂ O	6	5	[90]
BaCu(EDTA-4H)·4H ₂ O	6	5	[81]	[Cu ₂ (EDTA-4H)(9heade) ₂ (H ₂ O) ₄]·3H ₂ O	5×2	(6)	[91]
Ag[Cu(EDTA-3H)(H ₂ O)]·H ₂ O	6	5	[82]	{[Cu ₄ (phen) ₄ (OH) ₄ (H ₂ O) ₂]-[Cu(EDTA-4H)] ₂ } _n ·14H ₂ O	6	6	[92]
Mg[Cu(EDTA-4H)]·6H ₂ O	6	6	[83]				
Ba ₂ [Cu(EDTA-4H)](ClO ₄) ₂ ·6H ₂ O	6	6	[84]				
(7) Zn-EDTA 錯体							
[Zn ₂ (EDTA-4H)]·6H ₂ O	6	6	[93]	[Zn ₂ (EDTA-4H)(H ₂ O)]	6	5	[96]
[Mg(H ₂ O) ₄ Zn(EDTA-4H)] _n ·2nH ₂ O	6	6	[52]	[PbZn(EDTA-4H)]·H ₂ O	7	6	[97]
[Zn ₃ (EDTA-3H) ₂ (H ₂ O) ₆]	6	5	[94]	(H ₂ N) ₂ C=NH ₂ [Zn(EDTA-4H)]ClO ₄ ·H ₂ O	6	6	[98]

らのうち、Fe-EDTA キレートでは配位数 7 のものが多いことが見てとれる。特に、Fe²⁺に EDTA アニオンが配位している場合、EDTA アニオンが六座配位して 7 つ目の配位座を水分子などが占めており、すべて配位数 7 である。一方、Ni-と Cu-EDTA キレートでは配位数 7 のものはなく、Cu-EDTA の場合は、単核錯体のみならず、EDTA アニオンが Cu²⁺に対して 1:2 で結合した、エチレンジアミン部位についてシス型となった二核錯体があるのが特徴的である。そして Zn-EDTA キレートの結晶構造を確認した限り、EDTA が『配位数

4 の Zn²⁺に対しては四座配位子として 1:1 で結合し』(村上 2015) [100] (下線は筆者による)とした化学教育誌掲載記事の記述とは裏腹に、調べられた範囲では、Zn²⁺の配位数は 5 から 7 であり EDTA アニオンが四座配位子から六座配位子として結合している。

3. まとめ

後期第一系列遷移元素の金属-EDTA 錯体について、Stezowski & Hoard (1984) [99]で総説された数を大きく上回る計 100 種類の結晶中における配位数と配位座

数をまとめた。キレート滴定法で学ばれることの多い典型的な六座・6配位構造のものは全体の約33%にとどまった。他にCu-EDTAではEDTA:Cu²⁺=1:2の二核錯体が複数あることや、結晶中におけるZn-EDTAキレートは配位数5~7, EDTAアニオンの配位座数は四座から六座までであり、キレート滴定法を解説した化学教育誌の記述(配位数4・四座配位)(村上2015)[100]は誤りである可能性が高いことなども確認できた。主要族元素の金属-EDTAキレートの配位構造の比較(野口2023)[7]に引き続いて、後期第一系列遷移金属-EDTAキレートにおける構造多様性が再び示されたと考えている。

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