

EPISODIC KNOWLEDGE ON FIRST AND FOREMOST
CRYSTALLINE STRUCTURAL REPORT OF
ETHYLENEDIAMINETETRAACETIC ACID

D. NOGUCHI *

Graduate School of Integrated Science and Technology, Nagasaki University, Japan

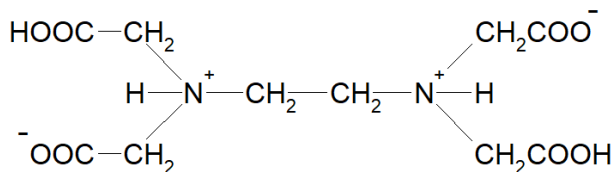
An investigation into the precise ethylenediaminetetraacetic acid (EDTA) crystalline structural report was initiated, as there appeared to be some ambiguity regarding the accurate notation of EDTA as a neutral molecule or a zwitterion. As a result, the first and foremost article reporting EDTA in zwitterionic form was determined after a difficult confirmation. Additionally, crystallographic data of the zwitterionic EDTA itself and non-chelated salts thereof registered on the CCDC were also mentioned herein. This episodic knowledge will be fundamental for not only chemical education but also related science and technology in the future.

<https://doi.org/10.46991/PYSUB.2024.58.3.166>

Keywords: analytical chemistry, chelator, polyaminocarboxylic acid.

Introduction. Ethylenediaminetetraacetate (EDTA; 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo)tetraacetate) is a commonly learned chelator in analytical chemistry owing to its ability to form stable metal complexes with four carboxylate groups (R-COO^-) and two tertiary amino groups (R-NR'R'') thereof. However, the accurate notation of EDTA itself appears somewhat ambiguous. This would be because there was a controversy about the chemical structure of EDTA itself around the middle of the 20th century [1, 2]. The one group interpreted EDTA as a neutral molecule [3–5], whereas the other group interpreted it as a zwitterion; i.e. $\text{HOOCCH}_2(\text{OOCCH}_2)\text{NH}^+\text{CH}_2\text{CH}_2\text{NH}^+(\text{CH}_2\text{COO}^-)\text{CH}_2\text{COOH}$ [6–8]. Even afterwards, there are still some textbooks of analytical chemistry that describe it as not a zwitterion, but a neutral molecule [9]. Precise understanding and revealing the historical origin of the chemical structure of EDTA itself should be significant not only for chemical educators, but also for scientific researchers. Therefore, I have investigated and analyzed the reported crystal structures of both zwitterionic EDTA themselves and its non-chelating salts; 27 entries have been demonstrated recently [10]. But at that time, the first and foremost article reporting the crystal structure of EDTA had not yet been determined. Eventually, according to a difficult task to confirm, it was found that the first and foremost crystal structure of EDTA was reported with zwitterionic fashion by Lu & Shao in 1961 and 1962 [11, 12] (see Scheme).

* E-mail: a.chemist.noguchi.d@gmail.com



Materials and Methods. Information as to crystal compounds at Cambridge Crystallographic Data Centre (CCDC) have been searched through the Internet.

Subsequently, Cotrait in 1972 reported another data of the crystal structure of EDTA with R index written in French [13]. Cotrait (1972) cited the above-mentioned article as “Tsin L.Y. & Chen S.M. (1962). Acta Sci. Sin. p. 469”. The journal name thereof is misleading; “Acta Sci. Sin.” is inaccurate, because “Acta” was unnecessary, and another confusing journal of “Acta Chim. Sin.” also exists. Moreover, the volume number was not included. Later, the further crystal structure of EDTA itself was also reported by Ladd & Povey (1973) [14], citing the aforementioned paper as “Lu Y. & Shao M. (1962) Sci. Sin. II, 469”. As you know by now, they mistaken the volume number “XI” for II!!! These incomplete citations are seemed like another reason for losing the worth of the first-reported invaluable knowledge. When Shkol’nikova & Porai-Koshits (1990) [15] reviewed the structures of uncharged, anionic, and cationic aminoalkylcarboxylic complexones including EDTA, the studies by Lu & Shao (1960, 1961) [11, 12] were not referenced, despite the fact that they were “Russian” scholars. Here should be also emphasized that none

of them ever mentioned the actual first and foremost report by Lu & Shao (1961) [11], even though posterior “Chinese” researchers, who rediscovered and deposited the crystal structural data of EDTA itself on the CCDC [16].

Further information shall be introduced. I also found additional entries of the non-chelation salts of EDTA such as $[\text{Mg}(\text{H}_2\text{O})_6](\text{EDTA}-2\text{H})$ by Tinnemans in 2023 [17], and two entries of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2(\text{EDTA}-2\text{H})$ and $\{(\text{HOCH}_2)_3\text{CNH}_3\}_2(\text{EDTA}-2\text{H})\cdot 3\text{H}_2\text{O}$ by Semenov et al. in 2023 [18] through this investigational process. Moreover, I found a crystal structure reporting $\text{Ag}(\text{EDTA}-3\text{H})$ [19]. Accordingly, a total of 34 entries related to EDTA themselves and non-chelating salts thereof were ensured after my previous work [20]. These existing data of the crystalline structures of zwitterionic EDTA itself and its non-chelational salts are expected to be valuable for both chemical education and materials science and engineering afterwards.

Conclusion. The first and foremost crystalline structural reports exhibiting an exact zwitterionic EDTA itself have provided valuable insights into its history in chemistry. However, the bibliographic data of this monumental article reported by Lu & Shao written in Russian was misinterpreted when registered in the CCDC, and subsequent studies also erroneously cited. This episodic knowledge would be of significance for not only science education, but also advanced research in the near future.

This work is an updated version of my preprint in EdArXiv. The language of the draft was edited using Paperpal, recruited by the NU’s Academic Support Office.

The author thanks the partial funding received from the Research Grant of NU WISE Programme for Global Health (2024).

Received 19.07.2024

Reviewed 19.09.2024

Accepted 10.10.2024

REFERENCES

1. Chapman D., Lloyd D.R., Prince R.H. An Infrared and Nuclear Magnetic Resonance Study of the Nature of Ethylenediaminetetra-acetic Acid and Some Related Substances in Solution: Hydrogen Bonding in α -Amino-polycarboxylic Acid Systems. *J. Chem. Soc. (Resumed)* (1963), 3645–3658. <https://doi.org/10.1039/JR9630003645>
2. Martynenko L.I., Pechurova N.I., et al. Infrared Spectroscopy Investigation of the Structure of Ethylenediaminetetraacetic Acid and Its Salts. *Russ Chem. Bull.* **19** (1970), 1172–1177. <https://doi.org/10.1007/BF00852653>
3. Busch D.H., Bailar J.C.Jr. The Stereochemistry of Complex Inorganic Compounds. XVII. The Stereochemistry of Hexadentate Ethylenediaminetetraacetic Acid Complexes. *J. Am. Chem. Soc.* **75** (1953), 4574–4575. <https://doi.org/10.1021/ja01114a054>
4. Chapman D. The Infrared Spectra of Ethylenediaminetetra-acetic Acid and Its Di- and Tetrasodium Salts. *J. Chem. Soc. (Resumed)* (1955), 1766–1769. <https://doi.org/10.1039/JR9550001766>
5. Langer H.G. Infrared Spectra of Ethylenediaminetetraacetic Acid (EDTA). *Inorg. Chem.* **2** (1963), 1080–1081. <https://doi.org/10.1021/ic50009a057>

6. Schwarzenbach G., Ackermann H., Komplexone V. Die Äthylendiamin-tetraessigsäure (Complexone V. The Ethylenediamine-tetraacetic Acid). *Helv. Chim. Acta* **30** (1947), 1798–1804 (in German).
<https://doi.org/10.1002/hlca.19470300649>
7. Nakamoto K., Morimoto, Y., Martell A.E. Infrared Spectra of Aqueous Solutions. III. Ethylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic Acid and Diethylenetriaminepentaacetic Acid. *J. Am. Chem. Soc.* **85** (1963), 309–313.
<https://doi.org/10.1021/ja00886a014>
8. Sawyer D.T., Tackett J.E. Properties and Infrared Spectra of Ethylenediaminetetraacetic Acid Complexes. IV. Structure of the Ligand in Solution. *J. Am. Chem. Soc.* **85** (1963), 314–316.
<https://doi.org/10.1021/ja00886a015>
9. Noguchi D. Confusion in the Notation of the Chemical Structure of EDTA: Molecule or Zwitterion? *J. Technol. Educ.* **28** (2021), 27–36.
<https://doi.org/10.13140/RG.2.2.25433.33120>
10. Noguchi D. Analysis of Specialties of Crystal Structure for Non-chelate Conformations of Ethylene-diaminetetraacetic Acid and Its Salts with Alkali and Alkaline Earth Metals. *Ukr. Chem. J.* **88** (2022), 55–69 (in Japanese).
<https://doi.org/10.33609/2708-129X.88.10.2022.55-69>
11. Lu Y., Shao M. The Crystal Structure of Ethylenediaminetetra Acetic Acid. *Acta Phys. Sin.* **17** (1961), 304–309 (in Chinese).
<https://doi.org/10.7498/aps.17.304>
12. Lu Y., Shao M. Определение кристаллической структуры этилендиамина четырех-уксусной кислоты (Determination of the Crystal Structure of Ethylenediamine Tetra-acetic Acid). *Sci. Sin.* **11** (1962), 469–476 (in Russian).
<https://doi.org/10.1360/ya1962-11-4-469>
13. Cotrait M. Structure Cristalline d'un Sel Birubidique de l'EDTA (Crystal Structure of an EDTA Dirubidium Salt). *Acta Cryst. B* **26** (1970), 1152–1161 (in French).
<https://doi.org/10.1107/S0567740870003758>
14. Ladd M.F.C., Povey D.C. Crystallographic and Spectroscopic Studies on Ethylenediamine-tetraacetic Acid (Edta) I. Crystal and Molecular Structure of β -Edta. *J. Cryst. Mol. Struct.* **3** (1973), 15–23.
<https://doi.org/10.1007/BF01270899>
15. Shkol'nikova L.M., Porai-Koshits M.A. Structure of the Uncharged, Anionic, and Cationic Forms of Aminoalkylcarboxylic and Aminoalkylphosphonic Complexones. *Russ. Chem. Rev.* **59** (1990), 40–43.
<https://doi.org/10.1070/RC1990v059n07ABEH003548>
16. Wang J., Zhang X., et al. Investigation on the Coordinate Structures of the Rare Earth Metal Complexes with Edta and Cydta Ligands. *Wuhan Univ. J. Nat. Sci.* **8** (2003), 1131–1137.
<https://doi.org/10.1007/BF02903686>
17. Tinnemans P. CCDC 2241171: Experimental Crystal Structure Determination. *CSD Commun.* (2023).
<https://doi.org/10.5517/ccdc.csd.cc2f73vn>
18. Semenov V.V., Zolotareva N.V., et al. Complexes of Ethylenediaminetetraacetic Acid with Amines. Molecular Structures of Bis(monoethanolaminium) Ethylenediaminetetraacetate and Bis[tris(hydroxymethyl)methylaminium] Ethylenediaminetetraacetate Trihydrate. *Crystallogr. Rep.* **68** (2023), 247–258.
<https://doi.org/10.1134/S1063774523020141>
19. Wimmer A., Urstoeger A., et al. Separating Dissolved Silver from Nano-Particulate Silver is the Key: Improved Cloud-point-extraction Hyphenated to Single Particle ICP-MS for Comprehensive Analysis of Silver-Based Nanoparticles in Real Environmental Samples Down to Single-digit nm Particle Sizes. *Anal. Chim. Acta* **1150** (2021), 238198.
<https://doi.org/10.1016/j.aca.2021.01.001>
20. Noguchi D. Episodic Knowledge on First and Foremost Crystal Structural Report of Ethylenediaminetetraacetic Acid (EDTA) Itself. *EdArXiv* (2024).
<https://doi.org/10.35542/osf.io/n9jf4>

Դ. ՆՈԳՈՒՉԻ

ԴՐՎԱԾՔԱՅԻՆ ԳԻՏԵԼԻՔ ԷԹԻԼԵՆԴԻԱՄԻՆՏԵՏՐԱՔԱՑԱԽԱԹԹՎԻ
ԲՅՈՒՐԵՂԱՅԻՆ ԿԱՌՈՒՑՎԱԾՔԻ ՎԵՐԱԲԵՐՅԱԼ ԱՌԱՋԻՆ ԵՎ
ՀԻՄՆԱԿԱՆ ՀԱՂՈՐԴՄԱՆ ՄԱՍԻՆ

Նախաձեռնվել է հետազոտություն էթիլենդիամինտետրաքալաթթվի (EDTA) բյուրեղային կառուցվածքի ներկայացման վերաբերյալ, քանի որ, ըստ երևույթին, որոշակի երկիմաստություն կար՝ կապված EDTA-ի ճշգրիտ նշման հետ՝ որպես չեզոք մոլեկուլի կամ ցվիտերիոնի: Արդյունքում, դժվար հաստատումից հետո հայտնաբերված է առաջին և հիմնական հոդվածը, որտեղ EDTA-ն ներկայացված է որպես ցվիտերիոնային ձև: Բացի այդ, այստեղ նշված են նաև ցվիտերիոնային EDTA-ի և դրա ոչ քելատային աղերի բյուրեղային կառուցվածքի տվյալները, որոնք գրանցված են CCDC-ում: Այս էպիզոդիկ գիտելիքները ապագայում հիմնարար նշանակություն կունենան ոչ միայն քիմիական կրթության, այլ նաև հարակից գիտության և տեխնոլոգիայի համար:

Д. НОГУЧИ

ЭПИЗОДИЧЕСКИЕ ЗНАНИЯ О ПЕРВОМ И ГЛАВНОМ ОТЧЕТЕ
О КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ
ЭТИЛЕНДИАМИНТЕТРАУКСУСНОЙ КИСЛОТЫ

Было начато исследование отчета о кристаллической структуре этилендиаминтетрауксусной кислоты (ЭДТА), поскольку, по-видимому, существовала некоторая двусмысленность относительно точного обозначения ЭДТА как нейтральной молекулы или цвиттер-иона. В результате после сложного подтверждения приводится первая и главная статья, сообщающая об ЭДТА как о цвиттер-ионной форме. Кроме того, здесь также упоминаются кристаллографические данные самой цвиттер-ионной ЭДТА и ее нехелатированных солей, зарегистрированных в Кембриджском центре кристаллографических данных. Эти эпизодические знания будут иметь основополагающее значение не только для химического образования, но и для смежных наук и технологии в будущем.