

# ANALYSIS OF SPECIALTIES OF CRYSTAL STRUCTURE FOR NON-CHELATE CONFORMATIONS OF ETHYLENE-DIAMINETETRAACETIC ACID AND ITS SALTS WITH ALKALI AND ALKALINE EARTH METALS

*Daisuke Noguchi*

*Division of Education and Research Support, Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, 8528521Nagasaki, Japan.*

*Email: a.chemist.noguchi.d@gmail.com*

In the present study, the crystal structures of non-chelating EDTA molecules and their non-chelation salts in a zwitterionic state, along with the EDTA-chelates of alkali and alkaline earth metals, were searched and overviewed. 25 non-chelating molecules of EDTA, and zwitterions of ethylenediammonium-diacetate diacetic acid  $\text{HOOC-CH}_2\text{-}(\text{OOC-CH}_2\text{-})\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{CH}_2\text{-COO}^-)\text{-CH}_2\text{-COOH}$  and their salts (ethylenediammonium-tetraacetic acid  $(\text{HOOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{CH}_2\text{-COOH})_2$ , ethylenediammonium-acetate triacetic acid  $(\text{HOOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{CH}_2\text{-COO}^-)\text{-CH}_2\text{-COOH}$ , and ethylenediammonium-tetraacetate  $(\text{OOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{CH}_2\text{-COO}^-)_2$  with counterions), as well as 17 types of EDTA-chelates of alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ) and alkaline earth metal ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) were analyzed using data from the Cambridge Crystallographic Data Center (CCDC). Each intramolecular contact distance between nitrogen and oxygen atoms ( $\text{NH}^+\cdots\text{O}$ ) has been examined and found to be around 2.7 Å. Investigation on the distribution of the intramolecular  $\text{NH}^+\cdots\text{NH}^+$ -distances of EDTA and non-chelated salts thereof also revealed that bulky counterion and certain crystal solvent molecules correspond to change in crystal packing, and that they influenced the conformers of EDTA molecules among gauche form to anti form. In the existing crystalline EDTA-chelates of alkali metals as well as alkaline earth metals, various coordination numbers (CN) and the denticity ( $\kappa$ ) of EDTA anions are displayed; CN 5 to 9, and tri- and hexadentate fashions. Intramolecular contact  $\text{N}\cdots\text{O}$  and  $\text{N}\cdots\text{N}$  distances correspond to the metal ion radii except for the case of Sr-EDTA chelate, probably due to differences of crystal packings in addition to the number of counterions and crystal solvent molecules. The existing data on crystalline EDTA and its salts have been gathered herein, which contributes to a further understanding and exploring applications hereafter.

**Keywords:** CCDC, EDTA, Hydrogen bonding, X-ray crystallography.

**INTRODUCTION.** Ethylenediaminetetraacetic acid (EDTA; abbreviated as  $\text{H}_4\text{Y}$ ) is widely known as a common chelator and well characterized as metal-chelates. Not just EDTA-chelates but EDTA itself and dozens of its existing non-chelating conformational salts of

inorganic acids, bases, alkali metals, and alkaline earth metals have been reported with crystal data so far. However, the structural systematization of other remaining EDTA species unlike the EDTA-chelates of heavy metals has rarely been documented, despite a recently

found function such as their unusual luminescence activity. Ethylenediaminetetraacetic acid (EDTA; Fig. 1), a typical chelating agent that forms complexes with various metal ions, has been given attention for molecular biology, chemical industry, and materials engineering (e.g., Blaurock-Busch 2016) [1]. Thus far, the crystalline structural studies of EDTA have been focused on chelate complexes with various metal ions (Lee 1972, Porai-Koshits et al. 1974, Nuttall & Stalker 1977, Stezowski & Hoard 1984, Davidovich 2005, Stavila et al. 2006, Wang et al. 2010, Noguchi 2022a) [2–9]. The crystal structures of non-chelating EDTA molecules have also been investigated in preceding studies; however, they are not well summarized compared to the large variety of existing heavy metal chelates of EDTA. Therefore, this study focused on a structural point of view, and conformations, including potential hydrogen-bonded contact nitrogen and oxygen atomic distances were overviewed utilizing crystallographic data deposited in the Cambridge Crystallographic Data Centre (CCDC).

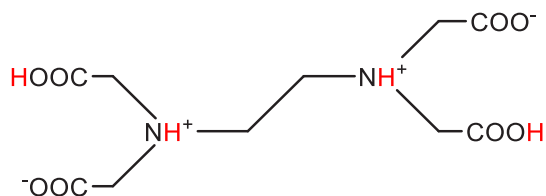


Fig. 1. Zwitterionic EDTA molecule ( $=H_4Y$ ).

*INVESTIGATION AND DISCUSSION OF THE RESULTS.* Based on the cif files available in the Cambridge Structural Database (Groom et al. 2016) [10], information on non-chelating zwitterionic EDTA molecules and their salts were summarized in Table 1 and shown in Fig. 2. 25 kinds of crystalline compounds were hit by searching; however, three cif files of CCDC Nos. 1148821, 1148825, and 1148828 could not be opened by crystal structure viewing software; Mercury 1.4.2. (build 2); i.e., crystal structure visualisation, exploration and analysis free-software. By checking the 22 kinds' cif files of the other by Mercury freeware, the distribution of intramolecular  $NH^+ \cdots O$  distances of non-chelate conformational zwitterions of EDTA and salts thereof was demonstrated in Table 2 and Fig. 3.

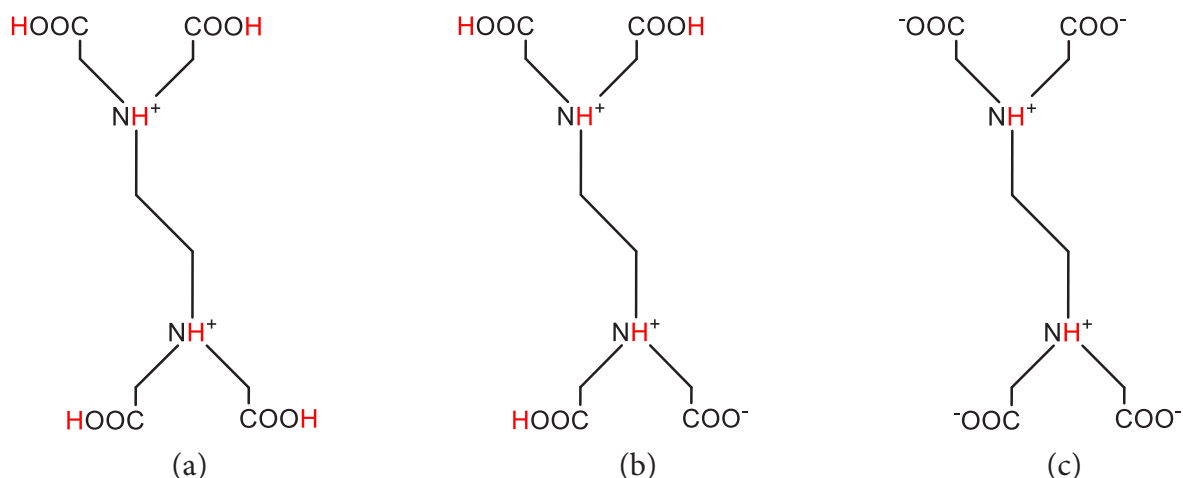


Fig. 2. Non-chelate conformational EDTA zwitterions in salts thereof; (a) ethylenediammonium-tetraacetic acid ( $(HOOC-CH_2)_2NH^+-CH_2-CH_2-NH^+(-CH_2-COOH)_2$  ( $=H_6Y^{2+}$ ), (b) ethylenediammonium-acetate triacetate ( $(HOOC-CH_2)_2NH^+-CH_2-CH_2-NH^+(-CH_2-COO^-)-CH_2-COOH$  ( $=H_5Y^+$ ), (c) ethylenediammonium-tetraacetate ( $(^-\text{OOC}-CH_2)_2NH^+-CH_2-CH_2-NH^+(-CH_2-COO^-)_2$  ( $=H_2Y^{2-}$ ).

Table 1

Non-chelating zwitterionic EDTA molecules and their salts with reported crystal structures (type, entry number, chemical formula, CCDC number, and references).

Type	Entry No.	Chemical Formula	CCDC No.	Ref.
$H_2EDTA^{2+}$ ( $H_6Y^{2+}$ )	1*	EDTA·2HCl·3H <sub>2</sub> O	657759	Kaluderović et al. 2007 [11]
	2*	EDTA·2HCl·3H <sub>2</sub> O	1163542	Mistryukov et al. 1987 [12]
	3	EDTA·H <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	1300053	Shkol'nikova et al. 1993 [13]
HEDTA <sup>+</sup> ( $H_5Y^+$ )	4	EDTA·HBr·H <sub>2</sub> O	1283049	Shkol'nikova et al. 1989 [14]
EDTA ( $H_4Y$ )	5	EDTA·0.39H <sub>2</sub> O	1101398	Ladd et al. 1974 [15]
	6*	EDTA	1148825	Lu & Shao 1962 [16]
	7*	EDTA	1148826	Cotrait 1972 [17]
	8*	EDTA	1148827	Ladd & Povey 1973 [18]
	9*	EDTA	1148828	Wang et al. 2003 [19]
	10	(H <sub>3</sub> O)Na <sub>2</sub> [Ni(EDTA-2H)] PW <sub>12</sub> O <sub>40</sub> ·EDTA·5H <sub>2</sub> O	1433251	Xiao et al. 2016 [20]
[EDTA-2H] <sup>2-</sup> ( $H_2Y^{2-}$ )	11	[Mn(H <sub>2</sub> O) <sub>6</sub> ][EDTA-2H]	285809	Ma & Niu 2003 [21]
	12	N <sub>2</sub> H <sub>5</sub> [EDTA-2H]	656243	Ragul et al. 2015 [22]
	13	(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> [EDTA-2H]	656246	
	14	Sr <sub>2</sub> [EDTA-2H]Cl <sub>2</sub> ·5H <sub>2</sub> O	686018	Polyakova et al. 2009 [23]
	15	Sr <sub>2</sub> [EDTA-2H](HCO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	686020	
	16	{HC <sub>3</sub> N <sub>3</sub> (NH <sub>2</sub> ) <sub>3</sub> } <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	741062	Vella-Zarb et al. 2014 [24]
	17*	K <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	838146	Krawczyk & Lis 2011 [25]
	18**	Na <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	1020814	Fronczek 2014 [26]
	19	(NH <sub>4</sub> )(N <sub>2</sub> H <sub>5</sub> )[EDTA-2H]·NH <sub>3</sub> ·2H <sub>2</sub> O	1033967	Sivasankar & Sonia 2015 [27]
	20	[Mg(H <sub>2</sub> O) <sub>6</sub> ][EDTA-2H]	1103464	Julian et al. 1973 [28]
	21	Rb <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	1147983	Cotrait 1970 [29]
	22*	K <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	1148821	Cotrait 1969 [30]
	23	Ca[EDTA-2H]·2H <sub>2</sub> O	1166578	Zabel et al. 2006 [31]
24**	Na <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	1171161	Font-Bardia et al. 1993 [32]	
25	Na <sub>2</sub> [Te(OH) <sub>6</sub> ][EDTA-2H]·2H <sub>2</sub> O	1309261	Cisarova et al. 1995 [33]	
26*	K <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	1968403	Meier & Massa 2019 [34]	
27**	Na <sub>2</sub> [EDTA-2H]·2H <sub>2</sub> O	2051489	Zheng et al. 2021 [1]	

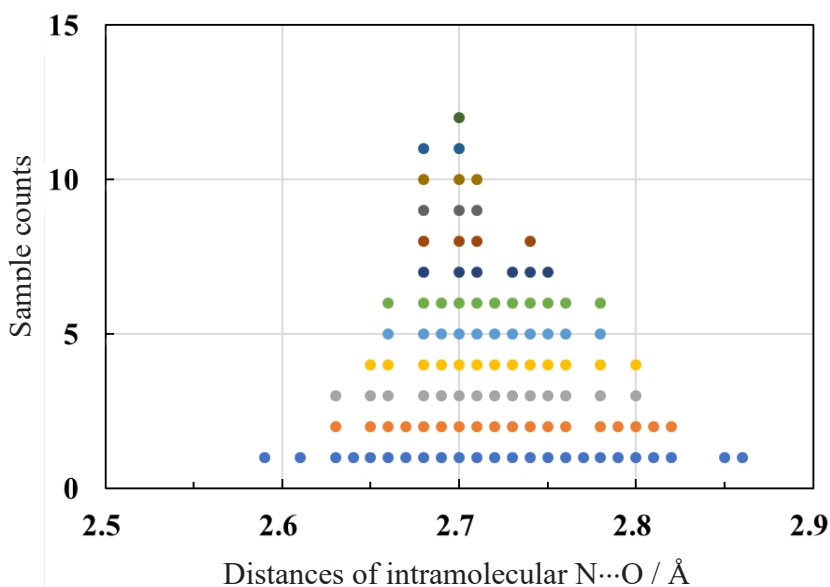


Fig. 3. Intramolecular hydrogen-bonded  $\text{NH}^+\cdots\text{O}$  distances of non-chelating zwitterionic EDTA molecules and their salts vs. sample counts of each hydrogen bonds.

Intramolecular distances between one ammonium-nitrogen atom and another ( $\text{NH}^+\cdots\text{NH}^+$ ) within every zwitterionic EDTA mole-

cule including its salt were also surveyed by checking cif files and shown in Table 2 (right) and Fig. 4.

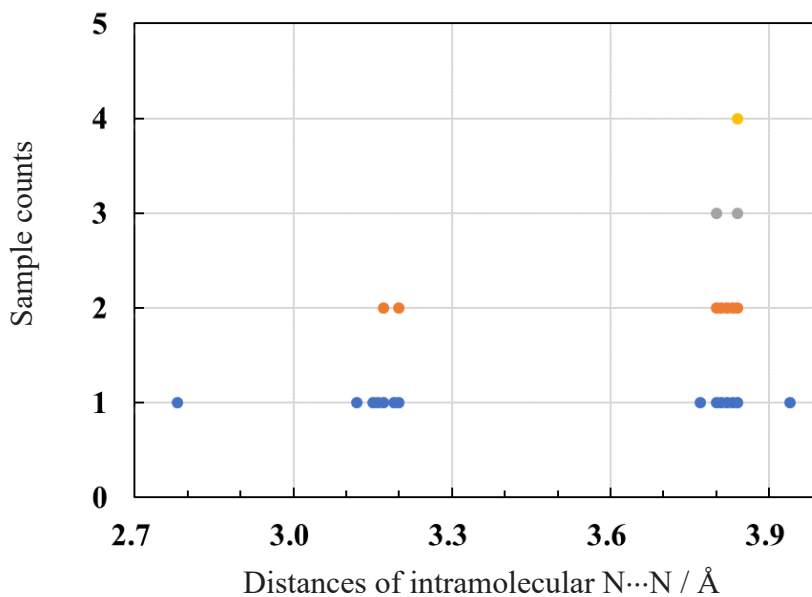


Fig. 4. Intramolecular  $\text{NH}^+\cdots\text{NH}^+$  distances of non-chelating zwitterionic EDTA molecules and their salts vs. sample counts.

Table 2  
**Intramolecular hydrogen-bonded ammonium-nitrogen and oxygen atomic (NH<sup>+</sup>...O), as well as one ammonium-nitrogen and other ammonium-nitrogen atomic (NH<sup>+</sup>... NH<sup>+</sup>) distances of non-chelating conformational EDTA zwitterions according to data available in CCDC.**

Entry	NH <sup>+</sup> ...O distances / Å						NH <sup>+</sup> ... NH <sup>+</sup> distances / Å	CCDC No.
1	2.684	2.689	2.822	2.684	2.689	2.822	3.163	657759
2	2.671	2.689	2.699	2.716			3.935	1163542
3	2.705	2.737	2.705	2.737			3.839	1300053
4	2.647	2.648	2.700	2.718			3.809	1283049
5	2.679	2.680	2.796	2.679	2.680	2.796	3.121	1101398
6							No data	1148825
7	2.682	2.748	2.788	2.682	2.748	2.788	3.195	1148826
8	2.675	2.751	2.780	2.675	2.751	2.780	3.199	1148827
9							No data	1148828
10	2.664	2.701	2.813	2.860			2.783	1433251
11	2.661	2.698	2.661	2.698			3.795	285809
12	2.699	2.710	2.699	2.710			3.840	656243
13	2.696	2.705	2.696	2.705			3.838	656246
14	2.757	2.780					3.837	686018
15	2.692	2.755	2.692	2.755			3.803	686020
16	2.698	2.723	2.698	2.723			3.820	741062
17	2.675	2.687	2.700	2.742	2.803		3.171	838146
18	2.739	2.751	2.739	2.751			3.830	1020814
19	2.674	2.727	2.762	2.728	2.780	2.800	3.192	1033967
20	2.660	2.708	2.660	2.708			3.803	1103464
21	2.592	2.612	2.632	2.633			3.772	1147983
22							No data	1148821
23	2.654	2.713	2.717	2.735	2.776	2.853	3.154	1166578
24	2.733	2.733	2.733	2.733			3.818	1171161
25	2.627	2.650	2.709	2.769			3.809	1309261
26	2.661	2.716	2.726	2.745	2.779	2.806	3.171	1968403
27	2.737	2.758	2.737	2.758			3.828	2051489

In terms of  $\text{NH}^+\cdots\text{NH}^+$  distances, there seem to be two groups; i.e., below  $3.3\text{ \AA}$  and above  $3.7\text{ \AA}$ . EDTA molecules have *gauche*-conformations within ethylenediamine moieties if  $\text{NH}^+\cdots\text{NH}^+$  distances are below  $3.3\text{ \AA}$ , whereas in the cases of  $\text{NH}^+\cdots\text{NH}^+$  distances distributing around  $3.8\text{ \AA}$ , they have *anti*-conformations (Fig. 5).

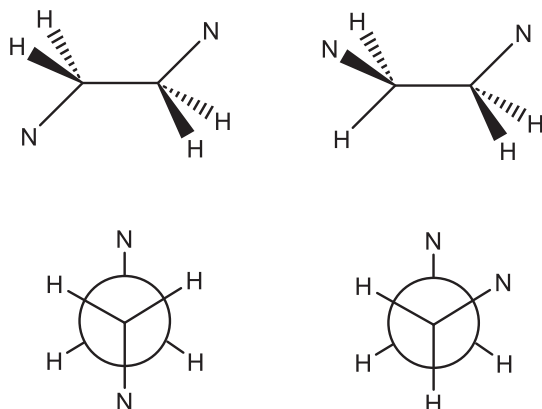


Fig. 5. *Anti*-conformer (left) and *gauche*-conformer (right) within an ethylenediamine moiety of EDTA (acetic acid groups are omitted for clarity).

If there are no other species neighboring the EDTA itself, *anti*-forms are more stable than *gauche*-forms due to the intra/inter-molecular repulsive forces. However, in certain cases, crystal packings stabilize *gauche*-EDTA rather than *anti*-EDTA, and the effect allows the existence of a small number of *gauche*-forms. Amongst the intramolecular  $\text{NH}^+\cdots\text{NH}^+$  distances, a noticeably short distance ( $2.783\text{ \AA}$ ) with a torsion angle of  $47.82^\circ$  of  $\varphi_{\text{N-C-C-N}}$  (indeed, typical angle is  $60^\circ$  for the *gauche* form) is characteristic of the EDTA molecule of CCDC No. 1433251 drawn in Fig. 6. In this case, except for the EDTA molecule itself, additional species such as “ $(\text{H}_3\text{O})\text{Na}_2[\text{Ni}(\text{EDTA}-2\text{H})]\text{PW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$ ”, including phosphododecatungstate  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , known as heteropolyacid salts having Keggin structure, is much larger than any other cases. Accordingly, it seems that the crystal packing by species except for EDTA molecules could strongly change intramolecular interactions in crystals.

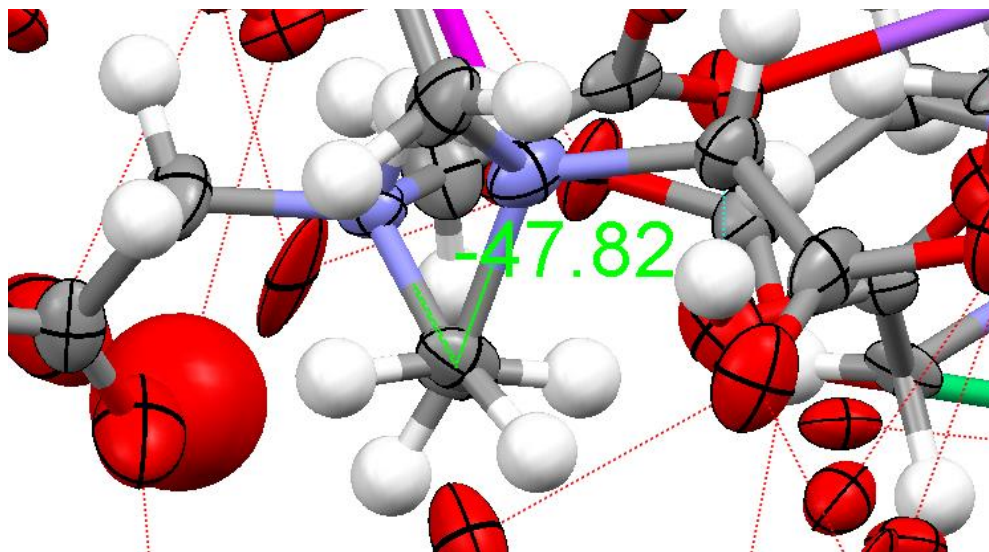


Fig. 6. *Gauche*-conformer of EDTA (torsion angle  $47.82^\circ$ ) in  $(\text{H}_3\text{O})\text{Na}_2[\text{Ni}(\text{EDTA}-2\text{H})]\text{PW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$  by ellipsoids of carbon (grey), nitrogen (blue), oxygen (red) (50% probability, respectively) with hydrogen (white sphere) (Xiao et al. 2016) [20].

It would be significant to analyze the dependence of the change in the intramolecular distances of N...O and N...N atoms on the value of the crystal radius in a series of alkali metals as well as alkaline earth metals; herein, nitrogen atom is coordinated to a metal ion. In order to compare with the cases of non-chelate

EDTA and salts thereof, crystal data of EDTA-chelates of alkali metals besides alkaline earth metals have been also searched for and displayed in Table 3. The intramolecular distances of nitrogen and oxygen atoms (N...O) were summarized in Table 4.

Table 3

**Type, Entry No., chemical formula, CCDC numbers of, and references to EDTA-chelates of alkali metals as well as alkaline earth metals with reported crystal structures.**

Type	Entry No.	Chemical Formula	CCDC No.	Ref.
[EDTA-3H] <sup>3-</sup> (HY <sup>3-</sup> )	28	[K <sub>3</sub> (EDTA-3H)]·2H <sub>2</sub> O	838147	Krawczyk & Lis 2011 [25]
[EDTA-4H] <sup>4-</sup> (Y <sup>4-</sup> )	29	[Ni(Phen) <sub>3</sub> ][Ba(EDTA-4H)(H <sub>2</sub> O) <sub>2</sub> ].12H <sub>2</sub> O Phen = 1,10-phenanthroline	196670	Sadikov et al. 2002 [38]
	30	[Ni(Phen) <sub>3</sub> ][Ca(EDTA-4H)(H <sub>2</sub> O) <sub>2</sub> ].10.5H <sub>2</sub> O	196671	Antsyshkina et al. 2002 [39]
	31	[Sr <sub>2</sub> (EDTA-4H)].5H <sub>2</sub> O	686019	Polyakova et al. 2009 [23]
	32	[Ba <sub>2</sub> (EDTA-4H)]	765935	Chen et al. 2010 [40]
	33*	[Ba <sub>2</sub> (EDTA-4H)].2.5H <sub>2</sub> O	765936	
	34	[Li <sub>4</sub> (EDTA-4H)].2H <sub>2</sub> O	809471	Cheng et al. 2013 [41]
	35	[K <sub>4</sub> (EDTA-4H)].3.92H <sub>2</sub> O	838148	Krawczyk & Lis 2011 [25]
	36*	[Ba <sub>2</sub> (EDTA-4H)].2.5H <sub>2</sub> O	1104933	Shao 1979 [42]
	37	[Ca <sub>2</sub> (EDTA-4H)].7H <sub>2</sub> O	1148812	Barnett et al. 1979 [43]
	38	[Co(NH <sub>3</sub> ) <sub>6</sub> ][Na(EDTA-4H)].3.5H <sub>2</sub> O	1148813	Schlemper 1977 [44]
	39	[Na <sub>4</sub> (EDTA-4H)].5H <sub>2</sub> O	1171162	Font-Bardia et al. 1993 [32]
	40	[Mg(H <sub>2</sub> O) <sub>6</sub> ][Mg(H <sub>2</sub> O)(EDTA-4H)].2H <sub>2</sub> O	1211677	Passer et al. 1977 [45]
	41	[Mg(H <sub>2</sub> O) <sub>6</sub> ][Mg(H <sub>2</sub> O)(EDTA-4H)].2H <sub>2</sub> O	1211678	Pozhidaev et al. 1974a [46]
	42	Na <sub>2</sub> [Mg(EDTA-4H)(H <sub>2</sub> O)].3H <sub>2</sub> O	1211717	Pozhidaev et al. 1974b [47]
	43	Na <sub>2</sub> [Mg(EDTA-4H)(H <sub>2</sub> O)].5H <sub>2</sub> O	1216509	Stezowski et al. 1973 [48]
	44	Sr[Ca(EDTA-4H)].5H <sub>2</sub> O	1286595	Arriortua et al. 1992 [49]

Table 4

Intramolecular distances of nitrogen and oxygen atoms (N...O) and one nitrogen and another nitrogen atom (N...N) of chelating alkali metal- and alkaline earth metals-EDTA complexes according to cif files available in CCDC.

Entry	N...O distances / Å				N...N distances / Å	CCDC No.
28	2.636	2.646	2.838	2.841	2.951	838147
29	2.725	2.742	2.747	2.747	3.054	196670
30	2.694	2.723	2.769	2.789	2.978	196671
31	2.706	2.731	2.745	2.762	3.019	686019
32	2.781	2.826	2.781	2.826	3.801	765935
33	2.711	2.749	2.750	2.767	2.998	765936
34	2.705	2.762	2.705	2.762	3.788	809471
35	2.777	2.795	2.826	2.828	3.040	838148
	2.784	2.791	2.780	2.862	3.078	
36	2.638	2.965	2.655	2.826	2.961	1104933
37	2.722	2.794	2.813	2.836	2.951	1148812
38	2.766	2.815	2.766	2.815	3.062	1148813
39	2.697	2.738	2.750	2.865	2.923	1171162
40	2.687	2.767	2.687	2.767	2.888	1211677
41	2.692	2.754	2.692	2.754	2.879	1211678
42	No data					1211717
43	2.675	2.679	2.675	2.679	2.906	1216509
44	2.684	2.698	2.706	2.711	2.953	1286595

The distribution of distances of intramolecular nitrogen and oxygen atoms (N...O) and nitrogen-nitrogen atoms (N...N) of these chelates listed in Table 4 is shown in Fig 7 and Fig. 8, except for  $\text{Na}_2[\text{Mg}(\text{EDTA}-4\text{H})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$  (Pozhidaev et al. 1974b) [47] because of being unavailable for checking 3D structure by the cif file (CCDC No. 1211717).

Averaged intramolecular N...O distances in EDTA-chelates of every metal are as follow: 2.734 Å of  $\text{Li}-\text{Y}([\text{Li}_4(\text{EDTA}-4\text{H})]\cdot 2\text{H}_2\text{O}$ , CCDC No. 809471), 2.777 Å of  $\text{Na}-\text{Y}$

( $[\text{Co}(\text{NH}_3)_6][\text{Na}(\text{EDTA}-4\text{H})]\cdot 3.5\text{H}_2\text{O}$ , 1148813;  $[\text{Na}_4(\text{EDTA}-4\text{H})]\cdot 5\text{H}_2\text{O}$ , 1171162), 2.805 Å of  $\text{K}-\text{Y}([\text{K}_4(\text{EDTA}-4\text{H})]\cdot 3.92\text{H}_2\text{O}$ , 838148), 2.709 Å of  $\text{Mg}-\text{Y}([\text{Mg}(\text{H}_2\text{O})_6][\text{Mg}(\text{H}_2\text{O})(\text{EDTA}-4\text{H})]\cdot 2\text{H}_2\text{O}$ , 1211677; 1211678;  $\text{Na}_2[\text{Mg}(\text{EDTA}-4\text{H})(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O}$ , 1216509), 2.745 Å of  $\text{Ca}-\text{Y}([\text{Ni}(\text{Phen})_3][\text{Ca}(\text{EDTA}-4\text{H})(\text{H}_2\text{O})_2]\cdot 10.5\text{H}_2\text{O}$ , 196671;  $[\text{Ca}_2(\text{EDTA}-4\text{H})]\cdot 7\text{H}_2\text{O}$ , 1148812;  $\text{Sr}[\text{Ca}(\text{EDTA}-4\text{H})]\cdot 5\text{H}_2\text{O}$ , 1286595), 2.736 Å of  $\text{Sr}-\text{Y}([\text{Sr}_2(\text{EDTA}-4\text{H})]\cdot 5\text{H}_2\text{O}$ , 686019), and 2.765 Å of  $\text{Ba}-\text{Y}([\text{Ni}(\text{Phen})_3][\text{Ba}(\text{EDTA}-4\text{H})(\text{H}_2\text{O})_2]\cdot 12\text{H}_2\text{O}$ , 196670;  $[\text{Ba}_2(\text{EDTA}-4\text{H})]$ ,



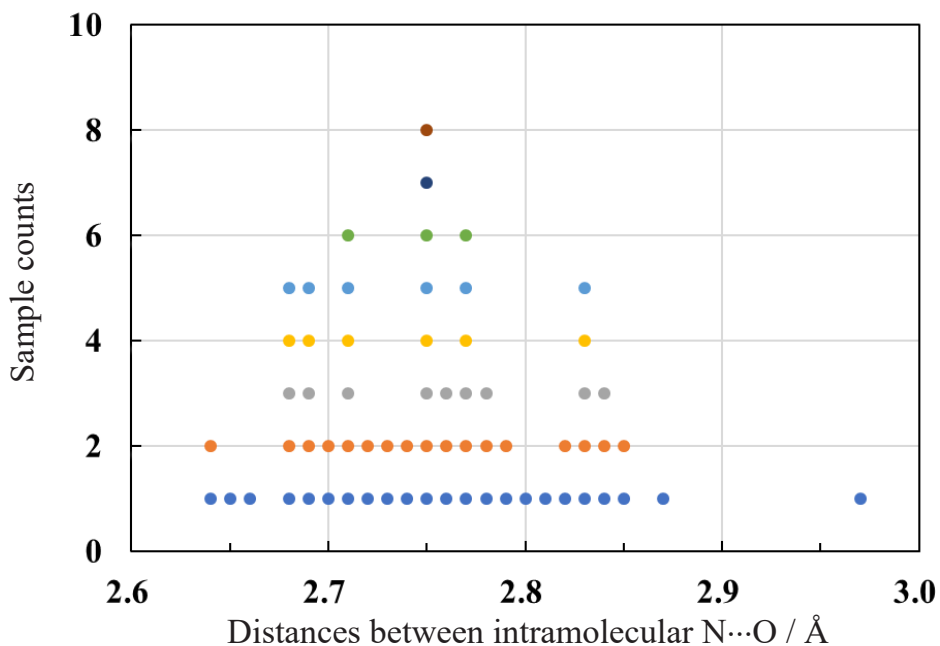


Fig. 7. Intramolecular N...O distances of EDTA-chelates of alkali metals as well as alkaline earth metals vs. sample counts.

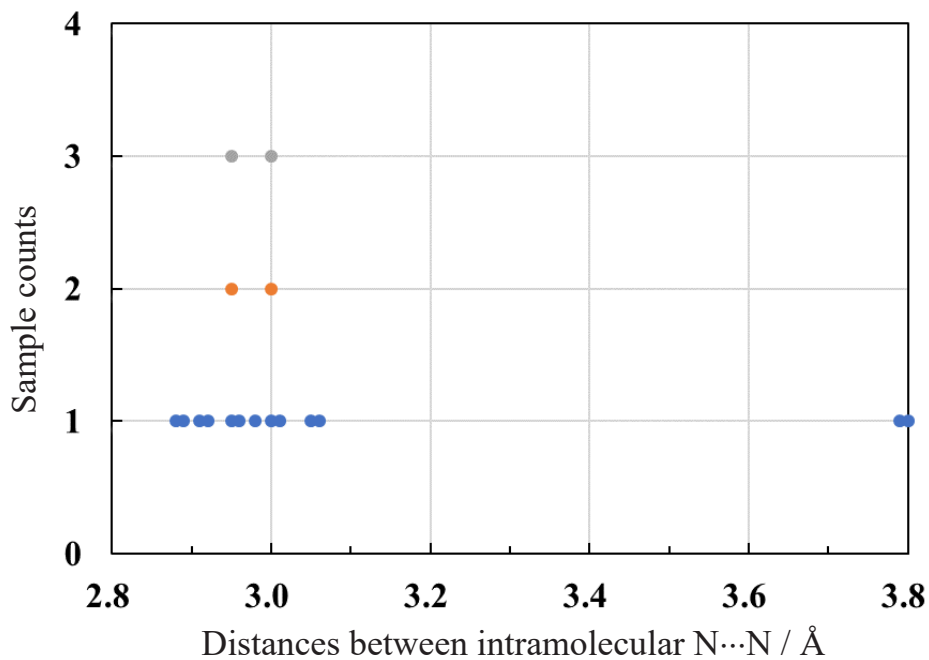


Fig. 8. Intramolecular N...N distances of EDTA-chelates of alkali metals and alkaline earth metals vs. sample counts.

765935;  $[\text{Ba}_2(\text{EDTA}-4\text{H})]\cdot 2.5\text{H}_2\text{O}$ , 765936; 1104933). On the other hand, averaged intramolecular N...N distances in the same EDTA-chelates are as follow: 3.788 Å of Li-Y, 2.993 Å of Na-Y, 3.059 Å of K-Y, 2.891 Å of Mg-Y, 2.961 Å of Ca-Y, 3.019 Å of Sr-Y, 3.204 Å of Ba-Y. These averaged intramolecular N...O distances in EDTA anions ( $=\text{Y}^{4-}$ ) in addition to coordination numbers (CN), denticity ( $\kappa$ ), and the crystal radii of metal ions by Shannon (1976) [50] are displayed in Table 5. It seems that only Sr-EDTA

chelates are out of the sequence of each metal ion radius for having a short N...O distance. Similarly, Polynova et al. (2009) noted that the Sr-N bonds in the Sr-Y complex (CCDC No. 686019) are somewhat shorter than those of strontium nitrilotriacetate; i.e.,  $\text{Sr}_3(\text{NTA})_2\cdot 8\text{H}_2\text{O}$  [23]. But, the reasons of this had not been pointed out. Only one crystal structure of the Sr-Y complex is known, so that the reason of the anomaly of shorter intramolecular N...O distance in Sr-Y seems to be difficult to explain.

Table 5

**Coordination numbers (CN), denticity ( $\kappa$ ), averaged intramolecular N...O distances in metal-chelates of EDTA anions ( $=\text{Y}^{4-}$ ), referring to the crystal radii of metal ions by Shannon 197 [50].**

	CN	Denticity	Averaged intramolecular N...O distances / Å	Averaged intramolecular N...N distances / Å	Crystal radii / Å from [50]
Li-Y	5	tri- $\times$ 2	2.734	3.788	0.73 (CN=4) 0.90 (CN=6)
Na-Y	7	hexa-	2.777	2.993	1.26 (CN=7)
K-Y	8	hexa-	2.805	3.059	1.65 (CN=8)
Mg-Y	7	hexa-	2.709	2.891	0.86 (CN=6) 1.03 (CN=8)
Ca-Y	8	hexa-	2.745	2.961	1.26 (CN=8)
Sr-Y	8	hexa-	2.736	3.019	1.40 (CN=8)
Ba-Y	9	tri- $\times$ 2, hexa-	2.765	3.204	1.61 (CN=9)

Recently, intramolecular distances between nitrogen and oxygen atoms (N...O) in room-temperature phosphorescence (RTP) emissive EDTA and salts thereof (CCDC Nos. 2051489 and 1148827) were revealed to be similar to those of the existing RTP-emissive clusteroluminogens according to Zheng et al. (2021) [35]. The intramolecular non-chelate HN<sup>+</sup>...O distances in EDTA and its salts as shown in Fig. 3 were found to be also similar with that of nonaromatic luminophores (Gong

et al. 2013 [36]; Chen et al. 2018 [37]). If intramolecular distances of nitrogen and oxygen atoms (N...O) determine the ability of RTP-emission in non-chelate EDTA as well as its salts in addition to the metal-chelates of alkali metals besides alkaline earth metals, integrated information about existing EDTA crystals described herein would support a forthcoming study on nonaromatic RTP, phenomenologically attracting much attention but still poorly understood in future.

**CONCLUSIONS.** Crystallographic data of zwitterionic ethylenediaminetetraacetic acid (EDTA) molecules and non-chelate salts thereof, besides the EDTA-chelates of both alkali metals and alkaline earth metals previously reported have been searched for and collected from the Cambridge Structural Database (CSD). Intramolecular contact distances of ammonium-nitrogen and oxygen atoms ( $\text{NH}^+\cdots\text{O}$ ) forming hydrogen bonds within zwitterionic EDTA molecules as well as intramolecular  $\text{NH}^+\cdots\text{NH}^+$  distances were examined. According to the investigation, intramolecular  $\text{NH}^+\cdots\text{O}$  distances are distributed around 2.7 Å. In addition,  $\text{NH}^+\cdots\text{NH}^+$  distances seem to be divided into two groups; i.e., a small number of *gauche*-forms and many *anti*-forms within ethylenediamine moiety in EDTA molecules. Especially, a large counterion seems to strongly influence the conformation of EDTA molecules. It means that crystal packings contribute to change in the stability of every conformer. The ionic radii of alkali metals as well as alkaline earth metals in EDTA-chelates also affect intramolecular atomic lengths, coordination numbers (CN), and denticity. In the Sr-EDTA complex, somewhat short  $\text{N}\cdots\text{O}$  distances compared with the series corresponding to each metal-ion radius are occurring.

The present article has been prepared on the basis in part of the technical reports and preprints (Noguchi 2022b-e) [51-54].



**ACKNOWLEDGEMENTS.** Thanks to the CCDC for making crystallographic data available freely. This study was partially funded by the Research Grant of Nagasaki University “Doctoral Program for World-leading Innovative and Smart Education” for academic year 2022.

## АНАЛІЗ ОСОБЛИВОСТЕЙ КРИСТАЛІЧНОЇ СТРУКТУРИ ДЛЯ БЕЗХЕЛАТНИХ КОНФОРМАЦІЙ ЕТИЛЕНДІАМІНОЦТОВОЇ КИСЛОТИ ТА ЇЇ СОЛЕЙ З ЛУЖНИМИ ТА ЛУЖНО-ЗЕМЕЛЬНИМИ МЕТАЛАМИ

*Дайсуке Нагочі*

*Відділ освіти та підтримки досліджень, Вища школа інженерії, Університет Нагасакі, Bunkyo-machi 1-14, Нагасакі 8528521, Японія*

*Email: a.chemist.noguchi.d@gmail.com*

У цьому дослідженні було проведено пошук і огляд кристалічних структур нехелатних молекул EDTA та їхніх нехелатних солей у стані цвіттер-іона, а також хелатів EDTA лужних і лужноземельних металів. Було проаналізовано 25 видів нехелатуючих молекул EDTA, цвіттер-іони етилендіамоній-діацетатдіоцтової кислоти  $\text{HOOC-CH}_2\text{-}(\text{OOC-CH}_2\text{-})\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{-CH}_2\text{-COO}^-)\text{-CH}_2\text{-COOH}$  та їхні солі (етилендіамоній-тетраоцтова кислота  $(\text{HOOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{-CH}_2\text{-COOH})_2$ , етилендіамоній-ацетат триоцтова кислота  $(\text{HOOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{-CH}_2\text{-COO}^-)\text{-CH}_2\text{-COOH}$  та етилендіамоній-тетраацетат  $(\text{OOC-CH}_2\text{-})_2\text{NH}^+\text{-CH}_2\text{-CH}_2\text{-NH}^+\text{-}(\text{-CH}_2\text{-COO}^-)_2$  з протиіонами), а також 17 видів EDTA-хелатів іонів лужних металів ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ) та іони лужноземельних металів ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) із використанням даних Кембриджського центру кристалічних даних (CCDC). Було вивчено кожну внутрішньомолекулярну контактну відстань між атомами азоту та кисню ( $\text{HN}^+\cdots\text{O}$ ), яка становить близько 2,7 Å.

Розрахунки розподілу внутрішньомолекулярних відстаней  $\text{HNH}^+ \dots \text{N}+\text{H}^+$  у молекулі ЕДТА та її нехелатних солях довели, що великий за об'ємом протиіон та молекули розчинника призводять до змін кристалічної упаковки через конформаційні перетворення від гош-форми до анти (транс) форми. В існуючих кристалічних ЕДТА-хелатах лужних металів, а також лужноземельних металів відображаються різні координаційні числа (CN) і щільність ( $\kappa$ ) аніонів ЕДТА; CN від 5 до 9, три- та шестизубчасті моди. Внутрішньомолекулярні контактні відстані  $\text{N}\dots\text{O}$  та  $\text{N}\dots\text{N}$  відповідають радіусам іонів металів, за винятком випадку хелату Sr-EDTA, ймовірно, через відмінності кристалічних упаковок на додачу до кількості протиіонів і молекул кристалічного розчинника. Існуючі дані про кристалічну ЕДТА та її солі було зібрані тут, що сприяє подальшому розумінню та дослідженню їхнього застосування у майбутньому.

**Ключові слова:** CCDC, ЕДТА, водневий зв'язок, рентгенівська кристалографія.

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Стаття надійшла 14.11.2022.