International Journal of Chemistry and Applications.
ISSN 0974-3111 Volume 9, Number 1 (2017), pp. 1-8

http://www.irphouse.com

# Structural Relationship of Ethylenediamine Monohydrogen-Squarate Polymorph's

**Louiza ZENKHRI *, Ahmed BOUTARFAIA**

*Univ Kasdi Merbah Ouargla, Chemistry Department,*
*Faculty of Mathematics and Matter Sciences,*
*BP 511 Route Ghardaia, Ouargla, Algeria - 30 000,*

**Abstract**

This report illustrates the structural relationship between two polymorph, ethylenediammonium bis(hydrogen squarate) monohydrate, with chemical formula $C_2H_{10}N_2^{2+}.2HC_4O_4^-.H_2O$ (I) and (II). The crystal structures of the two compounds have also been studied. The most important common feature of these compounds is the role of hydrogen bonding in the cohesion of their crystal lattice. In the crystal, the hydrogen bonds lead to a three dimensional network.

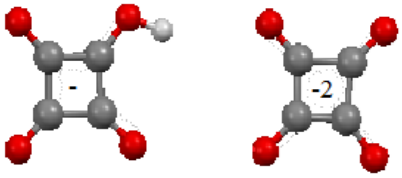
**Keywords:** Squaric acid, **hydrogenbonds, supramolecular**, Ethylenediamine.

## INTRODUCTION

When squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) is reacting with organic amines, it gives rise to supramolecular structure [1][2][3][4]. The oxoanion squarate is known by its coordinating diversity mode [5][6], leading to an of infinity coordination complex, because of its cyclic structure, possible aromaticity [7][8], and the proton donating and accepting capabilities for hydrogen bonding [9][10].It can form mono and dianions on deprotonation by amines (Figure 1) [11].

The monohydrogen squarate anions [$HC_4O_4^-$] form a head-to-tail chain or a head-to-head cyclic dimer or a tetramer, through strong O–H···O hydrogen bonds, it has an ability of donating and accepting hydrogen bonds confined to the molecular plane [11]. The result is some motifs linear chain (A), Cyclic dimer (B), Cyclic tetramer (C) [11] (Figure 2). Cyclic tetramer motif (D) [12] (Figure 2). It is used to generate

structural assemblies in solid state via hydrogen bonding [13]. Serth Matthew had classified the compounds according to their belonging to a specific type of motifs. However, ethylenediammonium a (hydrogen squarate) monohydrate (I) exhibit to motif A.




$HC_4O_4^-$ $C_4O_4^{-2}$

**Fig. 1:** Mono and dianions of squaric acid

Squarate compounds attract topic for various studies in the last three decade [14]. The design of the complex is not always easy. We meet during their preparations phases where the metal is absent in the compound of the resulting product, as a secondary phase accompanying a coordination complex. However, the study of these secondary phases, where the metal is deliberately omitted from the product composition gives a deeper idea to compression of cohesion of the crystal lattice and illustrates the profound role of hydrogen bonding in this cohesion.

$C_2H_{10}N_2^{2+}.2HC_4O_4^-.H_2O$ [15], the polymorph of ethylenediammonium bis(hydrogen squarate) monohydrate (I) was synthesized by slow evaporation of a mixture squarate, ethylenediamine and yttrium. It was obtained together with $\{(C_2H_{10}N_2)_{1.5}[Y(C_4O_4)_3(H_2O)_4]\}_n$ [16].

In this study, the hydrogen-bonded motifs formed in the two polymorph, generate layered structures. The monohydrogen squarate anions motifs are linked tougher through the strong O–H…O hydrogen bonds.

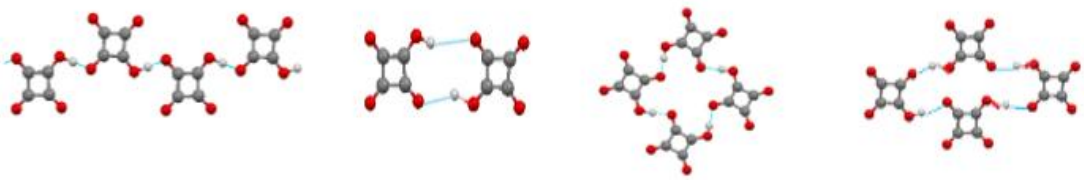



**Fig. 2:** Different motifs formed by Hydrogen bonds in squarate monoanion

The monohydrogen squarates of ethylenediamine (II) report by Suresh Mathew and al were prepared by slow evaporation from an aqueous solution of the squaric acid and ethylenediamine. The mixtures consist of 1 M solutions of one equivalent of the acid and two equivalents of the amine in water, at 80 °C for 5–6 h. the protonation of ethylenediamine, and identification of the presence of specific hydrogen bonds were confirmed by infrared spectra [17].

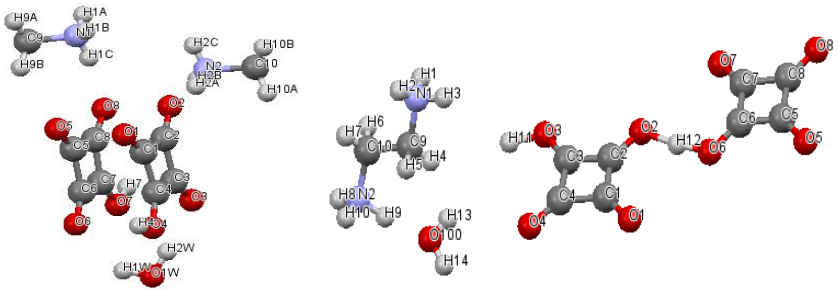
**Table I:** Experimental details of the two polymorphs

| | I | II |
|---|---|---|
| Empirical formula | $C_{10}H_{14}N_2O_9$ | $C_{10}H_{14}N_2O_9$ |
| Chemical formula weight (g/mol) | 306,23 | 306,23 |
| T(K) | 293 | 293 |
| Cell sitting | monoclinic | monoclinic |
| Space group | P2/c | $P2_1/c$ |
| a (Å) | 14.1907 | 10,40 |
| b (Å) | 9.0224 | 10,87 |
| c (Å) | 10.9412 | 11,59 |
| α (°) | 90 | 90 |
| β (°) | 111.789 | 105,82 |
| γ (°) | 90 | 90 |
| V ($Å^3$) | 1300,77 | 1263,05 |
| Z | 4 | 4 |

## RESULTS AND DISCUSSION

### Structures

A summary of Crystallographic data for (I) and (II) compounds is listed in Table I. Both of the two compounds crystallize in monoclinic system. (I) is in P2/c space group and (II) in P21/c, with the cell parameter's a = 14.190, b = 9.022, c = 10.941, β = 111.789, for (I) and a = 10.40, b= 10.87, c = 11.59, β = 105.82, for (II). The two symmetric units in (I) contain two hydrogen squarate anions, two half-molecules of protonated ethylenediamine arranged around a twofold axis and one water molecule (Fig 3 (I)). In asymmetric unit of (II) we found two $[HSQ]^-$ monoanions, one protonated amine and a water molecule (Fig 3 (II)).



(I) (II)

**Fig 3**: The labeled of asymmetric unit for the two polymorphs (I) and (II).

The study of hydrogen bounds between units of compound (I), shows that monohydrogen squarate exhibitmotif A, and form linear chain. These chains are interconnected by hydrogen bond created between monohydrogen squarate and ethylenediamine deprotonated and water molecule

In the table 2 is reported the bond lengths between atoms entities monohydrogen squarate, the ethylediamine, and the molecule of water respectively.The lengthsbetween atoms can be considered in the same order of magnitudein bothpolymorphs, and are consistent with the results reported in the works S. Mathew 2002. In compounds (I) and(II), eachmonohydrogen squarate ion has one C–O bond shorter than a normal single C–O bond, [C4-O4 = 1.2966 Å, C7-O7 = 1.2958 Å] and [C3-O3 = 1.274 Å, C6-O6=1.286Å] it is (1.426 Å in methanol [19]).while, C–O bond is between [1.2273 A ˚ and 1.275Å], and are typically C-O double bonds, it is 1.21Å in acetone [18]). Those results indicate that arromaticité is more pronounced in monohydrogen squarates of compound (I) than in compound (II), because of variation in bond length. [3].

**Table 2**. Selected bond lengths (Å) in compound (I) and (II).

| | bond lengths (Å) for the monohydrogen squarate in compound(I) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Squarate 1 | C1-C2 | C2-C3 | C3-C4 | C4-C1 | C1-O1 | C2-O2 | C3-O3 | C4-O4 | O4-H4 |
| | 1.498 | 1.471 | 1.412 | 1.454 | 1.2326 | 1.2273 | 1.2699 | 1.2966 | 1.0509 |
| Squarate 2 | C5-C6 | C6-C7 | C7-C8 | C8-C5 | C5-O5 | C6-O6 | C7-O7 | C8-O8 | O7-H7 |
| | 1.480 | 1.420 | 1.450 | 1.502 | 1.2253 | 1.2655 | 1.2958 | 1.22380 | 1.0597 |
| | bond lengths (Å) for the monohydrogen squarate in compound(II) | | | | | | | | |
| Squarate 1 | C1-C2 | C2-C3 | C3-C4 | C4-C1 | C1-O1 | C2-O2 | C3-O3 | C4-O4 | O3-H11 |
| | 1.440 | 1.409 | 1.463 | 1.492 | 1.241 | 1.276 | 1.274 | 1.2273 | 1.15 |
| Squarate 2 | C5-C6 | C6-C7 | C7-C8 | C8-C5 | C5-O5 | C6-O6 | C7-O7 | C8-O8 | O6-H12 |
| | 1.405 | 1.455 | 1.490 | 1.468 | 1.275 | 1.286 | 1.222 | 1.223 | 1.14 |

Bond lengths in the deprotonated ethylenediamine and water molecule are listed in the tables, respectively, for both compounds.

**Table 3**. Selected bond lengths (Å) for the two Ethylenediamine in the structures of ethylenediamine monohydrogensquarates (I) and (II).

| | Ethylenediamine | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ethylenediamine in (I) | C9-C10 | C9-N1 | C10-N2 | N1-H1A | N1-H2B | N1-H3C | N2-H2A | N2-H2B | N2-H2C |
| | 1.508 | 1.480 | 1.487 | 0.8933 | 0.8824 | 0.8806 | 0.8805 | 0.9002 | 0.9002 |
| Ethylenediamine in (II) | C9-C10 | C9-N1 | C10-N2 | N1-H1 | N1-H2 | N1-H3 | N2-H8 | N2-H9 | N2-H10 |
| | 1.472 | 1.476 | 1.469 | 0.98 | 0.79 | 0.97 | 0.88 | 1.02 | 0.95 |

**Table 4**. Selected bond lengths (Å) for the two water molecule in the structures of ethylenediaminemonohydrogensquarates (I) and (II).

| (I) | | (II) | |
|---|---|---|---|
| Ow-H1 | Ow-H2 | O100-H14 | O100-H13 |
| 0.92O3 | 0.9287 | 0.94 | 0.82 |

**Hydrogen Bounds**

The projection along axis b of the two structure shows that monohydrogensquarate entities generate parallel chain by O-H…O hydrogen bonds (Fig. 4, Table 5). Prallelto the c axis in the compound (I) with a spaced distance ranges from 3.279 Å to 3.435 Å. In compound (II), the monohydrogensquarate entities are aligned parallel to the b-axis, with a row spacing ranges from 3.519 Å to 3.473 Å

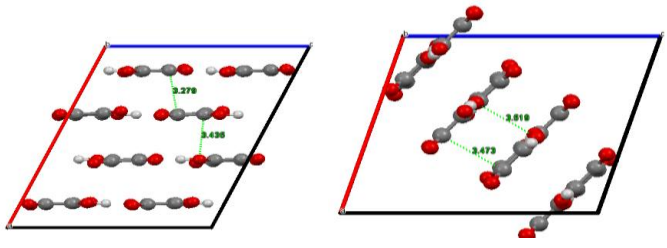


**Fig 4**: Packing diagram of the compounds (I) and (II)

In both of the compounds, these chains are linked each to other by ethylenediamine cation and water molecule's hydrogen bonds, N-H…O and OW-Hw…O, which are approximately equal, and generate 3D networks

**Table 5**. Hydrogen bonded length in the structures of ethylenediamine monohydrogen squarates

(I) and (II)

| | D-H…A | D-H | H…A | D…A | D-H…A |
|---|---|---|---|---|---|
| I | N-H…O | 0.89-0.90 | 1.92-2.14 | 2.77-2.92 | 146-169 |
| | O-H…O | 1.05-1.06 | 1.41-1-41 | 2.464-2.464 | 178-179 |
| | OW-Hw…O | 0.92-0.93 | 1.88-2.40 | 2.803-3.048 | 128-171 |
| II | N-H…O | 0.78-1.02 | 1.79-2.30 | 2.872-2.987 | 140-166 |
| | O-H…O | 1.04 | 2.35 | 2.579 | 154 |
| | OW-Hw…O | 0.82-0.94 | 1.84-2.02 | 2.759-2.759 | 156-164 |

**Structural relationship**

The monohydrogen squarate is stacked along the c axis with an interplanar distance of average 3.4 Å. The chains are built by a $HC_4O_4^-$ anion bridging between ethylenediamine cation and water molecule's hydrogen. The hydrogen bonding plays a very important role in the cohesion of the crystal lattice, and gives rise to a 3 D network

## CONCLUSION

Ethylenediamine monohydrogen squarate hydrate was generated in two different geometries, it consists of isolated entity. Very strong hydrogen bonds have contributed extensive network construction. In the compounds the monohydrogen squarate cristalize in chains. The study of this type of compounds clearly shows the way in which the cristal network in the organic compounds is maintained. This facilities the comprehension of the cohesion of the crystalline networks in the coordination complexes resulting from these chemical entities.

## REFERENCES

1. Köroglu, A., Bulut, A., Uçar , I., Nichol, G. S., Harrington, R. W., and Clegg, W., **2005**, "Proton sharing in bis(4-carbamoylpyridinium) squarate", Acta Crystallogr., **C59**, pp. o727.
2. Uçar, I., Bulut, A., Yesile, O. Z., and Büyükgüngör, O., **2004**, "Picolinamidium squarate and di-*p*-toluidinium squarate dehydrate", Acta Cryst., **C60**, pp. o585±o588.
3. Yesilel¸ O. Z., Odabasoglub, M., Olmez, H., and Büyükgüngör, O., **2006**, "Supramolecular Organization of Organoammonium Squarates", Z. Naturforsch., **61b**, pp. 1243 – 1248.

4. Yesilel¸ O. Z., Paş aoğ lu, H., Yılan, O. O., and Büyükgüngör, O., **2007**, "Syntheses, Spectral, Thermal and Structural Characterization of 2-Hydroxyanilinium and 2-Amino-3-hydroxy-pyridinium Squarates", Z. Naturforsch., **62b**, pp.823 – 828.

5. Greve, J., Jeβ, I., and Näther, C., **2003**, "Synthesis, crystal structures and investigations on the dehydration reaction of the new coordination polymers poly[diaqua-(μ2-squarato-O,O′)-(μ2-4,4′-bipyridine-N,N′)Me(II)] hydrate (Me=Co, Ni, Fe)", Journal of Solid State Chemistry., **175** pp. 328–340.

6. Dan, M., Sivashankar, K., Cheetham, A.K. and Rao, C.N.R. **2003**, "Amine-templated metal squarates, Journal of Solid State Chemistry"., **174**, pp. 60-68.

7. Frankenbach, G.M., Beno, M.A. Kini, A.M., Williams, J.M., Welp, U., Thompson, J.E., Whangbo, M.H., **1992**, "Structural, electronic and magnetic properties of the metal squarate tetrahydrate polymers $Fe(C_4O_4).4H_20$ and $Cu(C_4O_4).4H_20$", Inorg. Chim. Acta., **192**, pp. 19.

8. Erer, H., Yeseilil, O. Z., Dege, N., and Alpaslan, Y. B. **2010**, "One dimentioal coordination polymer of nickel(II)-Squarate with N,N,N',N'-tetramethylenediamine$\{[Ni(\mu\text{-}sq)(H_2O)_2\ (tmen).H_2O]\}_n$" J. Inorg. Organomet Polym., **20**, pp. 411.

9. Yesilel, O. Z., Odabasoglu, M., and Büyükgüngör, O., **2008**, "Supramolecular squarate and hydrogensquarate compounds with, Journal of Molecular Structure," J. Mol Struc., **874**(1-3), pp.151–158.

10. MacDonald, J. C., Dorrestein, P.C., Pilley, M. M., Foote, M. M. Lundburg, J. L., Henning, R. W., Schultz, A. J., and Manson, J. L., **2002,** "Design of Layered Crystalline Materials Using Coordination Chemistry and Hydrogen Bonds," J. Am. Chem. Soc., **122** (47), pp 11692.

11. Mathew, S., Paul, G., Shivasankar, K., Choudhury, A., and Rao, C. N. R. **2002**, "Supramolecular hydrogen-bonded structures in organic amine squarates," J. Mol Struc., **641**, pp. 263–279.

12. Gilli, G., Bertolasi, V., Gilli, P., Ferretti, V., **2001**, "Associations of squaric acid and its anions as multiform building blocks of hydrogen-bonded molecular crystals", Acta Crystallogr., **B57**, pp. 859.

13. Karle, I. L., Ranganathan, D., and Haridas, V., **1996**, "A Persistent Preference for Layer Motifs in Self-Assemblies of Squarates and hydrogen squarates by hydrogen bonding [X−H···O; X = N, O, or C]: A crystallographic study of five organic salts" J. Am. Chem. Soc., **118**(30), pp. 7128.

14. Van Ooijen, J.A.C., Reedijik, J., Spek. A.L., **1979**, "Crystal and molecular structure, spectroscopy, and magnetism of diaquobis(imidazole)catena-.mu.-(squarato-1,3)-nickel(II), A one-dimensional polymer", Inorg. Chem, **18**(5), pp. 1184.

15. Zenkhri, L., Bataille, T., and Audebrand, N., **2011**, "A second monoclinic polymorph of ethyl-enediammonium bis-(hydrogen squarate) monohydrate", Acta Cryst, **E67**, pp. o1118.

16. Zenkhri, L., Audebrandb, N., and Bataille, T., **2011**, "Yttrium ethyl-enediammonium squarate tetrahydrate", Acta Cryst, **E67**, pp. m529–m530.

17. Kanthers, J.A., Schouten,A., Kroon, J., and Grech, E., **1991**,"Structure of 8-Dimethylamino-l-dimethylammonionaphthalene Hydrogen Sqnarate", Acta Crystallogr, **C47**, pp. 807.

18. Bertolasi, V., Gilli, P., Ferretti, V., and Gilli, G., **2001**,"General rules for the packing of hydrogen-bonded crystals as derived from the analysis of squaric acid anions: aminoaromatic nitrogen base co-crystals", Acta Crystr. **B57**, pp. 591.