Two New Supramolecular Assemblies Obtained by Reaction Between Saccharin and Long-chain Diamines

Eduardo E. Castellano[a], Oscar E. Piro[b], Beatriz S. Parajón-Costa[c], and Enrique J. Baran[c]

[a] Instituto de Fisica de São Carlos, Universidade de São Paulo, 13560 São Carlos (SP), Brazil
[b] Departamento de Física and Instituto IFLP (CONICET), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina
[c] Centro de Química Inorgánica (CEQUINOR, CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina

Reprint requests to Dr. E. J. Baran. E-mail: baran@quimica.unlp.edu.ar

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The crystal structures of heptamethylenediammonium bis(saccharinate) monohydrate, [H_3N-$(CH_2)_7$-NH_3](sac)$_2$·H_2O (**1**) and octamethylenediammonium bis(saccharinate) hemihydrate, [H_3N-$(CH_2)_8$-NH_3](sac)$_2$·0.5H_2O (**2**), were determined by single-crystal X-ray diffraction methods. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with 2 molecules per unit cell, and **2** in the monoclinic space group $P2_1/a$ with $Z = 4$. The saccharinate moiety is planar in both compounds presenting bonding characteristics comparable to those found in other saccharinate salts. The ionic crystals are further stabilized by an extensive H-bonding network, which links the anions and cations into an infinite three-dimensional supramolecular assembly. The FTIR spectra of the adducts are briefly discussed in comparison with those of the constituent molecules.

Key words: Heptamethylenediammonium Bis(saccharinate) Monohydrate, Octamethylenediammonium Bis(saccharinate) Hemihydrate, Crystal Structures, Supramolecular Adducts, IR Spectra

Introduction

During the last years a number of interesting supramolecular structures of organic salts containing saccharin and different organic bases have been prepared and characterized [1 – 6], and we have extended these studies to some related species generated from thiosaccharin instead of saccharin [7, 8]. With the only exception of 1,6-hexanediamine [1, 7], in all the structures reported so far relatively small organic bases were always present. To explore the possibility of similar supramolecular assemblies with longer-chain diamines, we have prepared and characterized two new systems of this type containing 1,7-heptanediamine and 1,8-octanediamine, and the results are reported here.

Results and Discussion

Crystal and molecular structures

Fig. 1 shows an ORTEP-3 [9] drawing of the structure of [H_3N-$(CH_2)_7$-NH_3](sac)$_2$·H_2O (**1**). Selected bond lengths and angles are shown in Table 1.

As expected, both $C_6H_4(C{=}O)SO_2N^-$ saccharinate anions are planar (r. m. s. deviation of atoms from the corresponding least-squares plane are less than 0.01 Å). They are nearly perpendicular to each other [dihedral angle = 93.09(5)°], with the [H_3N-$(CH_2)_7$-NH_3]$^{2+}$ cation lying along the corner defined by the saccharinate planes. By translation along the crystallographic *a* and *b* axes an electrically neutral slab parallel to the *ab* plane with a wine cellar-like structure is generated, where the cellar walls are defined by the saccharinate anions and the stored bottles by the cations. The slab is further stabilized at its surfaces by $NH_3\cdots$N(sac) and N–H$\cdots$O(sulfoxide) bonds between the enclosed cations and their surrounding saccharinate anions. Neighboring slabs along the *c* axes, in turn, are linked to each other through $NH_3\cdots$O(carb), $NH_3\cdots$O (sulf) and bridging $NH_3\cdots$Ow–H$\cdots$N(sac) and (sac)-N$\cdots$H–Ow–H$\cdots$O(sulf) bonds. Fig. 2 presents an ORTEP-3 [9] drawing of these interactions. Further details of the H-bonding network are provided in the deposited material.

An ORTEP-3 [9] drawing of the structure of [H_3N-$(CH_2)_8$-NH_3](sac)$_2$·0.5H_2O (**2**) is shown in Fig. 3

Table 1. Selected bond lengths (Å) and angles (deg) in $[H_3N\text{-}(CH_2)_7\text{-}NH_3](sac)_2\cdot H_2O$ (**1**).

N(1)–C(1)	1.490(3)	C(15)–C(16)	1.379(4)
N(2)–C(7)	1.476(4)	C(25)–C(26)	1.376(4)
C(1)–C(2)	1.510(3)	C(16)–C(17)	1.382(3)
C(4)–C(5)	1.520(4)	O(1W)–H(1W)	0.826(19)
C(6)–C(7)	1.498(4)	O(1W)–H(2W)	0.83(2)
S(1)–O(13)	1.438(2)	S(2)–O(23)	1.439(2)
S(1)–O(12)	1.439(2)	S(2)–O(22)	1.445(2)
S(1)–N(11)	1.608(2)	S(2)–N(21)	1.589(2)
S(1)–C(17)	1.759(2)	S(2)–C(27)	1.761(2)
C(11)–O(11)	1.179(3)	C(21)–O(21)	1.237(3)
C(11)–N(11)	1.388(3)	C(21)–N(21)	1.355(3)
C(11)–C(12)	1.528(3)	C(21)–C(22)	1.504(3)
C(12)–C(17)	1.372(3)	C(22)–C(27)	1.376(4)
C(12)–C(13)	1.380(4)	C(22)–C(23)	1.386(3)
N(1)–C(1)–C(2)	111.0(2)	N(2)–C(7)–C(6)	113.7(3)
C(1)–C(2)–C(3)	112.6(2)	C(7)–C(6)–C(5)	115.5(3)
O(13)–S(1)–O(12)	114.14(14)	O(23)–S(2)–O(22)	112.14(11)
O(11)–C(11)–N(11)	125.7(2)	O(21)–C(21)–N(21)	123.8(2)
S(1)–N(11)–C(11)	113.46(17)	S(2)–N(21)–C(21)	111.48(17)
C(13)–C(12)–C(11)	127.3(2)	C(23)–C(22)–C(21)	129.9(2)
H(W)–O(W)–H(W)	96(5)	C(26)–C(27)–S(2)	129.7(2)

Table 2. Selected bond lengths (Å) and angles (deg) in $[H_3N\text{-}(CH_2)_8\text{-}NH_3](sac)_2\cdot 0.5H_2O$ (**2**).

N(1)–C(1)	1.489(4)	C(15)–C(16)	1.389(6)
N(2)–C(8)	1.478(5)	C(25)–C(26)	1.378(6)
C(1)–C(2)	1.502(5)	C(16)–C(17)	1.379(5)
C(3)–C(4)	1.520(5)	C(26)–C(27)	1.383(5)
C(7)–C(8)	1.551(7)	C(24)–C(25)	1.366(6)
S(1)–O(13)	1.446(2)	S(2)–O(23)	1.443(3)
S(1)–O(12)	1.436(2)	S(2)–O(22)	1.437(3)
S(1)–N(11)	1.595(3)	S(2)–N(21)	1.612(3)
S(1)–C(17)	1.764(3)	S(2)–C(27)	1.764(3)
C(11)–O(11)	1.244(4)	C(21)–O(21)	1.246(4)
C(11)–N(11)	1.348(4)	C(21)–N(21)	1.340(5)
C(11)–C(12)	1.500(4)	C(21)–C(22)	1.493(4)
C(12)–C(17)	1.379(5)	C(22)–C(27)	1.378(5)
C(12)–C(13)	1.381(5)	C(22)–C(23)	1.379(5)
N(1)–C(1)–C(2)	111.4(3)	N(2)–C(8)–C(7)	112.1(4)
C(1)–C(2)–C(3)	111.9(3)	C(8)–C(7)–C(6)	122.0(7)
O(13)–S(1)–O(12)	112.48(15)	O(23)–S(2)–O(22)	113.53(18)
O(11)–C(11)–N(11)	123.5(3)	O(21)–C(21)–N(21)	124.8(3)
S(1)–N(11)–C(11)	111.0(2)	S(2)–N(21)–C(21)	111.5(2)
C(13)–C(12)–C(11)	129.7(3)	C(23)–C(22)–C(21)	128.3(3)
C(16)–C(17)–S(1)	130.2(3)	C(26)–C(27)–S(2)	131.3(3)

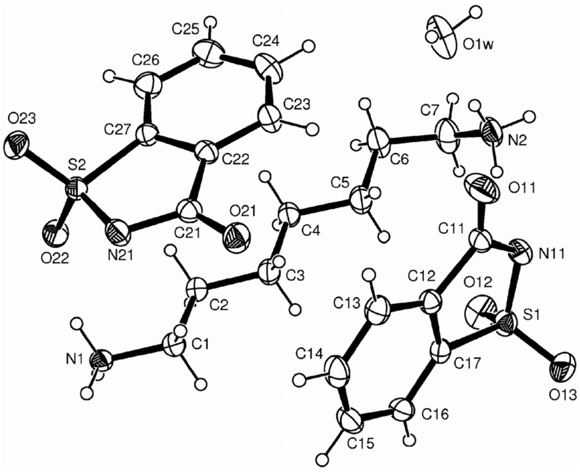

Fig. 1. Molecular structure of $[H_3N\text{-}(CH_2)_7\text{-}NH_3](sac)_2\cdot H_2O$ (**1**) in the crystal showing the labeling of the non-H atoms (displacement ellipsoids at the 30 % probability level).

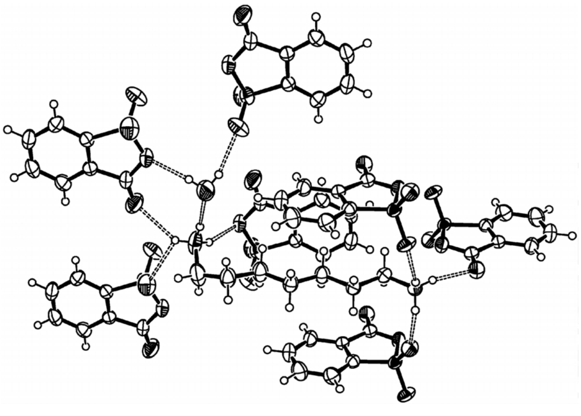

Fig. 2. Molecular packing of $[H_3N\text{-}(CH_2)_7\text{-}NH_3](sac)_2\cdot H_2O$ (**1**) in the crystal. Sulfur, oxygen and nitrogen atoms are indicated by hatched ellipsoids and carbon atoms by crossed ones. Hydrogen bonds are denoted by dashed lines.

and selected bond lengths and angles are shown in Table 2.

As for $[H_3N\text{-}(CH_2)_7\text{-}NH_3](sac)_2\cdot H_2O$ (**1**), both saccharinate anions are planar (r. m. s. deviation of atoms from the least-squares plane less than 0.018 Å) and present a similar supramolecular arrangement around the longer $[H_3N\text{-}(CH_2)_8\text{-}NH_3]^{2+}$ cation. In fact, the two saccharinate planes now subtend an angle of 100.89(7)° with each other and bind the cation which extends along the edge defined by the planes. The symmetry of the crystal lattice gives rise to neutral slabs parallel to the crystallographic *ab* plane which stack along the *c* axes, with the cellar-like structure described for **1**. As for this salt, each slab is further stabilized at its surfaces by $NH_3\cdots$N(sac) and $NH_3\cdots$O(sulf) bonds between the enclosed cations and their surrounding saccharinate anions. Neighboring slabs along the *c* axes, in turn, are linked to each other through $NH_3\cdots$O(carb) and $NH_3\cdots$O(sulf) interactions. Further details of the H-bonding network are provided in the deposited material.

Finally, a comparison of bond lengths and angles of the two described adducts with those found

Table 3. Assignment of some of the most characteristic IR bands of saccharinate in the sodium salt, of the two free amines and of the two new adducts **1** and **2** (band positions in cm^{-1}).[a]

$NaSac \cdot H_2O$	$NH_2(CH_2)_7NH_2$	$NH_2(CH_2)_8NH_2$	**1**	**2**	Assignment
	3320 s	3353 m			$\nu_{as}(NH_2)$
		3270 sh			$\nu_s(NH_2)$
			3202 vs	3170 vs	$\nu(NH_3^+)$
	2927 s	2924 s	2935 s	2933 s	$\nu_{as}(CH_2)$
	2856 m	2853 m	2860 m	2863 m	$\nu_s(CH_2)$
			2039 m	2054 m	see text
1642 vs			1629 vs	1632 vs	$\nu(C{=}O)$
1590 s			1585 s	1581 s	$\nu(C–C) + \delta_{as}(NH_3^+)$
	1577 vs	1580 vs			$\delta_{sciss}(NH_2)$
1460 m			1463 m	1462 m	$\nu(C–C)$
1336 m			1334 m	1335 m	$\nu_s(CNS)$
1258 vs			1260 vs	1259 vs	$\nu_{as}(SO_2)$
1150 vs			1146 vs	1141 vs	$\nu_s(SO_2)$
	1085 w	1044 m	1052 s	1051 s	$\nu(CN)_{amine}$
970 s				980 w	$\gamma(CH)$
950 m			956 s	943 m	$\nu_{as}(CNS)$
794 w			796 m	798 w	$\delta(CO)$
	821 w	818 m			$\delta_{wagg}(NH_2)$
677 m			681 m	680 m	$\delta(CCC)$
610 m			604 s	606 s	$\delta(SO_2)$
			486 m	481 w	$\tau(NH_3^+)$

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

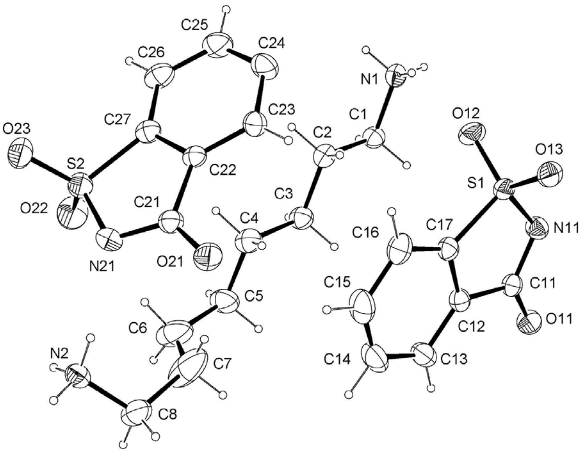

Fig. 3. Molecular structure of $[H_3N\text{-}(CH_2)_8\text{-}NH_3](sac)_2 \cdot 0.5H_2O$ (**2**) in the crystal showing the labeling of the non-H atoms (displacement ellipsoids at the 30 % probability level).

in some ionic saccharinates, for example $Na(C_7H_4NO_3S) \cdot 2/3H_2O$ [10], $Mg(C_7H_4NO_3S)_2 \cdot 7H_2O$ [10] or $K_2Na(C_7H_4NO_3S)_3 \cdot H_2O$ [11], shows very similar values for all of them. A further comparison with data of free saccharin [12] shows in all cases the expected shortening of the C–N and S–N bonds upon deprotonation [13], whereas the C–O and S–O bonds are less affected than expected.

Infrared spectra

We have measured the FTIR spectra of the two new adducts as well as those of the two free diamines employed in their synthesis. The assignment of some of the most characteristic bands of these molecules was performed with the aid of standard references [14, 15]. In Table 3 we compare the most characteristic IR bands of the adducts, the diamines and the saccharinate in its sodium salt [16].

As it can be appreciated, the typical $\nu(C{=}O)$ stretching vibration of the saccharinate anion is slightly displaced to lower frequencies upon adduct formation, surely due to the involvement of this group in hydrogen bonding. The stretching vibrations of the SO_2 groups are less affected, although the $\nu_s(SO_2)$ mode shows a definite displacement to lower frequencies. Skeletal saccharinate bands are practically not affected.

As expected, most of the typical amine NH_2 vibrations are replaced by NH_3^+ vibrations in the adducts. Interestingly, a combination band, which is typical and often appears in the case of ammine salts [14], could be clearly identified as a medium intensity band at 2039 cm^{-1} (adduct **1**) and 2054 cm^{-1} (adduct **2**).

Experimental Section

Synthesis of the adducts

All reagents were commercially available (saccharin and diamines from Aldrich, solvents from Merck) and were used as purchased. The adducts were obtained by addition of 1.0 mmol of the respective diamine to a methanolic solution (30 mL) containing 2.0 mmol of saccharin. The mixtures were heated with stirring for 15 min at 40 °C. The re-

Table 4. Crystal and structure refinement data of [H_3N-$(CH_2)_7$-NH_3](sac)$_2$·H_2O (**1**) and [H_3N-$(CH_2)_8$-NH_3](sac)$_2$·$0.5H_2O$ (**2**).

	1	**2**
Formula	$C_{21}H_{30}N_4O_7S_2$	$C_{22}H_{31}N_4O_{6.5}S_2$
Formula weight	514.61	519.63
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/a$
a, Å	7.9404(4)	16.5660(5)
b, Å	8.2119(5)	8.0522(3)
c, Å	18.8831(7)	19.5757(6)
α, deg	98.036(3)	90
β, deg	92.324(3)	106.107(2)
γ, deg	92.821(2)	90
V, Å^3	1216.32(11)	2508.75(14)
D_c, g cm^{-3}	1.405	1.376
Z	2	4
$F(000)$, e	544	1100
θ range data collection, deg	2.51 – 25.93	2.49 – 26.00
Index ranges *hkl*	$-9 \le h \le 8$	$-20 \le h \le 20$
	$-9 \le k \le 10$	$-9 \le k \le 7$
	$-23 \le l \le 23$	$-24 \le l \le 22$
Reflections coll. / indep.	10513 / 4694	16663 / 4912
R_{int}	0.0600	0.0655
Observ. reflect. [$I \ge 2\sigma(I)$]	3482	3423
Data / restraints/ ref. param.	4694 / 2 / 315	4912 / 0 / 316
Final $R1$ / w$R2$ [$I \ge 2\sigma$(I)]	0.0488 / 0.1179	0.0651 / 0.1702
Final $R1$ / w$R2$ (all data)	0.0745 / 0.1305	0.0996 / 0.1952
Goodness-of-fit on F^2	1.041	1.034
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.38 / −0.51	1.26 / −0.88

sulting solutions were filtered, and the filtrates were slowly evaporated at r. t. After a few days an abundant quantity of crystalline material precipitated from the solution. Similar assays performed under the same conditions with 1,9-nonanediamine, and using a variety of solvents and solvent mixtures, were unsuccessful as it was impossible to isolate single crystals adequate for structural work from the solid precipitates.

Crystal structure determination

X-Ray diffraction data were collected on an Enraf-Nonius Kappa-CCD diffractometer at 293(2) K with graphite-monochromatized MoK_α (λ = 0.71073 Å) radiation. Colorless crystals of dimensions 0.19 × 0.12 × 0.08 mm^3 (**1**) and 0.25 × 0.18 × 0.08 mm^3 (**2**) were used in the experiments. Crystal data and refinement results are summarized in Table 4. The final unit cell parameters were based on all reflections. Data collections were made using the program COLLECT [17]; integration and scaling of the reflections were performed with the HKL DENZO-SCALEPACK system of programs [18]. Absorption corrections were deemed unnecessary. The structures were solved by Direct Methods with SHELXS-97 [19], and the molecular model was refined by full-matrix least-squares on F^2 by means of SHELXL-97 [20]. All hydrogen atoms were stereochemically positioned and refined with the riding model, except the water hydrogens, which in the case of compound **1** were found in a difference map and refined restrained to a target O–H distance of 0.82(2) Å. In the case of compound **2** a disordered water molecule was modeled with an occupation factor of 0.5; its H atoms could not be located in the final difference map and were not included in the model. Besides, the diammonium cation in this same compound shows some degree of disorder at carbon atom C7 as indicated by a peak of 1.26 e Å^{-3} in the final difference map. However, though attempts to model the disorder setting C7 in two different positions did improve the $R1$ factor slightly, it did not produce a significantly better stereochemistry of this moiety, and the procedure was therefore discarded. As a consequence of this disorder, interatomic distances involving C7 are somewhat dubious.

CCDC 736974 (**1**) and CCDC 736975 (**2**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Spectroscopic measurements

The infrared spectra of the two compounds, as well as those of the respective free diamines, were recorded in the spectral range between 4000 and 400 cm^{-1} on a FTIR-Bruker-EQUINOX-55 instrument, using KBr pellets.

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