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# SYNTHESIS OF TETRAHYDRATED Na (I) SALT OF 4-CARBOXY 2-NITRO TEREPHTHALATE AND ITS STRUCTURAL STUDY

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***Abstract:*** *An acid sodium salt of 2-nitro-terephthalic acid was synthesized and its molecular and crystal structures were studied. The crystallographic parameters of the new compound are as follows: the chemical formula – $C_8H_8NNaO_8$, Cambridge Crystallographic Database Code: 2332574, molecular weight – 269.14, the temperature during measurement of the crystal parameters – 100.0 K, monocrystalline dimension 0.18mm×0.21mm×0.15mm, Radiation $CuK_\alpha$ λ= 1.54184, the minimum value of theta 4, 0250, the maximum value of theta 749580, the number of obtained reflections 9169, the number of independent reflections 2040, syngony - triclinic, space-group P-1, the specific gravity of the monocrystal d= 1.716 g/cm$^3$, unit cell parameters – a = 6.5034 Å, b = 7 .4080 Å, c= 11.1553 Å, the volume of the crystal lattice V=520.79 Å$^3$, the number of molecules in the lattice Z=2, the axial angles in the triclinic system α = 92.6990°, β= 100.1720°, γ= 99.0840°, final R factor = 0.0267. Metallic sodium ionically coordinates with the ligand. Distance between atoms – Na(1)–O(1)=2,3357 Å, Na (1)–O(4)=2,3236 Å, Na(1)–O(7)= 2,3855 Å.*

***Key words****: tetrahydrated Na (I) salt of 4-carboxy 2-nitro terephthalate, molecular and crystal structures, triclinic syngony, ionic structure, acid salt*
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## Introduction

2-nitroterephthalic and 2-aminoterephthalic acids, which contain two carboxyl groups, have attracted the attention of researchers as complex-forming ligands, and their crystal and molecular structures were studied by synthesizing new complex compounds with several metals. [1-9]. Since the nitro group - $NO_2$ and the amino group - $NH_2$, located in the benzene ring, are in the middle position for one carboxyl group, and in the meta position for the other, this position, which affects the reactivity of the ligand, leads to the fact that the hydrogen atom is more easily replaced by alkaline metals, due to increasing its activity in the carboxyl group. This so-called "moderating effect" is manifested in other benzoic acid derivatives, salicylic acid, and para-aminosalicylic acid, as well as in other mid-substituted derivatives [10, 11].

In this research, Na salt of nitroterephthalic acid was synthesized and used in the synthesis of the other metal coordination compounds.

The crystal structure of Na 2 - nitroterephthalate salt has not been found in the literature. Therefore, the high-quality single crystals of Na 4 - carboxy 2 - nitro terephthalate salt were obtained for X-ray structural analysis and its molecular and crystal structures were studied.

## Experimental part

New Na 2 - nitroterephthalate salt was synthesized as follows: 0.84 grams (0.01 mol) of $NaHCO_3$ salt is dissolved in 100 ml of distilled water and 0.211 g (0.01 mol) of 2-nitroterephthalic acid is added. The sodium salt will be produced by replacing the hydrogen ion

in one of the carboxyl groups of the ligand with a sodium ion. The solution of the resulting salt was filtered through filter paper and left in the dark place at room temperature. After a few days, transparent prismatic single crystals began to fall out. The single crystals were filtered and dried in a desiccator over anhydrous $CaCl_2$ to constant weight. The yield of the reaction was 82.4%.

Monocrystals were selected under a microscope and collected the reflexes needed to identify the crystal structure of the suitable monocrystals for X-ray structure analysis in automated diffractometer operating at XtaLAB ARC 11 (RNC) of the University of Virginia in the United States of America, and the molecular and crystal structures were determined based on special programs [12-16]. The crystallographic parameters of the crystal structure are listed in **Table 1**.

**Table 1.** Crystallographic data of the Sodium Nitro-terephthalate compound

| | | | |
|---|---|---|---|
| Chemical formula | $C_8H_8NNaO_8$ | Dimension of the crystal lattice | $0.18\times0.21\times0.15 mm^3$ |
| Molecular weight | 269.14 g/mol | Parameters of the crystal lattice | a=6.5034 Å<br>b=7.4080 Å |
| Temperature during measurement | 100.00 K | | c=11.1553 Å |
| | | Volume of the crystal lattice | v=520.79 $Å^3$ |
| Syngony | triclinic | | |
| Space-group | *P-1* | The number of the molecules in the lattice | z=2 |
| Density | 1.716 $g/cm^3$ | Triclinic angles | $\alpha= 92.699^0$<br>$\beta= 99.084^0$ |
| Radiation | $CuK_\alpha$ = 1.54184 | | $\gamma= 100.172^0$ |
| Minimal value of Theta | $4.025^0$ | | |
| Maximal value of Theta | $74.958^0$ | | |
| Measured reflexes | 9169 | final R- factor | R= 0.267 |
| Independent reflexes | 2040 | | |

**Table 2** lists the coordinates of the atoms in the molecule and their corresponding temperature factors. The interatomic distances, valence angles and coordinates of the hydrogen atoms are given in **Tables 3, 4** and **5**, respectively.

**Table 2.** Coordinates of the atoms ($x10^4$) and their temperature factors

| Atom | x | y | z | Ueq |
|---|---|---|---|---|
| Na1 | 2409,8(7) | 1241.6(6) | 805.5(4) | 13.04(15) |
| O2 | 7882,0(14) | 11641.6(11) | 6114.8(7) | 14.2(2) |
| O8 | 8514,5(14) | 13905.9(11) | 8016.1(8) | 14.0(2) |
| O4 | 4371,4(13) | 3972.3(11) | 1810.2(8) | 14.6(2) |
| O3 | 7809,5(14) | 3824.7(12) | 1951.1(8) | 16.3(2) |
| O1 | 8807,0(14) | 9562.0(12) | 7395.5(7) | 16.0(2) |
| O7 | 1058,0(14) | -1798.7(12) | -84.8(8) | 14.7(2) |
| O6 | 6636,3(15) | 7598.1(12) | 1065.6(8) | 19.2(2) |
| O5 | 5423,8(15) | 9861.1(12) | 1837.5(8) | 18.4(2) |

| | | | | |
|---|---|---|---|---|
| N1 | 6214.3(16) | 8475.8(13) | 1928.2(9) | 12.7(2) |
| C7 | 7101.9(18) | 9151.6(16) | 4123.1(10) | 11.5(2) |
| C6 | 6715.9(18) | 7835.9(16) | 3147.4(10) | 10.9(2) |
| C8 | 6297.0(19) | 4488.0(15) | 2233.2(10) | 12.0(2) |
| C2 | 7696.2(18) | 8618.6(16) | 5288.4(10) | 11.5(2) |
| C5 | 6851.1(18) | 5997.9(15) | 3274.6(10) | 11.0(2) |
| C3 | 7874.8(19) | 6791.3(17) | 5447.5(11) | 13.9(3) |
| C4 | 7441.8(19) | 5497.9(16) | 4455.1(11) | 13.7(3) |
| C1 | 8182.3(18) | 9976.8(16) | 6376.1(10) | 12.3(2) |

**Table 3.** Interatomic distance (d)

| **Chemical bond** | **d, Å** | **Chemical bond** | **d, Å** |
|---|---|---|---|
| Na(1) – O(4) | 2.3236(9) | N(1) – O(5) | 1.2277(13) |
| Na(1) – O(1) | 2.3357(9) | N(1) – C(6) | 1.4684(14) |
| Na(1) – O(7) | 2.3855(10) | C(7) – C(6) | 1.3874(16) |
| Na(1)- O($7^1$) | 2.3762(9) | C(7) – C(2) | 1.3924(16) |
| Na(1) – O(6) | 2.4268(9) | C(6) – C(5) | 1.3923(16) |
| Na(1) – O(5) | 2.5139(10) | C(8) – C(5) | 1.5276(15) |
| O(2) – C(1) | 1.3210(14) | C(2) – C(3) | 1.3961(16) |
| O(1) – C(1) | 1.2182(15) | C(2) – C(1) | 1.4953(15) |
| C(8) – O (4) | 1.2508(15) | C(5) – C(4) | 1.3984(16) |
| C(8) – O(3) | 1.2497(15) | C(3) – C(4) | 1.3890(16) |
| N(1) – O(6) | 1.2295(13) | | |

**Table 4.** Valence angles (ω)

| **Angles** | **ω°** | **Angles** | **ω°** | **Angles** | **ω°** |
|---|---|---|---|---|---|
| O(4)-Na(1)-O(1) | 89.70(3) | O(6)-Na(1)-O(5) | 107.83(3) | C(6)-N(1)-Na(1) | 129.64(7) |
| O(4)-Na(1)-O(7) | 106.94(3) | C(8)-O(4)Na(1) | 133.05(7) | C(6)-N(1)-Na($1^1$) | 145.40(7) |
| O(4)-Na(1)-O($7^1$) | 167.98(4) | C(1)-O(1)-Na(1) | 141.21(8) | C(6)-C(7)-C(2) | 118.46(10) |
| O(4)-Na(1)-O(6) | 87.56(3) | Na(1)-O(7)-Na($1^1$) | 94.93(3) | C(7)-C(6)-N(1) | 119.75(9) |
| O(4)-Na(1)-O(5) | 83.93(4) | N(1)-O(6)-Na(1) | 127.40(7) | C(7)-C(6)-C(5) | 123.39(10) |
| O(1)-Na(1)-O(7) | 86.93(3) | N(1)-O(5)-Na(1) | 145.96(8) | C(5)-C(6)-N(1) | 116.75(10) |
| O(1)-Na(1)O($17^1$) | 90.25(3) | Na(1)-N(1)-Na(1) | 84.72(2) | O(4)-C(8)-Na(1) | 30.90(5) |
| O(1)-Na(1)-O(6) | 171.95(4) | O(6)-N(1)Na(1) | 35.47(5) | O(4)-C(8)-C(5) | 116.50(10) |
| O(1)-Na(1)-O(5) | 79.37(3) | O(6)-N(1)-Na($1^1$) | 109.23(7) | O(3)-C(8)-Na(1) | 97.74(7) |
| O(7)-Na(1)-O($7^1$) | 85.07(3) | O(6)-N(1)-O(6) | 117.72(9) | O(3)-C(8)-O(4) | 127.13(11) |
| O(7)-Na(1)-O(6) | 86.63(3) | O(15)-N(1)-Na(1) | 23.03(5) | O(3)-C(8)-C(5) | 116.20(10) |
| O(7)-Na(1)-O(5) | 162.55(4) | O(5)-N(1)-Na($1^1$) | 92.32(7) | C(5)-C(8)-Na(1) | 142.9(8) |
| O(7)-Na(1)-O($5^1$) | 84.24(3) | O(5)-N(1)-O(6) | 124.28(9) | C(7)-C(2)-C(3) | 119.67(10) |
| | | O(5)-N(1)-C(6) | 118.00(9) | C(7)-C(2)-C(1) | 121.17(10) |

**Table 5.** Coordinates of hydrogen atoms ($\times 10^4$) and their temperature factors

| **Atom** | **x** | **y** | **z** | **U eq** |
|---|---|---|---|---|
| H2 | 8142.63 | 12337.64 | 6758.2 | 21 |
| H8A | 9700(20) | 14630(20) | 8030(15) | 21 |
| H8B | 7590(20) | 14590(20) | 8063(15) | 21 |
| H7 | 6963.92 | 10387.5 | 3998.92 | 14 |

| | | | | |
|---|---|---|---|---|
| H3 | 8296.02 | 6429.46 | 6241.23 | 17 |
| H4 | 7548.43 | 4255.83 | 4580.11 | 16 |
| H7A | 1110(30) | -2520(30) | -487(18) | 31(5) |
| H7B | 1620(30) | -2280(30) | -613(19) | 38(5) |

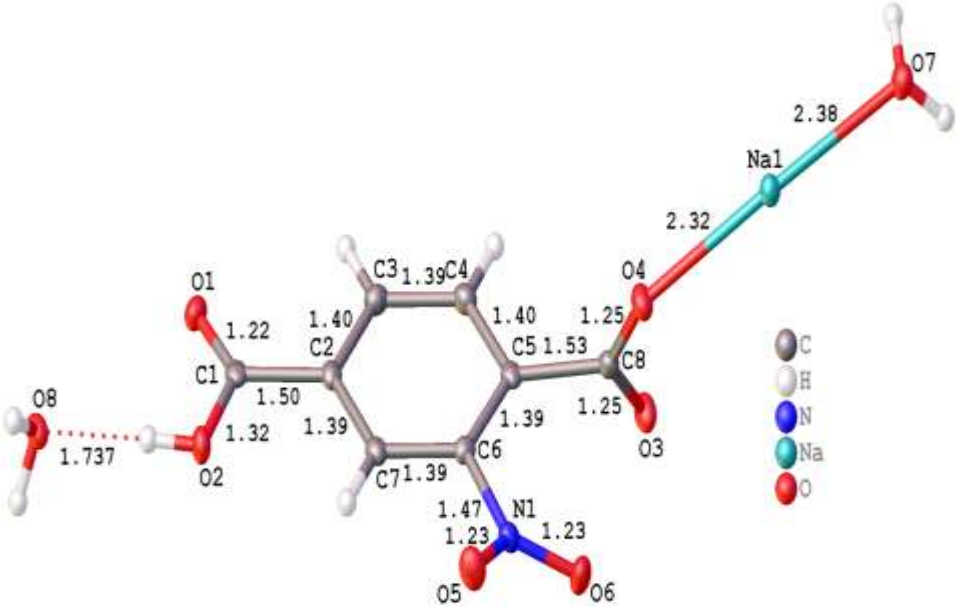


**Fig. 1**. The crystal structure of the Sodium 2- nitroterephthalic monomer molecule

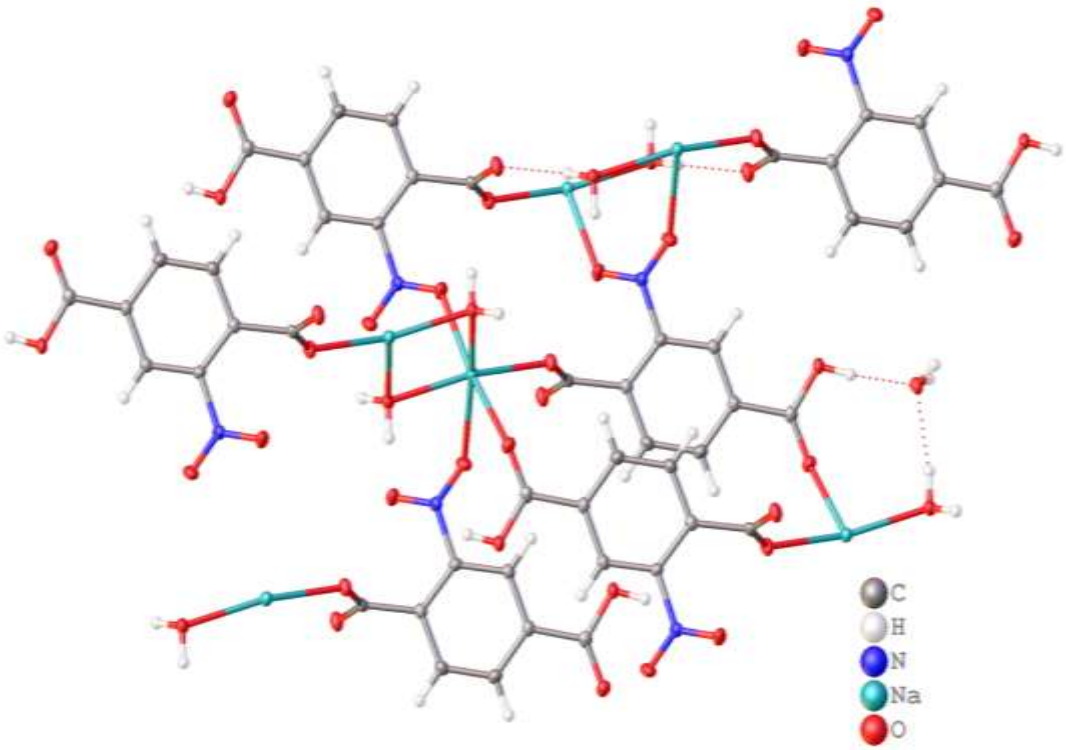


**Fig. 2**. The crystal structure of the polymer molecule in the crystal lattice

**Figure 1** shows the structure of the molecule, and **Figure 2** exhibits the structure of the molecule located in the lattice and connected by strong hydrogen bonds.

**Analysis of the obtained results.** As shown in **Figure 1**, sodium metal replaces one of the hydrogens in dibasic 2-nitroterephthalic acid and forms an acid salt. As expected, the structure is ionic, one of the oxygens in the carboxyl group is coordinated with sodium metal Na(1) – O(1) = 2.3357Å. The other oxygen of the carboxyl group forms a strong hydrogen bond with the water molecules included in the structure. Two water molecules coordinate with sodium metal and form an aqua complex Na (1) – O(4) = 2.3236 Å, Na(1) – O(7) = 2.3855 Å. Two water molecules that do not coordinate with the metal molecules form a polymer molecule located in a crystal lattice by connecting monomer molecules with strong hydrogen bonds (**Figure 2**).

## Conclusion

1. The coordination compound of 2-nitroterephthalic acid and acid salt of Na metal was synthesized, the molecular and crystal structures of the obtained single crystals was identified in an automated diffractometer. It was found that Na metal replaces one hydrogen atom of the carboxyl group and forms an ionic compound. The hydrogen atom in the second carboxyl group of the ligand is not replaced by a metal atom and an acid salt of the ligand is obtained. The C-C bonds of the benzene ring in the ligand are 1.89 Å in length, similar to other benzoic acid derivatives.
2. Since there is an ionic structure, the carbon-oxygen bond in the carboxyl group is identical.

## References


1. Smith A., Sinqh W., Carter K.P. Catena-(tris-2-nitroterftalato) – tris-aqua Nd(III) // New J. Chen. –London. 2018, № 40, p.7338-7342.
2. Smith A., Carter K.P., Lough A.J. Catena-(tris-2-nitroterftalato)- tris-aqua-di-Europium(III)- dihydrate // New J. Chen.-London. 2015, №37, p. 2163-2167.
3. Panyarel K., Surinwoung S., Prior T.J. Catena- tris (2- nitroterftalato) –diaqna-di Thulium(III). // Micropordus and Mesoporous meterials. (Germany), 2017, № 251, pp.155-159.
4. Panyarel K., Surinwoung S., Prior T.J., Konno T. Catena- tris (2-nitroterephalato)-tetra-aqua- di- Lantanium(III) // Microporous and Mesoporous materials, (Germany), 2017, № 251, p. 213-219.
5. Lun B., Sho L., Cuo Q. Catena- tetraakis-dimetieforamido- tris-(2-aminoterephtalic acid)- di Neodium-dihidrate // Inorg. Chem. 2017, № 17, p. 18-24.
6. Hui T., Hong N., Zhung L. Catena (tris-2-aminoterephtalato)-tetraaqua Nd(III) // J. Mol. Structure, Coimbra (Portugal), 2018, № 654, p.183-187.
7. Tao H., Nerq W.Z., Zhong Q.L. Catena (Bis-2-aminoterephtalato)- mono-aminoterephalato- Dy(III)- tetrahydrate // J. Mol. Structure, 2013, № 846, p. 197-202.
8. Aliyeva G.M., Rakhmanova S.Y., Alakbarova F.J., Munshieva M.K., Movsumov E.M., Imanova N.A., Mammadova N.A., Mammadova H.F., Mansurova K.A. Synthesis and structural study of bis-(nitrotereftalato)-monopyridino Co (II) hexahydrate // Azerbaijan Chemical Journal, 2023, № 2, p.138-145
9. Hasanova S.S. Synthesis, physicochemical study and crystal structure of bi-(p-nitrobenzoate)-di-(pyrazine) nickel(II)-dihydrate // Chemical problems, 2022, vol. 20, no.1, p. 95-101
10. Rzaeva M.F., Movsumov E.M., Sergienko V.S., Ilyukhin A.B. Crystal structure of complexes of divalent Co, Ni, Cd with anions of 2-acetylamino-5-nitrobenzoic acid. // Crystallography, 2012, Vol. 57, No. 2, pp. 256-260.
11. Rzaeva M.F., Movsumov E.M., Lysenko K.A. Synthesis and structural study of 5-nitro-2 acetamidobenzoato Mn(II) XXV. International Chugaev Conference on

Coordination Chemistry. Suzdal, Russia, 2011, p. 347.
12. Hasanova S.S. Synthesis and crystal structure study of bis-(3,5-dinitrobenzoato)-di(pyridino) di-cadmium(II) catena complex compound // Sumgayit State University Scientific News, Department of Natural and Technical Sciences - 2022, Vol. 22, No. 1, pp. 25-30.
13. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program // Journal of applied crystallography, 2009, Vol. 42 (2), p. 339-341
14. Sheldrick G.M. SHELXT – Integrated space – group and crystal – structure determination // Acta crystallographica. Section A, Foundations and advances, 2015, Vol. 71 (1), p. 3-8
15. Hasanova S.S., Yolchueva E.A., Aliyeva Q.M., Shabbir M., Ashfaq M., Movsumov E.M., Khurram Sh.M., Tahir M.N., Al-Sehemi A.G., Alarfaji S.S. Synthesis, characterization, crystal structures, and supramolecular assembly of copper complexes derived from nitroterephthalic acid along with Hirshfeld Surface Analysis and quantum chemical studies // ACS Omega, 2023, https://doi.org/10.1021/acsomega.2c07686
16. Bourhis L.J., Dolomanov O.V., Gildea R.J., Howard J.A.K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment – Olex2 dissected // Acta crystallographica. Section A, Foundations and advances, 2015, Vol. 71 (1), p. 59-75.

## 4-HİDRO KARBOKSİ 2-NİTRO TEREFTALAT Na (1) DUZUNUN SİNTEZİ VƏ KRİSTAL QURULUŞUNUN ÖYRƏNİLMƏSİ

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**Xülasə:** 4-karboksi 2-nitrotereftal turşusunun Na turş duzu sintez olunaraq molekulyar və kristal quruluşu öyrənilmişdir. Triklin sinqoniyada kristallaşan yeni birləşmənin kristalloqrafik parametrləri aşağıdakı kimidir: kimyəvi formulu $C_8H_8NaO_8$, molekul kütləsi 269.14 reflekslərin ölçülməsi zamanı temperatur 100,0K, monokristalın ölçüləri 0.18mm×0.21mm×0.15mm, radiasiya $CuK_\alpha$ $\lambda$ =1.54184, Teta minimum 4.025°, Teta maksimum 74.958°, ölçülmüş reflekslərin sayı 9169, asılı olmayan reflekslərin sayı – 2040, sinqoniya – triklin, fəza qrupu – P-1, monokristalın sixlığı d=1,716 q/sm$^3$, kristal qəfəsin parametrləri $a$ = 6.5034 Å, $b$ = 704080Å, $c$ = 11.1553 Å, kristal qəfəsin həcmi V=520.79 Å$^3$, qəfəsdə olan molekulların sayı Z=2. Triklin bucaqlar α=92.084°, β= 99.084°, γ=100.172°, son R faktoru =0.0267. Natrium metalı liqantla ion tipli koordinasiya yaradır. Burada atomlararası məsafə Na(1)–O(1)=2.3357 Å, Na (1)–O(4)=2.3236 Å, Na(1)–O(7)=2.3855 Å kimidir.

**Açar sözlər:** natrium (1) 4-karboksi-2-nitrotereftalat duzunun tetrahidratı, molekulyar və kristal quruluş, triklin sinqoniya, ion quruluşu, turş duz

# СИНТЕЗ Na (1) ТЕТРАГИДРАТНОЙ СОЛИ 4-КАРБОКСИ-2-НИТРОТЕРЕФТАЛАТА И ЕГО СТРУКТУРНОЕ ИЗУЧЕНИЕ

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**Аннотация:** Синтезирована кислая натриевая соль 2-нитротерефталевой кислоты и изучена ее молекулярная и кристаллическая структура. Кристаллографические параметры нового соединения следующие: химическая формула – $C_8H_8NNaO_8$, молекулярная масса – 269.14, температура при измерении параметров кристалла – 100.0 К, размер монокристалла 0.18×0.21×0.15 мм, излучение $CuK_\alpha$ λ= 1.54184, минимальная значение теты 4.0250, максимальное значение теты 749580, количество полученных отражений 9169, количество независимых отражений 2040, сингония - триклинная, пространственная группа P-1, удельный вес монокристалла d= 1.716 г/см$^3$, параметры элементарной ячейки – *a* = 6.5034 Å, *b* = 7.4080 Å, *c* = 11.1553 Å, объем кристаллической решетки V=520.79 Å$^3$, число молекул в решетке Z=2, углы триклинной сингонии α = 92.6990°, β= 100.1720°, γ= 99.0840°, окончательный R-фактор = 0.0267. Металлический натрий ионно координируется с лигандом. Расстояние между атомами Na(1)–O(1)=2.3357 Å, Na(1)–O(4)=2.3236 Å, Na(1)–O(7)= 2.3855 Å.

**Ключевые слова**: тетрагидратная Na(1) соль 4-карбокси-2-нитротерефталата, молекулярная и кристаллическая структура, триклинная сингония, ионное строение, кислая соль