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Research Article

SYNTHESIS AND CRYSTAL CHARACTERIZATION OF BIS-(GUANIDINIUM) 3,3-DIMETHYLGLUTARATE HYDRATE

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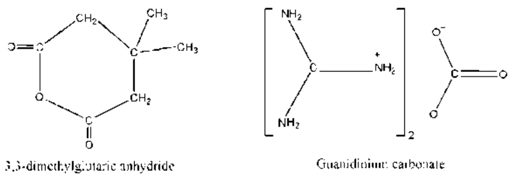
ABSTRACT

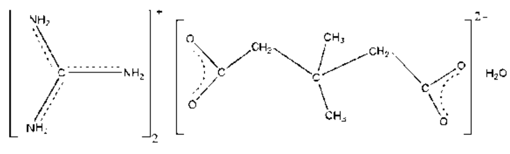
The salt$\{[NH_2C(NH_2)_2]_2\}(\underline{C_7H_{10}O_4})(H_2O)$(**I**) was isolated from reaction between aqueous solutions of 3,3-dimethylglutaric anhydride and guanidinium carbonate. It crystallizes in the triclinic space group *P-1* with $Z = 2$, $a = 8.7314(10)$ Å, $b = 9.1938(19)$ Å, $c = 10.9182(18)$ Å, $\alpha = 73.118(13)°$, $\beta = 79.067(13)°$, $\gamma = 76.353(13)°$ and $V = 808.1\ (2)$ Å^3. The asymmetric unit is comprised of a guanidinium cation, a 3,3-dimethylglutarate anion and a molecule of water. In the structure, guanidinium cations, 3,3-dimethylglutarate anions and water molecules are connected through expanses N–H···O and O–H···O inter species hydrogen bonds leading to a supramolecular three dimensional structure.

INTRODUCTION

Guanidinium with its six proton donors/acceptors may easily give rise to polydimensional topology self-assemblies. The possible propagation of multidirectional hydrogen bonding interactions makes guanidinium a useful candidate in crystal engineering. Several inorganic-organic hybrid materials with guanidinium have shown a great variety of networks (Halevas *et al.*, 2017; Thuery and Harrowfield, 2016; Han *et al.*, 2012; Galloway *et al.*, 2010; Moggach *et al.*, 2009). Videnova-Adrabinska and coworkers earlier reported some guanidinium dicarboxylates crystal structures among with guanidinium hydrogen glutarate, illustrating the prospective arrangement of guanidinium to grow two-dimensional hydrogen-bonded networks (Videnova-Adrabinska *et al.*, 2007). 3,3-dimethylglutarate and some related (glutarate substituted at the 3-position) have been used to synthesize and structurally characterize by single crystal crystallographic analysis, some compounds that exhibit diverse topologies (Nettleman *et al.*, 2010). An interesting structure with a two-fold interpenetration of layers has also been isolated and characterized (Contejean and La Duca, 2018). Diverse copper (II) compounds containing 3,3-dimethylglutarate or mixed ligands such as 3,3-dimethylglutarate/2,2′-bipyridine were reported to be able to kill both liver and kidney cell lines at very low concentrations (Devereux *et al.*, 2006). The Dakar group has focused on glutarate and N,N,N′,N′-tetramethylguanidinium, and has already published some articles (Boye *et al.*, 2007a, b; Ndiaye *et al.*, 2016a, b, 2017). Continuing our investigations on glutarate, especially on 3,3-dimethylglutarate and guanidinium, we investigated in this work the interactions between 3,3-dimethylglutaric anhydride and guanidinium carbonate which has afforded crystals of the salt **I**, namely bis (guanidinium) 3,3-dimethylglutarate hydrate (Scheme **1**), whose crystal characterization is reported herein.



3,3-dimethylglutaric anhydride Guanidinium carbonate



Studied Compound I

Scheme 1 Molecular representations of 3,3-dimethylglutaric anhydride and guanidinium carbonate reagents, and compound **I** related to this study.

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MATERIALS AND METHODS

Synthesis and crystallization

All chemicals were purchased from Aldrich Company and were used without any further purification. To 1.30 g of 3,3-dimethylglutaric anhydride, $C_7H_{10}O_3$ 99 % purity was added 25 mL hot water at 333 K. The mixture was first homogenized by stir then 25mL hot aqueous solution (333 K) of guanidinium carbonate, $\{[NH_2C(NH_2)_2]CO_3\}$ 98 % purity prepared by dissolving 1.66 g in 25 mL, was added slowly. The resulting clear solution was stirred 2h in the opened atmosphere. Submitted to a forced evaporation in an oven at 333 K, colorless prism like crystals of the salt **I** suitable for a X-ray crystallographic analysis were obtained after some days.

X-ray crystallography

A crystal of approximate dimensions 0.226×0.192×0.032 mm was used for data collection. The X-ray crystallographic data were collected using a Nonius Kappa CCD diffractometer operating at $T = 293$ (2) K. Data were measured using φ and ω scans using Mo*K*α radiation (λ = 0.71073 Å) using a collection strategy to obtain a hemisphere of unique data determined by *COLLECT* (Nonius, 2003). Cell parameters were determined and refined using *Dirax (*Duisenberg, 1992*)*. Data were corrected for absorption correction using *Eval CCD (*Duisenberg *et al.,* 2003*)*. The structure was solved using *SHELXS* (Sheldrick, 2015a) and the structure refined using least-squares minimization *SHELXL* (Sheldrick, 2015b).

Programs used for the representation of the molecular and crystal structures: *Olex2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008). The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. CCDC 1995963 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Table 1 Crystal data and structure refinement

Parameters	Compound **I**
Empirical formula	$C_7H_{10}O_4{\cdot}2(CH_6N_3){\cdot}H_2O$
Formula weight	269.34
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	a = 8.7314 (10)Å α = 73.118 (13)° b = 9.1938 (19)Å β = 79.067 (13)° c = 10.9182 (18)Å γ = 76.353(13)°
Volume	808.1 (2)Å^3
Z	2
Calculated density	1.218 g cm^{-3}
Absorption coefficient	0.099 mm^{-1}
F(000)	320
Crystal size	0.226× 0.226× 0.226 mm^3
Theta range for data collection	3.439–28.496°
Limiting indices	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$
Reflections collected/unique	27442/4082
R_{int}	0.0368
Absorption correction	Multi-scan
Max. and min. transmission	0.7457 and 0.7216
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4082/0/189
Goodness-of-fit on F^2	1.065
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0497$, $wR_2 = 0.1145$
R indices (all data)	$R_1 = 0.0813$, $wR_2 = 0.1018$
Largest diff. peak and hole	0.209 and -0.185e Å^{-3}

$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.2475P]$ where $P = (F_o^2 + 2F_c^2)/3$

Table 2 Selected bond lengths (Å) and angles (°)

Atom-Atom	Bond length	Atom-Atom	Bond length
O1—C3	1.2588 (17)	C7—O4	1.2446 (18)
O2—C3	1.2507 (17)	C7—O3	1.2636 (19)
C2—N6	1.322 (2)	N2—C1	1.316 (2)
C2—N4	1.3235 (19)	N1—C1	1.319 (2)
C2—N5	1.318 (2)	C1—N3	1.327 (2)
Atom-atom-atom	Angle value	Atom-atom-atom	Angle value
O1—C3—C4	118.26 (13)	O4—C7—C6	119.57 (14)
O2—C3—O1	122.63 (13)	O4—C7—O3	122.19 (14)
N6—C2—N4	119.20 (14)	N2—C1—N1	120.32 (14)
N5—C2—N6	120.28 (14)	N2—C1—N3	120.90 (15)
N5—C2—N4	120.52 (14)	N1—C1—N3	118.78 (15)

RESULTS

Compound **I** was isolated from reaction between two reagents, an anhydride and a carbonate salt, in aqueous solution. 3,3-dimethylglutaric anhydride, $C_7H_{10}O_4$ was preliminary dissolved in water at 333 K giving a clear solution. To this clear aqueous solution was added an equimolaraqueous solution of guanidinium carbonate, $\{[NH_2C\ (NH_2)_2]CO_3\}$. The resulting clear solution was stirred 2h. Colorless single crystals grew (Eq. 1) from the limpid solution and were characterized as **I**, $\{[NH_2C(NH_2)_2]_2\}[(C_7H_{10}O_4)(H_2O)]$.

$$C_7H_{10}O_3 + 2H_2O + \{[NH_2C(NH_2)_2]CO_3\} \xrightarrow{60°C} \underset{\text{Studied Compound}}{\{[NH_2C(NH_2)_2]_2\}[(C_7H_{10}O_4)(H_2O)]} + H_2CO_3 \quad \text{(Eq.1)}$$

DISCUSSION

Salt **I** crystallizes in the triclinic space group P-1. Its asymmetric unit depicted in Fig. 1 is comprised of two independent guanidinium cations, one 3,3-dimethylglutarate anion and a water molecule linked through strong H-bonds. The geometric parameters within the 3,3-dimethylglutarate are in accordance with those already reported in the literature (Arıcı *et al.*, 2019; Yeşilel & Wriedt, 2019; Nettleman *et al.*, 2010). The C–O bond lengths from 1.2446 (18) Å to 1.2636 (19) Å indicate a π delocalization, the slight difference is due to the involvement fashion in hydrogen bonding interactions. Angle and bond distance values for the guanidinium cation well corroborate those found in known containing guanidinium compounds (Videnova-Adrabinska *et al.*, 2007; Peng *et al.*, 2010). The guanidinium cations C–N distances, whose C–N_{amine} and C=N_{imine} cannot be differentiated, as well as the sum of the angles at C1 and C2 carbon atoms of 360° indicate a π delocalization and a perfect planar arrangement, respectively.

In a supramolecular point of view, in the crystal of **I** the 3,3-dimethylglutarates are organized into dimers *via* O–H···O hydrogen bonds involving two water molecules. The hydrogen bonded dimers are strongly linked into chains by the cations (N4, N5, N6) through N–H···O and N–H···O_{water}. The chains are interconnected through N4–H4D···O2 and N6–H6D···O2 hydrogen bonds giving rise to layers represented in Fig. 2.The layers are then linked *via* the remaining cations (N1, N2, N3) and the carboxylate O atoms through N–H···O hydrogen bonds (see Table 3). Each 3,3-dimethylglutarate anion is linked to six cations and to two water molecules through N–H···O and O–H···O hydrogen bonds. The carboxylate oxygen atoms are each one involved in three H-bonds with two cations (O2 and O4) or with two cations and one molecule of water (O1 and O3), leading thus to tetrahedral environments at these O atoms. This hydrogen bonding interconnections fashion explains the slight difference of C–O bonds. The two longer C–O bonds involve two oxygen atoms (O1 and O3) that support two N–H···O and one stronger O–H···O hydrogen bonds while the shorter ones (O2 and O4) support three N–H···O hydrogen bonds. Each water molecule interacts with two O carboxylate atoms of two 3,3-dimethylglutarates and one guanidinium, through two O–H···O and one N–H···O hydrogen bonding interactions. Thus, the geometry around the O water is pyramidal. The inter species interactions exhibit five types of self-assemblies describing a 6-membered, a 8-membered and a 12-membered hydrogen bonded macrocycles involving both cations and anions, and a 8-membered and a 12-membered hydrogen bonded rings involving cations, anions and water molecules. Two different 8-membered and one 12-membered hydrogen bonded self-assemblies enable the junction between hydrogen bonded dimers, which grow into chains.The 12-membered hydrogen bonded macrocycle as well as the 6-membered ring comes from the joining chains. The rings encountered within the chains are fused, those allowing the sheets to grow as well. The extensive hydrogen bonding interactions between cations, anions and water molecules give rise to a three-dimensional supramolecular structure depicted in Fig. 3.

Table 3 Hydrogen-bond geometry (Å, º) [Symmetry codes: (i) −*x*+1, −*y*+1, −*z*−3; (ii) −*x*+1, −*y*, −*z*−2; (iii) *x*+1, *y*−1, *z*; (iv) −*x*+1, −*y*+1, −*z*−2; (v) *x*, *y*, *z*+1; (vi) −*x*, −*y*+1, −*z*−2.]

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*C*···O4^{i}	0.86	2.08	2.9217 (18)	167
N6—H6*D*···O2	0.86	2.22	2.9664 (18)	146
N4—H4*C*···O1^{ii}	0.86	2.07	2.9173 (19)	167
N4—H4*D*···O2	0.86	2.10	2.8789 (19)	151
N5—H5*A*···O3^{i}	0.86	2.01	2.8528 (18)	165
N5—H5*B*···O5^{iii}	0.86	2.20	2.9919 (19)	153
N2—H2*A*···O2	0.86	2.18	3.0216 (18)	166
N2—H2*B*···O5^{iv}	0.86	2.23	3.075 (2)	167
N1—H1*A*···O1	0.86	1.96	2.8238 (17)	178
N1—H1*B*···O4^{v}	0.86	2.18	2.9070 (18)	142
N3—H3*A*···O3^{iv}	0.86	2.18	2.977 (2)	155
N3—H3*B*···O4^{v}	0.86	2.21	2.9246 (19)	141
O5—H5*C*···O1^{vi}	0.85 (3)	1.94 (3)	2.7623 (17)	160 (2)
O5—H5*D*···O3	0.85 (2)	1.83 (2)	2.6689 (18)	168 (2)

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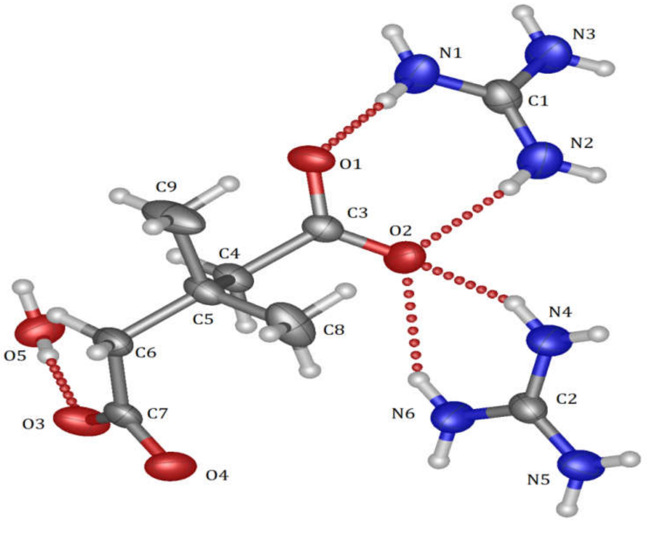

Fig 1 The molecular structure of salt **I** showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

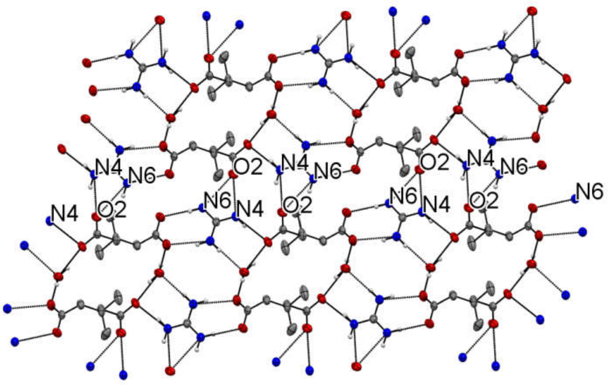

Fig 2 Partial packing diagram of **1** showing the hydrogen-bonded chains connected into sheets parallel to (0 1 1). Only hydrogen atoms involved in the interactions are shown. Symmetry identifiers are those found in Table 3.

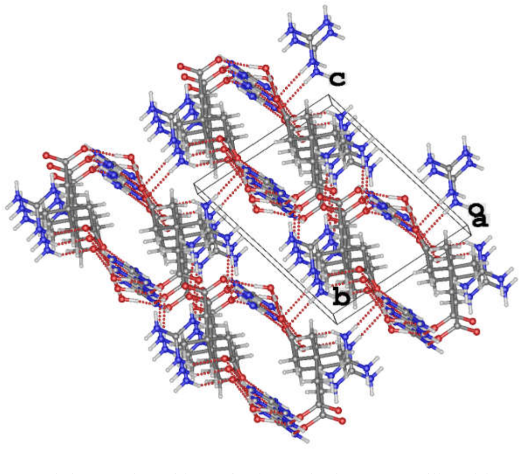

Fig 3 The partial crystal packing of salt **I**. Displacement ellipsoids are drawn at the 50% probability level.

References

1. Halevas, E., Chatzigeorgiou, E., Hadjispyrou, S., Hatzidimitriou, A. G., Psycharis, V. and Salifoglou, A. 2017.pH- and ligand structure-specific synthesis, structure-lattice dimensionality and spectroscopic fingerprint in novel binary In(III)-hydroxycarboxylic acid materials.*Polyhedron*, 127:420-431.
2. Thuery, P. and Harrowfield, J. 2016.

Tetrahydrofurantetracarboxylic Acid: An Isomerizable Framework-Forming Ligand in Homo- and Heterometallic Complexes with UO_2^{2+}, Ag^+, and Pb^{2+}.*Cryst. Growth Des.*,16:7083-7093.

3. Han, J., Yau, C. W., Chan, C. W. and Mak, T. C. W. 2012. Anionic Host Layers Constructed with Guanidinium−Hydrogen Carbonate Dimer 2:1 Rosette-Ribbons and Bridging Carboxylate Connectors. *Cryst.Growth Des*.12:4457-4465.
4. Galloway, K. W., Moggach, S. A., Parois, P., Lennie, A. R., Warren, J. E., Brechin, E. K., Peacock, R. D., Valiente, R., Gonzalez, J., Rodriguez, F., Parsons, S. and Murrie, M. 2010.Pressure-induced switching in a copper(II) citrate dimer.*CrystEngComm.*,12:2516-2519.
5. Moggach, S. A., Galloway, K. W., Lennie, A. R., Parois, P., Rowantree, N., Brechin, E. K., Warren, J. E., Murrie, M. and Parsons, S. 2009. Polymerisation of a Cu(II) dimer into 1D chains using high pressure. *CrystEngComm.,*11:2601-2604.
6. Videnova-Adrabinska, V., Obara, E. and Lis, T. 2007. Two-dimensional hydrogen-bonded networks in guanidinium hydrogen Dicarboxylates.*New J. Chem*., 31:287-295.
7. Nettleman, J. H., Szymanski, P. J., Sposato, L. K., and LaDuca, R. L. 2010. Diverse dimensionalities and structures in copper coordination polymers incorporating substituted aliphatic dicarboxylate ligands and 4,4′-bipyridine. *Inorg.Chim.Acta*, 363:225-233.
8. Contejean, Z. I. and LaDuca, R. L. 2018. Nitroaromatic-detecting zinc and cadmium coordination polymers with methyl-substituted aliphatic dicarboxylate and 4,4′-dipyridylamine ligands and diverse topologies*J. Solid State Chem*.,266:44-53.
9. Devereux, M., McCann, M., O'Shea, D., O'Connor, M., Kiely, E., McKee, V., Naughton, D., Fisher, A., Kellett, A., Walsh, M., Egan, D. and Deegan, C. 2006. Synthesis, superoxide dismutase mimetic and anticancer activities of metal complexes of 2,2-dimethylpentanedioic acid(2dmepdaH2) and 3,3-dimethylpentanedioic acid(3dmepdaH2): X-ray crystal structures of [Cu(2dmepda)(bipy)2]·7.5H2O and [Cu(3dmepda)(bipy)2]·5H2O (bipy = 2,2′-bipyridine) *Bioinorg. Chem. Appl.,* ID-80283:1-11.
10. Boye, M. S., Diassé-Sarr, A., Molloy, K. C., Kociok-kohn, G. and Mahieu, B. 2007a. Poly[bis(trimethyltin)-μ-glutarato]. *Acta Cryst*. E63:m1724-m1726.
11. Boye, M. S. and Diassé-Sarr, A. 2007b. “Synthèse et caractérisation par spectroscopies Infrarouge et Mossbauer de nouveaux dérivés glutarato, 3,3-diméthylglutarato et hydrogénooxolato contenant des résidus SnR_2 [R= Me,Bu]”. C. R. Chimie 10:489-92.
12. Ndiaye, M., Samb, A., Diop, L. and Maris, T. 2016a. *ActaCryst*.Crystal structure of catena-poly[N,N,N′,N′-tetra-methyl-guanidinium [(chlorido-cadmate)-di-μ-chlorido]. E72:1-3.
13. Ndiaye, M., Samb, A., Diop, L. and Maris, T. 2016b. Crystal structure of bis(*N*,*N*,*N*′,*N*′-tetra methyl-guanidinium) tetrachloridocuprate(II). *ActaCryst*. E72:1047-1049.
14. Ndiaye, M., Samb, A., Diop, L., Cattey, H., Pourchet, S. and Plasseraud, L. 2017.Synthesis, characterization, and thermal properties of N,N,N′,N′-tetramethylguanidiniumtribromidocadmate (II) exhibiting an unusual coordination geometry. *Main Group Met. Chem*., 40:137-143.
15. Nonius. 2003. *COLLECT*. Nonius BV, Delft, The netherlands.
16. Duisenberg, A. J. M. 1992.Indexing in single-crystal diffractometry with an obstinate list of reflections.*J. Appl. Cryst.*,25:92-96.
17. Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. and Schreurs, A. M. M. 2003. An intensity evaluation method: EVAL-14. *J. Appl. Cryst*., 36:220-229.
18. Sheldrick, G. M. 2015*a*. SHELXT - Integrated space-group and crystal-structure determination. *ActaCryst*., A71:3-8.
19. Sheldrick, G. M. 2015*b*. Crystal structure refinement with SHELXL.*ActaCryst*., C71:3-8.
20. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. 2009. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*., 42:339-341.
21. Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. and Wood, P. A. 2008. Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. *J. Appl. Cryst*., 41:466-470.
22. Arıcı, M., Erer, H., Karaçam, S. and Yeşilel, O. Z. 2019.Coordination polymers based on 3,3-dimethylglutarate and 1,4-bis((1H-imidazol-1-yl)methyl)benzene: Hydrothermal synthesis and characterizations. *J. Solid State Chem*., 277:811–818.
23. Yeşilel, O. Z. and Wriedt, M. 2019. Lanthanide(III) coordination polymers constructed from 2,2- and 3,3-dimethylglutarate ligands. *Polyhedron*,169:32-38.
24. Peng, B., Peng, Q., Zhou, W. and Zhou, Z. 2010. Guanidinium L-glutamate. *Acta Cryst*., E66:o2679.

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