

Reaction of Hydrazine Hydrate with Oxalic Acid: Synthesis and Crystal Structure of Dihydrazinium Oxalate

Rajendran Selvakumar,¹ Thathan Premkumar,^{1,2,*} Vadivelu Manivannan,³
Kaliannan Saravanan¹ and Subbiah Govindarajan^{1,*}

¹Department of Chemistry, Bharathiar University, Coimbatore – 641 046, India.

²The University College/Department of Chemistry, Sungkyunkwan University, Suwon 440-746, South Korea.

³Department of Materials Science, Ponnaiyah Ramajeyam Institute of Science and Technology, Prist University, Thanjavur– 613 403, India.

Received 15 July 2013, revised 28 November 2013, accepted 10 December 2013.

ABSTRACT

The reaction of oxalic acid with hydrazine hydrate (in appropriate mole ratio) forms the dihydrazinium oxalate under specific experimental condition. The title compound is a molecular salt containing two discrete hydrazinium cations and an oxalate anion. The oxalate anion is perfectly planar and there is a crystallographic centre of symmetry in the middle of the C-C bond. The C-O bond distances are almost equal indicating the presence of resonance in the oxalate ion. The crystal packing is stabilized by intermolecular N-H...O and N-H...N hydrogen bonds. The oxalate ions are linked together end to end through hydrogen bonds (via $N_2H_5^+$ ions) and run parallel to the [101] direction. It is interesting to note that each oxalate group in the structure is surrounded by six hydrazinium ions through hydrogen bonding. Similarly, each hydrazinium ion is surrounded by three oxalate and one hydrazinium ion.

KEY WORDS

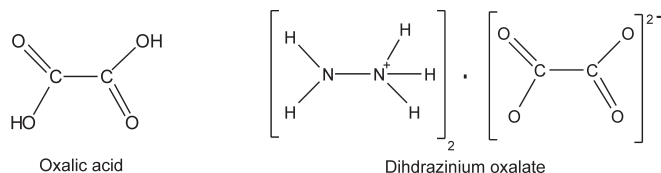
Hydrazine, oxalic acid, dihydrazinium oxalate, crystal structure.

1. Introduction

Hydrazine, a weaker base than ammonia, is a diacidic base that forms $N_2H_5^+$ [hydrazinium (+1)] and $N_2H_6^{2+}$ [hydrazinium (+2)] ionic salts with mineral as well as carboxylic acids. Hydrazinium (+1) salts are more common and they can be obtained with a wide variety of acids whereas hydrazinium (+2) salts are formed only with strong acids. Dibasic acids are known to form N_2H_5HA , $(N_2H_5)_2A$ and $N_2H_5HA.H_2A$ type of salts (H_2A = dibasic acid) with hydrazine. Though a number of hydrazinium salts of the former two types with different dibasic acids have been reported, it appears that no report is available in literature on the hydrazinium salts of the third type, viz. $N_2H_5HA.H_2A$, except that of oxydiacetic acid.¹

Hydrazine forms two types of salts with oxalic acid, viz. $N_2H_4.H_2C_2O_4$ and $2N_2H_4.H_2C_2O_4$. Pratt and Richards² studied these compounds with proton magnetic resonance and satisfactorily explained that these compounds could be formulated as $N_2H_5.HC_2O_4$ and $(N_2H_5)_2C_2O_4$, respectively. To prepare $(N_2H_5)_2C_2O_4$, Pratt and Richards first prepared $N_2H_6C_2O_4$ salt which was then treated with an aqueous solution of hydrazine hydrate.² The structure of $N_2H_5.HC_2O_4$ was extensively and thoroughly studied by X-ray^{3,4} and neutron⁵ diffraction methods and found to consist of chains of $N_2H_5^+$ and $HC_2O_4^-$ ions. The chains are cross-linked by N-H...O bonds from the $N_2H_5^+$ ions, thus forming a three-dimensional network. Though much has been reported on the $N_2H_5HC_2O_4$ salt, the crystal structure of $(N_2H_5)_2C_2O_4$ has not been determined. The structures of oxalic acid and its salt are shown below.

The spectral and thermal properties of this salt have been well studied,⁶ but the crystal structure has not been reported so far.



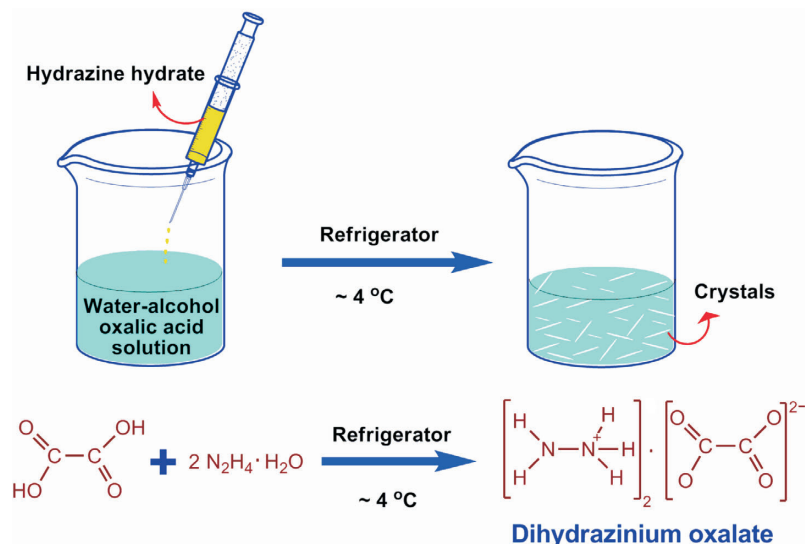
The preparation of the single crystals (suitable for single crystal X-ray analysis) of dihydrazinium oxalate is difficult (the crystals obtained only in ice-cold conditions). When the reaction was carried out above 25 °C, the title compound was not obtained; instead only monohydrazinium oxalate was realized showing the thermal transformation of the dihydrazinium oxalate to the monohydrazinium salt. This may be the main reason that the crystal structure of dihydrazinium oxalate $[(N_2H_5)_2C_2O_4]$ salt has not been reported so far, though the crystal structure of monohydrazinium salt of oxalic acid has been realized around four decades ago (~1973).^{3,4} Interestingly, a successful attempt has been made to determine the crystal structure of the $(N_2H_5)_2C_2O_4$ and the results are presented in this paper.

2. Experimental

2.1. Preparation of Dihydrazinium Oxalate, $(N_2H_5)_2C_2O_4$

Dihydrazinium oxalate was prepared by dissolving hydrazine hydrate and oxalic acid (in the mole ratio 2:1) in equal volume of water-alcohol mixture, in ice-cold conditions (yield: 85 %; mp 147 °C). When the reaction was carried out above 25 °C the title compound was not obtained; instead only monohydrazinium oxalate was realized showing the thermal transformation of the dihydrazinium oxalate to the mono salt. Elemental analysis: C (%): 15.35 (Cald. 15.58); H (%): 6.28 (6.54); N (%): 36.40 (36.36);

*To whom correspondence should be addressed.
E-mail: T.P.: thathanpremkumar@gmail.com; S.G.: drsgovind@yahoo.co.in



Scheme 1

Scheme and reaction showing the simple experimental procedure for the preparation of dihydrazinium oxalate salt.

and % hydrazine: 41.0 (Cald. 41.58). The hydrazine content of the salt was determined volumetrically using a standard KIO_3 (0.025 M) solution under Andrews' conditions.⁷

2.2. Single Crystal X-ray Diffraction Analysis

Preliminary examination and data collection were performed using a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer at 218 K using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) equipped with a sealed tube X-ray source. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages⁸ were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids. Collected data were corrected for systematic errors using SADABS⁹ based on the Laue symmetry using equivalent reflections. Structure solution and refinements were carried out using the SHELXTL software package.¹⁰

3. Results and Discussion

The dihydrazinium oxalate crystals are colourless and soluble in water. The detailed experimental procedure and reaction involved for the preparation of titled salt are explained in Scheme 1. The analytical data (elemental and volumetric analyses) agree well with the proposed formula for the $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$ salt. The hydrazine content (41.0 %) of the salt was determined volumetrically using a standard KIO_3 (0.025 M) solution under Andrews' conditions,⁷ which was consistent (calculated value 41.58 %) with the formula of the salt, $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$, determined by single crystal X-ray diffraction method.

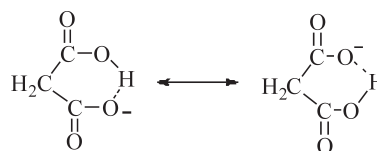
It is interesting to note that oxalic⁶ and succinic acids¹¹ form both hydrazinium and dihydrazinium salts, whereas malonic acid forms only mono-hydrazinium salt, viz. $\text{N}_2\text{H}_5(\text{HOOC}-\text{CH}_2-\text{COO})$. The reasons are very difficult to generalize.

As reported,⁶ oxalic acid forms both salts. The hydrogenoxalate

anion which is represented as $\text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$ has a strong $-\text{I}$ effect

due to the $-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$ group that makes the O-H bond more labile. This leads to the formation of a dihydrazinium salt. In the case of hydrogenmalonate anion, the O-H bond is stabilized by the

formation of a six-membered ring anion due to strong intramolecular hydrogen bonding.

Table 1 Crystal data for $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$.

Empirical formula	$\text{C}_2\text{H}_{10}\text{N}_4\text{O}_4$
Formula weight	154.14
Temperature	223(2) K
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 12.9415(11) \text{ \AA}$ $b = 3.7098(3) \text{ \AA}$ $c = 12.3455(11) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 95.478(2)^\circ$ $\gamma = 90^\circ$
Volume	$590.01(9) \text{ \AA}^3$
Z	4
Density (calculated)	1.735 g/cm^3
Absorption coefficient	0.133 mm^{-1}
F(000)	328
Crystal size	$0.22 \times 0.19 \times 0.18 \text{ mm}^3$
Theta range for data collection	3.16 to 31.02
Index ranges	$-10 \leq h \leq 18, -5 \leq k \leq 5,$ $17 \leq l \leq 17$
Reflections collected	2364
Independent reflections	918 [R(int) = 0.0168]
Completeness to theta	31.02 97.0 %
Absorption correction	SADABS
Max. and min. transmission	0.9828 and 0.6602
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	918 / 16 / 67
Goodness-of-fit on F^2	1.093
Final R indices [I > 2sigma(I)]	$\text{R1} = 0.0342, \text{wR2} = 0.1009$
R indices (all data)	$\text{R1} = 0.0386, \text{wR2} = 0.102$
Largest diff. peak and hole	0.469 and $-0.275 \text{ e \AA}^{-3}$

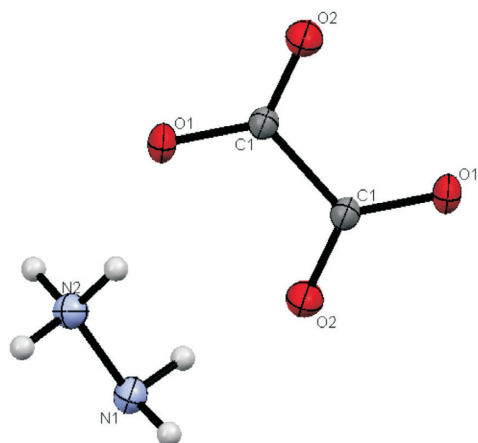


Figure 1 ORTEP diagram of $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$ with thermal ellipsoids at 60 % probability.

Hence a proton cannot be abstracted by a weak base like N_2H_4 , which prevents the formation of dihydrazinium salts. In hydrogensuccinate anion, the intramolecular hydrogen bonding is not preferred due to an increase in size of the ring. Also the $-I$ effect of the carboxylate group makes the O-H bond more labile. This helps to form the dihydrazinium salt.

Single crystals obtained for $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$ salt has been studied using single crystal X-ray diffraction methods. The crystal data including experimental details, bond length, bond angle and hydrogen bonding parameters are given in Tables 1–3.

The ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of the title compound is shown in Fig. 1. The oxalate ions are linked together into infinite chains by $\text{O}\cdots\text{H}-\text{N}$ bonds and the bond distances vary from 2.8095 (9) to 3.6974 (12) Å. The $\text{C}_2\text{O}_4^{2-}$ skeleton is perfectly planar and there is a crystallographic centre of symmetry in the middle of C-C bond. The covalent bond distances within the $\text{C}_2\text{O}_4^{2-}$ ion are C-C = 1.5597 (15), C-O1 = 1.2613 (9) and C-O2 = 1.2477 (9) Å. The C-O bond distances are almost equal

Table 2. Bond lengths/Å and angles/ $^\circ$ for $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$.

C(1)-O(2)	1.2477(9)	O(2)-C(1)-O(1)	126.24(7)
C(1)-O(1)	1.2613(9)	O(2)-C(1)-C(1)#1	117.61(8)
C(1)-C(1)#1	1.5597(15)	O(1)-C(1)-C(1)#1	116.15(8)
N(1)-N(2)	1.4478(10)	N(2)-N(1)-H(1A)	105.6(8)
N(1)-H(1A)	0.911(11)	N(2)-N(1)-H(1B)	106.2(8)
N(1)-H(1B)	0.925(11)	H(1A)-N(1)-H(1B)	105.9(11)
N(2)-H(2B)	0.906(10)	N(1)-N(2)-H(2B)	112.5(8)
N(2)-H(2A)	0.893(10)	N(1)-N(2)-H(2A)	108.8(8)
N(2)-H(2C)	0.900(11)	H(2B)-N(2)-H(2A)	110.5(10)
		N(1)-N(2)-H(2C)	105.8(9)
		H(2B)-N(2)-H(2C)	110.3(10)
		H(2A)-N(2)-H(2C)	108.9(10)

Table 3 Hydrogen bond lengths/Å and angles/ $^\circ$ for $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$.

	D-H	H A	D A	D-H A
N1-H1A...O2(i)	0.911(11)	2.592(13)	3.0010(9)	108.0(9)
N2-H2B...O1(ii)	0.906(10)	2.142(11)	3.0018(9)	157.9(11)
N2-H2C...N1(ii)	0.900(11)	2.843(12)	3.2270(10)	107.3(9)
N2-H2C...O1(iii)	0.900(11)	2.547(14)	2.8842(9)	102.9(9)
N2-H2A...O1(iv)	0.893(10)	1.923(10)	2.8095(9)	171.8(11)
N2-H2A...O2(iv)	0.893(10)	2.969(11)	3.5359(10)	123.0(9)
N2-H2C...N1(v)	0.900(11)	2.079(10)	2.9335(10)	158.2(12)
N2-H2C...N2(v)	0.900(11)	2.928(11)	3.6974(12)	144.4(11)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x, y-1, z$; (iii) $-x+1, y-1, -z+1/2$; (iv) $-x+1, y, -z+1/2$; (v) $-x+3/2, y-1/2, -z+1/2$.

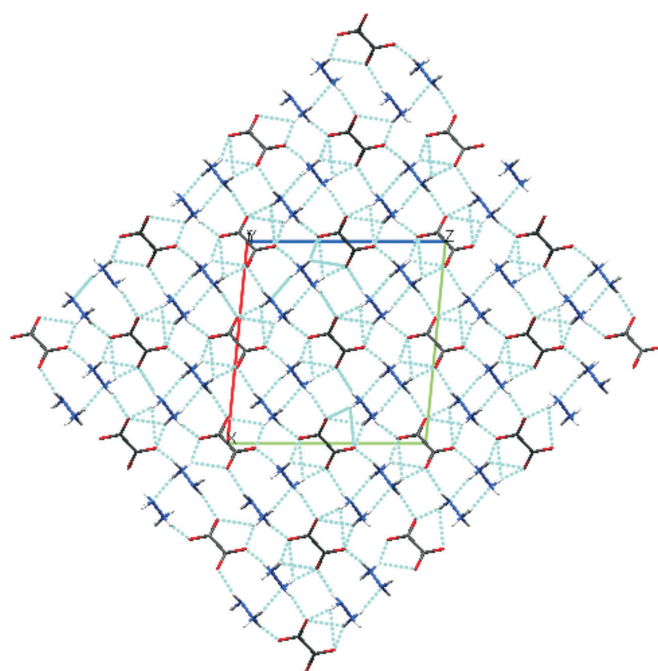


Figure 2 Packing diagram of $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$ viewed down the b axis.

indicating the presence of resonance in the oxalate ion. The N–N distance of the N_2H_5^+ ion is 1.4478 (10) Å which is in agreement with the value reported for $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ (N–N bond length is 1.443 (5) Å) and $\text{CH}_3\text{COON}_2\text{H}_5$ (N–N bond length is 1.462 (12) Å). The bond angles within the N_2H_5^+ ion are all fairly close to tetrahedral and there seems to be a significant difference between the two ends. In the NH_2 end, the bond angles are equal and nearer to 106° , whereas in the NH_3 end the angles are around 110° .

The structure is built from N_2H_5^+ and $\text{C}_2\text{O}_4^{2-}$ ions, which are joined by hydrogen bonds (Fig. 2). The oxalate ions are linked together end to end through hydrogen bond (*via* N_2H_5^+ ions) and run parallel to [101] direction. The chains are cross-linked by $\text{N}-\text{H}\cdots\text{O}$ bonds from the donor N_2H_5^+ ions, thus forming a three-dimensional network. In the lattice, the adjacent N_2H_5^+ ions are also linked to each other through $\text{N}-\text{H}\cdots\text{N}$ bond, with the NH_2 part of one hydrazinium ion to the NH_3 end of another. It is interesting to note that each oxalate group in the structure is surrounded by six hydrazinium ions through hydrogen bonding. Similarly, each hydrazinium ion is surrounded by three oxalate and one hydrazinium ion.

4. Conclusions

The reaction of oxalic acid with hydrazine hydrate (in appropriate mole ratio) forms the dihydrazinium oxalate at specific

experimental conditions. Note that when the reaction is carried out above 25 °C the title compound was not obtained; instead only monohydrazinium oxalate was realized showing the thermal transformation of the dihydrazinium oxalate to the mono salt. The crystal structure of dihydrazinium oxalate was determined. In the salt, the cations and anions form a rigid three-dimensional network through hydrogen bonding. It is interesting to note that each oxalate group in the structure is surrounded by six hydrazinium ions through hydrogen bonding. Similarly, each hydrazinium ion is surrounded by three oxalate and one hydrazinium ion.

References

- 1 S. Yasodhai and S. Govindarajan, *J. Therm. Anal.*, 2000, **62**, 737–745.
- 2 I.L. Pratt and R.E. Richards, *Trans. Faraday Soc.*, 1953, **49**, 744–751.
- 3 N.B.K. Ahmed, R. Liminga and I. Olovsson, *Acta Chem. Scand.*, 1968, **22**, 88–96.
- 4 J.O. Thomas, *Acta Cryst. B*, 1973, **29**, 1767–1776.
- 5 A. Nilsson, R. Liminga and I. Olovsson, *Acta Chem. Scand.*, 1968, **22**, 719–731.
- 6 D. Gajapathy, S. Govindarajan and K.C. Patil, *Thermochim. Acta*, 1983, **60**, 87–92.
- 7 A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 4th edn., Longman, London, 1986.
- 8 *Bruker Analytical X-ray; APEX2 and SAINT*; Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
- 9 R.H. Blessing, *Acta Cryst. A*, 1995, **51**, 33–38.
- 10 G.M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122.
- 11 K. Kuppusamy, B.N. Sivasankar and S. Govindarajan, *Thermochim. Acta*, 1995, **259**, 251–262.