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Halogenides of dimethylglycine in comparison with respective salts of glycine, sarcosine and betaine

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ABSTRACT

We investigated salts formation in the DMG(dimethylglycine)–HCl–H_2O, DMG–HBr–H_2O and DMG–HI–H_2O systems. In addition to previously known dimethylglycinium chloride (DMGH)Cl, we obtained and characterized (structurally and spectroscopically) the following crystals: (DMGH)Br, (DMGH)I as well as the first salts of DMG with dimeric (DMG···DMGH) cation: (DMG···DMGH)Cl, (DMG···DMGH)Br, (DMG···DMGH)I. Obtained results are compared with results of known or newly obtained respective salts of glycine, sarcosine (monomethylglycine) and betaine (trimethylglycine).

1. Introduction

Among salts of glycine (Gly) and its *N*-methyl derivatives, monomethylglycine (sarcosine, Sar), dimethylglycine (DMG) and trimethylglycine (betaine, Bet), the salts of dimethylglycine are least studied [1]. Recently we started a systematic investigation of salts and molecular adducts of dimethylglycine with various inorganic and organic acids (more than 30 salts and adducts) [2].

Dimethylglycine and its first salt dimethylglycine hydrochloride were synthesized by Clarke et al., in 1933 [3]. Both are very hygroscopic. The crystal structure of dimethylglycine hydrochloride was reported in 1983 [4], while the crystal structure of dimethylglycine remained unknown until 2012. Crystals of hemihydrate of DMG and two anhydrous (orthorhombic and monoclinic) forms were obtained and investigated in the group of Boldyreva [5–8]. Rodrigues et al. obtained trifluoroacetate of dimethylglycine [9] as well as those of glycine, sarcosine and betaine [10–12]. Anioła et al. studied the reaction of glycine, sarcosine, dimethylglycine and betaine with squaric acid [13]. All these three salts of dimethylglycine have centrosymmetric structure. In Ref. [14] it was shown that in the system Sar–CF_3COOH–H_2O, in addition to previously obtained sarcosinium trifluoroacetate [11], one more salt exists with dimeric sarcosine sarcosinium cation, which is the first salt with dimeric cation of an amino acid with trifluoroacetate anion.

In this regard, we wondered if it is possible to obtain salts with a dimeric (DMG···DMGH) cation. For this purpose, we conducted a systematic investigation of salts and molecular adducts of dimethylglycine with various inorganic and organic acids [2].

In the present paper, we report our results on salts formed in the DMG–HCl–H_2O, DMG–HBr–H_2O and DMG–HI–H_2O systems. These results are compared with published data on respective salts of glycine, sarcosine and betaine. For completeness, we tried to obtain single crystals of absent salts or single crystals of salts which were known but the structures were not determined.

2. Experimental

2.1. Synthesis

As initial reagents, we used *N,N*-dimethyglycine (≥98.0%) both from Shanghai Worldyang Chemical Co. and Alfa Aesar Co., glycine

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Table 1
Crystallographic data and details of the structure refinement for (DMGH)Cl (**I**), (DMGH)Br (**II**) and (DMGH)I (**III**).

Crystal	(I)	(II)	(III)
Empirical Formula	$C_4H_{10}ClNO_2$	$C_4H_{10}BrNO_2$	$C_4H_{10}INO_2$
Formula mass	139.58	184.02	231.03
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, Z	$P2_1/c$, 4	$P2_1/n$, 8	$P2_1/n$, 8
a (Å)	7.0447(14)	10.585(2)	10.779(2)
b (Å)	7.2110(10)	10.027(2)	10.022(2)
c (Å)	13.863(3)	14.505(3)	15.282(3)
α (°)	90	90	90
β (°)	99.72(3)	110.77(3)	110.27(3)
γ (°)	90	90	90
V (Å^3)	694.1(2)	1439.5(5)	1548.5(5)
$\rho_{calc.}$(g cm^{-3})	1.336	1.698	1.982
Temperature (K)	200(2)	200(2)	200(2)
2θ	65.06	65.26	65.26
μ (mm^{-1})	0.470	5.633	4.064
F(000)	296	736	880
Absorption-correction	Multi-scan	Multi-scan	Multi-scan
Index ranges	±10, ±10, ±20	−15/16, ±15, ±21	±16, ±15, ±23
Reflections collected	9409	19456	20637
Independent reflections (R_{int})	2506	5226	5524
Data with $F_o > 4\sigma$ (F_o)	2215	4090	5214
Parameters refined/restrained	83	166	166
R_1^a/wR_2^b ($I > 4\sigma(I)$)	0.0239	0.0271	0.0162
R_1^a/wR_2^b (for all F_o^2)	0.0669	0.0609	0.0380
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.392/-0.213	0.758/-0.771	0.812/-0.901

Table 2
Selected bond lengths (in Å) and angles (in °) for (DMGH)Cl (**I**), (DMGH)Br (**II**) and (DMGH)I (**III**).

	(I)	(II)A	(II)B	(III)A	(III)B
C1–O1	1.3243(10)	1.319(2)	1.312(2)	1.3210(17)	1.3145(17)
C1–O2	1.2044(10)	1.201(2)	1.204(2)	1.2039(17)	1.2048(17)
C1–C2	1.5122(11)	1.507(2)	1.509(2)	1.5043(17)	1.5115(18)
C2–N1	1.4869(11)	1.4833(19)	1.486(2)	1.4839(16)	1.4844(17)
N1–C3	1.4923(11)	1.493(2)	1.491(2)	1.4985(18)	1.4947(18)
N1–C4	1.4945(11)	1.495(2)	1.493(2)	1.4952(17)	1.4943(18)
O2–C1–O1	125.83(8)	125.32(15)	126.26(16)	125.44(13)	126.17(13)
O2–C1–C2	124.85(7)	124.03(14)	123.63(15)	124.60(12)	123.80(12)
O1–C1–C2	109.31(7)	110.63(14)	110.09(14)	109.95(11)	110.02(12)
N1–C2–C1	112.52(6)	111.96(12)	110.57(13)	112.01(10)	110.56(10)
C2–N1–C3	109.99(6)	112.12(12)	111.09(13)	112.33(10)	111.17(11)
C2–N1–C4	113.36(6)	110.41(12)	111.46(13)	109.85(10)	111.60(11)
C3–N1–C4	110.37(7)	110.64(13)	110.25(14)	110.83(11)	110.22(11)
N–C–C═O	1.31(11)	2.3(2)	−8.5(2)	4.0 (2)	−6.34(19)

(≥99.0%, TLC) and hydriodic acid (57% w/w, distilled, stabilized with <1.5% hypophosphorous acid, 99.95%) from Sigma-Aldrich Co., and hydrochloric (32% w/w, chemically pure grade) and hydrobromic (40.5% w/w, ultrapure grade) acids from Reakhim Co. Crystalline compounds have been obtained by slow evaporation at room temperature from aqueous solution containing a

Table 3
Hydrogen bond parameters (in Å and °) for (DMGH)Cl (**I**), (DMGH)Br (**II**) and (DMGH)I (**III**).

	D-H···A	D-H	H···A	D···A	DHA
(**I**)	O1–H1···Cl1^{i}	0.871(16)	2.147(17)	3.0044(8)	168.0(13)
	N1–H11···Cl1	0.899(12)	2.217(12)	3.0900(9)	163.7(10)
(**II**)	O1A-H1A···Br1^{ii}	0.85(3)	2.28(3)	3.1204(14)	174(2)
	N1A-H11A···Br2 ^{iii}	0.87(2)	2.52(2)	3.3255(18)	154.2(16)
	O1B–H1B···Br2^{iv}	0.74(3)	2.41(3)	3.1393(16)	169(3)
	N1B–H11B···Br1	0.86(2)	2.63(2)	3.3546(17)	143.0(17)
(**III**)	O1A-H1A···I1^{ii}	0.80(3)	2.57(3)	3.3685(13)	175(3)
	N1A-H11A···I2 ^{iii}	0.819(18)	2.888(18)	3.5909(17)	145.1(15)
	O1B–H1B···I2^{iv}	0.74(3)	2.66(3)	3.3943(14)	173(3)
	N1B–H11B···I1	0.86(2)	2.84(2)	3.5629(15)	142.3(16)

Symmetry code: (i) -x+1, -y+2, -z+1; (ii) x+1, y, z; (iii) x+1/2, y+1/2, z+1/2; (iv) -x+1/2, y-1/2, -z+1/2.