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Crystal and Molecular Structure of 1:1 Complex of *N*-Methylmorpholine Betaine with Salicylic Acid*

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The structure of a 1:1 complex of *N*-methylmorpholine betaine (MMB) with salicylic acid (SAL) has been determined by single crystal X-ray analysis. The crystals are orthorhombic, space group *Pbca*, with $a = 9.4702(6)$, $b = 13.0559(7)$ and $c = 45.226(2)$ Å (at 140 K). The asymmetric unit is comprised of two $MMB^+ \cdot SAL^-$ units (**A** and **B**), each formed by a short, nearly linear O–H···O hydrogen bond (2.542(2) and 2.474(2) Å) between the carboxylic group of the betaine cation and the carboxylate group of the anion. The salicylate anions form short intramolecular O–H···O hydrogen bonds of 2.472(2) and 2.525(2) Å (O–H···O angles 160(2) and 149(2)°) for anion **A** and **B**, respectively, between the *ortho* hydroxyl donor and the COO^- group, but the carboxylate acceptor O atom is in each case different. The morpholine rings are in chair conformation with the $-CH_2COOH$ group in equatorial and the methyl group in axial positions. FTIR, and ^1H and ^{13}C NMR spectra of the complex are discussed.

Key words: *N*-methylmorpholine betaine, salicylic acid, hydrogen bonds, X-ray diffraction, FTIR, NMR spectra

Prodrugs can be used to mask the side-effects and toxicity of drugs, *e.g.* salicylic acid is a good painkiller, but causes gastric bleeding because of the free phenolic group. This is overcome by masking the phenol as an ester (aspirin). The ester is later hydrolyzed by esterases to free the active drug [1]. Salicylic acid is a commonly used anionic drug component, *e.g.* with benzylamine, chloroquine, choline, quinine, morpholine, picolylamine, *etc.* Because of its own pharmacological and biological activity (analgesic, antipyretic, antiinflammatory activity), salicylic acid cannot be regarded as an inert salt-forming acid [2].

Betaines have found uses in medicine, pharmacy, biology and other scientific applications. The antimicrobial effectiveness of betaines is not comparable to that of cationic surfactants, however, certain betaine-derived compounds are active against specific strains or potentiate the effects of other compounds [3].

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* Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

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Recently, we have studied the effect of the OH group, as an additional substituent in proton-donor or proton-acceptor molecules, on the structure and hydrogen bonding of betaine–acid complexes [4–7]. In this paper, we extend this study and report on the preparation and structure of a new complex of *N*-methylmorpholine betaine with salicylic acid.

EXPERIMENTAL

N-Methylmorpholine betaine (*N*-carboxymethyl-*N*-methylmorpholinium inert salt, MMB) was obtained as described [8]. A complex of MMB with salicylic acid (SAL) was prepared by mixing one equivalent of MMB with one equivalent of SAL in methanol. The complex was recrystallized from acetonitrile and dried over P_2O_5; m.p. 104–105°C. The deuterated complex was prepared by three-fold recrystallization from CH_3OD and dried over P_2O_5 in vacuum. Analysis for $C_{14}H_{19}NO_6$: confirmed the composition. ^{1}H, ppm, DMSO-d_6: 3.35 (s, 3H, C(7)H), 3.56 (m, 2H, C(2)H and C(6)H, ax), 3.74 (m, 2H, C(2)H and C(6)H, eq), 3.93 (m, 4H, C(3)H and C(5)H), 4.16 (s, 2H, C(8)H), 6.84 (d, 1H, C(13)H), 7.37 (t, 1H, C(14)H), 6.81 (t, 1H, C(5)H), 7.74 (d, 1H, C(6)H), 13.49 (1H, OH). ^{13}C, ppm, DMSO-d_6: 47.02 C(7), 59.12 C(2) and C(6), 59.79 C(3) and C(5), 62.56 C(8), 115.92 C(11), 161.44 C(12) 117.80 C(13), 133.68 C(14), 116.83 C(15) 130.01 C(16), 165.29 C(10), 171.90 C(17).

FTIR spectra were measured on a Bruker IFS 113 v instrument, which was evacuated to avoid water and CO_2 absorptions. Each spectrum consisted of 250 scans at 31°C. Solid state spectra were recorded in Nujol and Fluorolube suspensions using KBr plates. NMR spectra were recorded on a Varian-Gemini 300VT spectrometer operating at 300.07 and 75.46 MHz for ^{1}H and ^{13}C, respectively. Spectra were measured in DMSO-d_6 relative to TMS as internal standard. The 2D spectra were obtained with standard Varian software. The sample concentration was 0.3 M.

Single crystals of the complex were grown from a $ClCH_2CH_2Cl$:CH_3CN mixture (5:1) over P_2O_5 in a desiccator. A colorless plate with dimensions 0.4 × 0.4 × 0.03 mm was used for X-ray measurements. The intensities were collected at 140 K using a KM4-CCD diffractometer equipped with an Oxford low temperature device [9], and graphite-monochromated MoKα radiation generated from a sealed-tube operated at 50 kV and 40 mA. 1092 ω scans were collected in four orientations of the crystal with 60.2 mm crystal-detector distance. Each scan covered 0.42° rotation recorded in 20 s. The images were indexed, integrated, and scaled using CrysAlis version 1.169 [10]. The final data set consisted of 41271 observations which were reduced in the *mmm* Laue group to 7329 unique data (R_{int} = 0.045, redundancy 5.4). Experimental details and crystal data are given in Table 1. The structure was solved by direct methods using SHELXS [11] and refined by least-squares minimization of $\Sigma w(F_o^2 - F_c^2)^2$ for all reflections (SHELXL, [12]). All acidic hydrogen atoms were derived from a difference Fourier map. All atoms were included in the refinement, with anisotropic (non-H atoms) and isotropic (H atoms) displacement parameters. The final atomic coordinates are given in Table 2. Crystallographic data for structure reported have been deposited at Cambridge Crystallographic Data Centre (No. CCDC 216 556) and can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{14}H_{19}NO_6$
Formula weight	297.3
Temperature	140 K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	a = 9.4702(6) Å

Table 1 (continuation)

	b = 13.0559(7) Å
	c = 45.226(2) Å
Volume	V = 5592(3) Å^3
Z	16
Calculated density	1.413 g/cm^3
Absorption coefficient	0.111 mm^{-1}
F(000)	2528
Crystal size	0.40 × 0.40 × 0.03 mm
θ range for data collection	2.70–29.32°
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 17$, $-61 \le l \le 61$
Reflections collected/unique	41271/7329 (R_{int} = 0.045)
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	7329/0/532
Goodness-of-fit	1.022
Final R indices [$I \ge 2\sigma(I)$]	R_1 = 0.046, wR_2 = 0.091
R indices (all data)	R_1 = 0.095, wR_2 = 0.108
Largest difference peak and hole	0.302 and –0.226 $e\cdot$ Å^{-3}

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for 1:1 complex of *N*-methylmorpholine betaine with salicylic acid. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
O(5A)	7376(1)	819(1)	4250(1)	42(1)
O(6A)	6679(1)	2373(1)	4128(1)	40(1)
O(7A)	8916(1)	483(1)	4681(1)	39(1)
C(11A)	8124(2)	2170(1)	4557(1)	23(1)
C(12A)	8904(2)	1496(1)	4736(1)	26(1)
C(13A)	9692(2)	1868(2)	4972(1)	36(1)
C(14A)	9661(2)	2899(2)	5036(1)	43(1)
C(15A)	8859(2)	3572(2)	4869(1)	40(1)
C(16A)	8113(2)	3208(1)	4628(1)	31(1)
C(17A)	7340(2)	1767(1)	4294(1)	28(1)
C(7A)	7055(2)	5281(1)	3078(1)	28(1)
C(8A)	8187(2)	5211(1)	3567(1)	24(1)
C(9A)	7258(2)	4381(1)	3694(1)	24(1)
O(1A)	6017(1)	4266(1)	3642(1)	32(1)
O(2A)	8011(1)	3821(1)	3876(1)	28(1)
O(4A)	6859(1)	8027(1)	3210(1)	27(1)
N(1A)	7504(1)	5897(1)	3341(1)	20(1)
C(2A)	8604(2)	6684(1)	3254(1)	26(1)

Table 2 (continuation)

C(3A)	7992(2)	7524(1)	3065(1)	28(1)
C(5A)	5769(2)	7314(1)	3277(1)	27(1)
C(6A)	6273(2)	6473(1)	3477(1)	24(1)
O(5B)	2516(2)	5709(1)	3172(1)	41(1)
O(6B)	1582(2)	4234(1)	3316(1)	48(1)
O(7B)	3961(2)	5805(1)	2704(1)	43(1)
C(11B)	3173(2)	4223(1)	2910(1)	25(1)
C(12B)	3939(2)	4780(1)	2703(1)	30(1)
C(13B)	4730(2)	4270(2)	2488(1)	39(1)
C(14B)	4720(2)	3217(2)	2479(1)	44(1)
C(15B)	3945(2)	2652(2)	2678(1)	40(1)
C(16B)	3174(2)	3151(1)	2893(1)	33(1)
C(17B)	2352(2)	4729(1)	3152(1)	30(1)
C(7B)	2985(2)	7813(2)	4393(1)	36(1)
C(8B)	1563(2)	7922(1)	3941(1)	28(1)
C(9B)	2352(2)	7099(1)	3773(1)	26(1)
O(1B)	3591(1)	6914(1)	3799(1)	35(1)
O(2B)	1475(1)	6641(1)	3596(1)	37(1)
O(4B)	3221(1)	10577(1)	4341(1)	33(1)
N(1B)	2400(1)	8523(1)	4162(1)	22(1)
C(2B)	1403(2)	9292(1)	4300(1)	31(1)
C(3B)	2170(2)	10035(2)	4498(1)	36(1)
C(5B)	4227(2)	9882(1)	4223(1)	33(1)
C(6B)	3565(2)	9129(1)	4015(1)	28(1)

RESULTS AND DISCUSSION

X-ray crystallography: Fig. 1 presents the molecular structure and atomic numbering of the $MMB^+ \cdot SAL^-$ units. The bond lengths, bond angles, and selected torsion angles are given in Table 3. The asymmetric unit consists of two (**A** and **B**) 1:1 complexes between *N*-methylmorpholine betaine (cationic component) and salicylic acid (anionic component). In both cases, the proton has been transferred from the salicylic acid molecule to the betaine moiety. Each of the $MMB^+ \cdot SAL^-$ complexes is formed by a short hydrogen bond between the carboxylic group of the betaine component and the carboxylate group of the salicylate anion. These intermolecular O–H···O bridges are close to linearity (171(2) and 167(3)°) with O···O distances of 2.542(2) and 2.474(2) Å in **A** and **B**, respectively (Table 4). The geometry of the COO groups of the betaine moieties (Table 3) confirms their protonated character. Also, the refined positions of the hydrogen atoms in the intermolecular O–H···O hydrogen bonds corroborate the carboxyl status of the betaine molecules. However, the O–H bonds in the two

carboxylic groups are different, in agreement with the O···O distances. In particular, the O–H bond in betaine **B** is 1.07(3) Å and indicates a very strong O–H···O hydrogen bond.

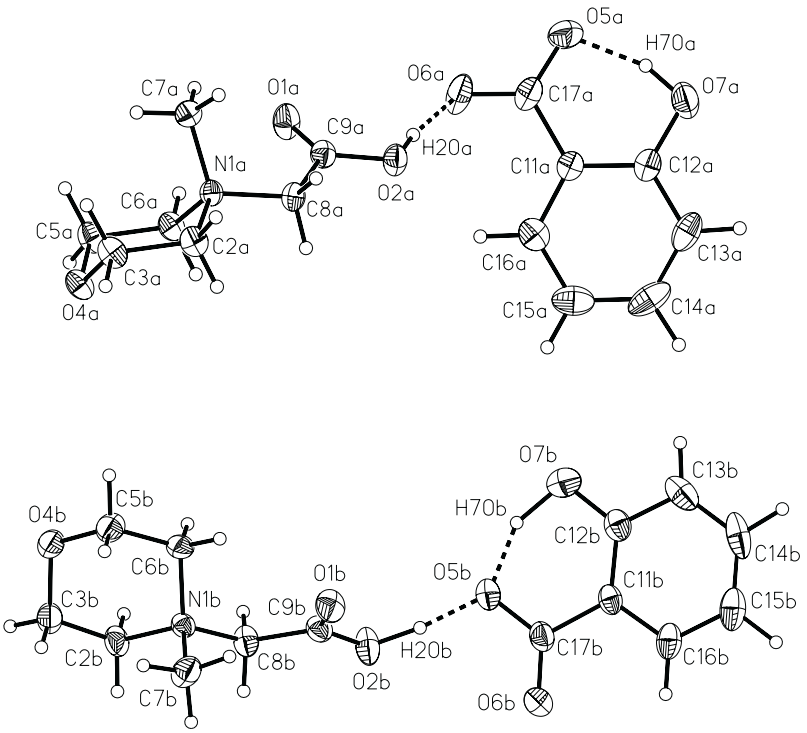

Figure 1. The structure of *N*-methylmorpholine betaine complex with salicylic acid at 140 K. Top: complex **A**, bottom: complex **B**. The displacement ellipsoids are plotted at 50% probability level.

Table 3. Bond lengths (Å), bond angles (°), and selected torsion angles (°).

N-methylmorpholine betaine cation	**A**	**B**
Bond lengths		
C(9)–O(1)	1.208(2)	1.203(2)
C(9)–O(2)	1.311(2)	1.301(2)
C(8)–C(9)	1.510(2)	1.513(2)
N(1)–C(8)	1.503(2)	1.499(2)
N(1)–C(7)	1.500(2)	1.501(2)
N(1)–C(2)	1.516(2)	1.512(2)
N(1)–C(6)	1.517(2)	1.513(2)
C(2)–C(3)	1.505(2)	1.508(2)
C(3)–O(4)	1.419(2)	1.412(2)
C(5)–O(4)	1.422(2)	1.420(2)
C(5)–C(6)	1.503(2)	1.501(3)

Table 3 (continuation)

Bond angles		
C(9)–O(2)–H(20)	109(1)	113(1)
N(1)–C(8)–C(9)	115.8(1)	116.5(1)
O(1)–C(9)–O(2)	125.6(2)	126.2(2)
O(1)–C(9)–C(8)	125.6(1)	125.1(2)
O(2)–C(9)–C(8)	108.8(1)	108.7(1)
C(3)–O(4)–C(5)	110.1(1)	110.0(1)
C(7)–N(1)–C(8)	110.0(1)	109.7(1)
C(7)–N(1)–C(2)	110.5(1)	110.7(1)
C(8)–N(1)–C(2)	106.6(1)	107.0(1)
C(7)–N(1)–C(6)	111.7(1)	111.1(1)
C(8)–N(1)–C(6)	110.6(1)	111.4(1)
C(2)–N(1)–C(6)	107.3(1)	106.9(1)
C(3)–C(2)–N(1)	112.2(1)	111.8(2)
O(4)–C(3)–C(2)	111.6(1)	111.3(2)
O(4)–C(5)–C(6)	112.1(1)	112.0(2)
C(5)–C(6)–N(1)	111.2(1)	111.7(1)
Torsion angles		
N(1)–C(8)–C(9)–(1)	–4.3(2)	–2.0(3)
N(1)–C(8)–(9)–O(2)	177.2(1)	178.8(1)
C(9)–C(8)–N(1)–C(7)	–62.1(2)	–60.0(2)
C(9)–C(8)–N(1)–C(2)	178.0(1)	179.9(2)
C(9)–C(8)–N(1)–C(6)	61.7(2)	63.5(2)
C(7)–N(1)–C(2)–C(3)	69.7(2)	68.0(2)
C(8)–N(1)–C(2)–C(3)	–170.8(1)	–172.5(2)
C(6)–N(1)–C(2)–C(3)	–52.3(2)	–53.1(2)
C(5)–O(4)–C(3)–C(2)	–59.4(2)	–60.1(2)
N(1)–C(2)–C(3)–O(4)	57.3(2)	58.7(2)
C(3)–O(4)–C(5)–C(6)	60.4(2)	60.0(2)
O(4)–C(5)–C(6)–N(1)	–58.2(2)	–57.7(2)
C(7)–N(1)–(6)–C(5)	–68.9(2)	–68.3(2)
C(8)–N(1)–C(6)–C(5)	168.3(1)	169.1(1)
C(2)–N(1)–C(6)–C(5)	52.4(2)	52.6(2)
Salicylate anion	**A**	**B**
Bond lengths		
C(17)–O(5)	1.254(2)	1.292(2)
C(17)–O(6)	1.260(2)	1.224(2)
C(12)–O(7)	1.346(2)	1.339(2)
C(11)–C(17)	1.497(2)	1.496(2)
C(11)–C(16)	1.393(2)	1.402(3)
C(11)–C(12)	1.405(2)	1.392(2)
C(12)–C(13)	1.390(2)	1.397(2)
C(13)–C(14)	1.378(3)	1.375(3)
C(14)–C(15)	1.387(3)	1.378(3)
C(15)–C(16)	1.381(3)	1.381(3)
Bond angles		
C(12)–O(7)–H(70)	101(2)	104(1)
C(16)–C(11)–C(12)	118.8(2)	119.0(2)
C(16)–C(11)–C(17)	121.5(2)	118.8(2)
C(12)–C(11)–C(17)	119.8(2)	122.2(2)
O(7)–C(12)–C(13)	118.7(2)	118.1(2)
O(7)–C(12)–C(11)	121.0(2)	121.9(2)
C(13)–C(12)–C(11)	120.3(2)	120.0(2)
C(14)–C(13)–C(12)	119.5(2)	119.6(2)
C(13)–C(14)–C(15)	121.0(2)	121.3(2)

Table 3 (continuation)

C(16)–C(15)–C(14)	119.5(2)	119.4(2)
C(15)–C(16)–C(11)	120.9(2)	120.7(2)
O(5)–C(17)–O(6)	122.6(2)	123.5(2)
O(5)–C(17)–C(11)	117.4(2)	115.2(2)
O(6)–C(17)–C(11)	120.0(2)	121.3(2)
Torsion angles		
C(16)–C(11)–C(12)–O(7)	178.1(1)	178.8(2)
C(17)–C(11)–C(12)–O(7)	–2.5(2)	–1.4(2)
C(16)–C(11)–C(12)–C(13)	–2.5(2)	–2.1(2)
C(17)–C(11)–C(12)–C(13)	176.8(1)	177.6(2)
O(7)–C(12)–C(13)–C(14)	–178.2(2)	–179.3(2)
C(11)–C(12)–C(13)–C(14)	2.5(2)	1.6(3)
C(12)–C(13)–C(14)–C(15)	–0.2(3)	–0.1(3)
C(13)–C(14)–C(15)–C(16)	–1.9(3)	–0.7(3)
C(14)–C(15)–C(16)–C(11)	1.8(3)	0.0(3)
C(12)–C(11)–C(16)–C(15)	0.4(2)	1.3(2)
C(17)–C(11)–C(16)–C(15)	–179.0(2)	–178.5(2)
C(16)–C(11)–C(17)–O(5)	–178.3(2)	173.3(2)
C(12)–C(11)–C(17)–O(5)	2.4(2)	–6.5(2)
C(16)–C(11)–C(17)–O(6)	1.8(2)	–7.0(3)
C(12)–C(11)–C(17)–O(6)	–177.5(2)	173.2(2)

Table 4. Hydrogen bonds and short contacts in the crystal structure of 1:1 complex of *N*-methylmorpholine betaine with salicylic acid.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(2A)–H(20A)···O(6A)	0.90(2)	1.65(2)	2.542(2)	171(2)
O(2B)–H(20B)···O(5B)	1.07(3)	1.42(3)	2.474(2)	167(3)
O(7A)–H(70A)···O(5A)	0.95(2)	1.56(3)	2.472(2)	160(2)
O(7B)–H(70B)···O(5B)	1.18(3)	1.44(3)	2.526(2)	149(2)
C(6A)–H(6AB)···O(1A)	0.95(2)	2.35(2)	2.986(3)	124(1)
C(7A)–H(7AB)···O(1A)	0.98(2)	2.39(2)	3.039(2)	123(1)
C(6A)–H(6AB)···O(1B)	0.95(2)	2.57(2)	2.984(2)	107(1)
C(5A)–H(5AB)···O(1B)	0.93(2)	2.58(2)	3.180(2)	122(1)
C(6B)–H(6BA)···O(1B)	0.95(2)	2.41(2)	3.051(3)	124(1)
C(7B)–H(7BA)···O(1B)	0.99(2)	2.29(2)	2.986(2)	127(1)
C(2A)–H(2AB)···O(2B)[a]	0.93(2)	2.57(2)	3.129(2)	120(1)
C(8A)–H(8AA)···O(5A)[b]	0.96(2)	2.48(2)	3.237(2)	136(1)
C(7B)–H(7BB)···O(4B)[c]	1.00(2)	2.50(2)	3.144(3)	122(1)
C(6B)–H(6BB)···O(6B)[d]	0.95(2)	2.47(2)	3.165(2)	131(1)
C(8B)–H(8BB)···O(1A)[d]	0.94(2)	2.51(2)	3.297(2)	142(1)
C(8B)–H(8BA)···O(6A)[d]	0.98(2)	2.37(2)	3.264(2)	152(1)
C(5A)–H(5AB)···O(6B)[d]	0.93(2)	2.57(2)	3.357(2)	142(1)
C(3B)–H(3BB)···O(7A)[e]	0.95(2)	2.51(2)	3.244(2)	134(1)
C(5B)–H(5BA)···O(5A)[f]	0.99(2)	2.49(2)	3.226(2)	130(1)

Symmetry codes: (a) 1 + x, y, z; (b) 1.5 – x, 0.5 + y, z; (c) 0.5 – x, y – 0.5, z; (d) 0.5 – x, 0.5 + y, z; (e) x – 1, 1 + y, z; (f) x, 1 + y, z.

In both cases (**A** and **B**), the morpholine ring adopts a chair conformation with the CH_2COOH group in the equatorial position and the methyl group in the axial position. The hydrogen atoms of the COOH groups of the MMB^+ cations are situated at the oxygen atoms, which are *anti* to the betaine nitrogen atoms, the

N(1)–C(8)–C(9)–O(2) torsion angles being 177.2(1) and 178.8(2)° for **A** and **B**, respectively.

The salicylate anions in both cases are stabilized by short intramolecular O(7)–H(70)···O(5) hydrogen bonds with the hydroxyl groups acting as donors and the carboxylate groups as acceptors. Those O–H···O bridges are short, 2.472(2) Å in **A** and 2.525(2) Å in **B**, but because of their intramolecular constraint deviate by, respectively, 20(2) and 31(2)° from strict linearity (Table 4). However, there is no simple correlation between the O···O distances and the O–H bonds, as the longer O–H distance is found in anion **B** (1.18(3) Å). This lengthening of the O(7)–H(B) distance is perhaps not an artifact, as it is accompanied by a shortening of the O(7)–C(12B) distance (Table 3). The question about the O(7)H···O(5) separation in the intramolecular bond in SAL^- (**B**) may be related to the constrained situation of the O(5B) atom, which has to fulfill a dual-acceptor role, as it is involved in both the intra- and intermolecular bonds. The fact that it is an acceptor in two short hydrogen bonds is reflected in the dimensions of the COO^- group of anion **B**, which, despite its deprotonation, is characterized by two distinctly different C–O bond lengths (Table 3). The situation is quite different in complex **A**, where each of the two O···O hydrogen bonds (intra- and intermolecular) is accepted by a different O atom of the salicylate carboxylate group. Accordingly, the salicylate C–O bond lengths show a high degree of equalization. It has to be noted, that the O(5) atom of salicylate **A** also has a double-acceptor role, but the additional bond is a weak intermolecular C–H···O interaction (Table 4).

There are numerous proton–donor···oxygen atom interactions in the crystal connecting the $MMB^+ \cdot SAL^-$ units into a three-dimensional network. Since conventional hydrogen-bond acceptors (O atoms) highly outnumber conventional donors (OH groups) in this structure, all those lattice interactions are formed by C–H donors [13] (Table 4). Those donors include all types of aliphatic (but not aromatic) C–H groups in the crystal, *i.e*. the methylene groups (both in the morpholine and acetyl moieties) and the methyl groups. The acceptors in those C–H···O interactions are predominantly the carbonyl O atoms of the betaine cations, with only sporadic connections to other O atoms (ether group of MMB^+, carboxylate group of SAL^-). It is interesting to note that the phenolic OH groups of the salicylate units are not involved in any intermolecular interactions. In the crystal packing, it is possible to distinguish sub-networks of H-bonded complexes **A** and **B** (Fig. 2). The basic motifs of those sub-networks are helical columns of the $MMB^+ \cdot SAL^-$ units running along [010]. Those columns alternate along the [001] direction, with columns **A** sitting at $z = 0, 1/2, \ldots$ and columns **B** at $z = 1/4, 3/4, \ldots$. The sub-networks **A** and **B** are interconnected by additional C–H···O hydrogen bonds, as illustrated in Fig. 3 and in Table 4.

The relatively high density of the crystals (Table 1), which consist of atoms not heavier than O, is a consequence of (i) the electrostatic attraction between the MMB^+ cations and the SAL^- anions, (ii) the strong intermolecular O···O hydrogen bonds between the MMB^+ cations and the SAL^- anions, and (iii) the numerous C–H···O interactions.

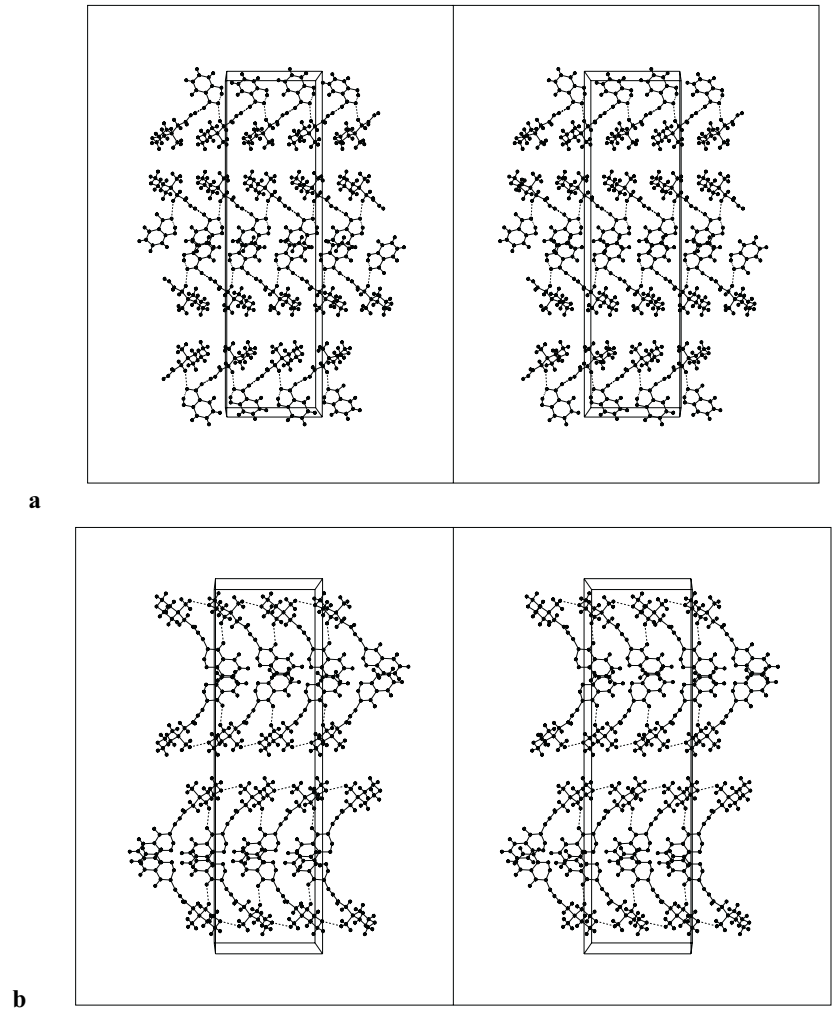

Figure 2. Stereoview of the molecular packing projected along [100] ([001] down, [010] across) showing hydrogen bonds (dashed lines). (a) The sub-network formed by complex **A**, (b) the sub-network formed by complex **B**.

Infrared spectra: Fig. 4 shows powder FTIR spectra of the investigated complex and of its deuterated analogue. According to the crystal structure, there are four O–H···O hydrogen bonds of different length/character, which can be grouped, according to the O···O distances, into two shorter ones (2.472 Å – intramolecular, 2.474 Å – intermolecular) and two longer ones (2.526 Å – intramolecular, 2.542 Å – intermolecular). The νOH vibration attributed to the longer O–H···O bonds, both intra- and intermolecular, is observed in the spectrum as a broad absorption in the 2710–2300 cm^{-1} region, and shifts to the 1930 cm^{-1} region after deuteration. The broad and strong absorption in the 1500–400 cm^{-1} region, with the center of gravity at *ca* 1100 cm^{-1} is due to the νO–H···O vibration of the shorter hydrogen bonds. On deuteration, only its

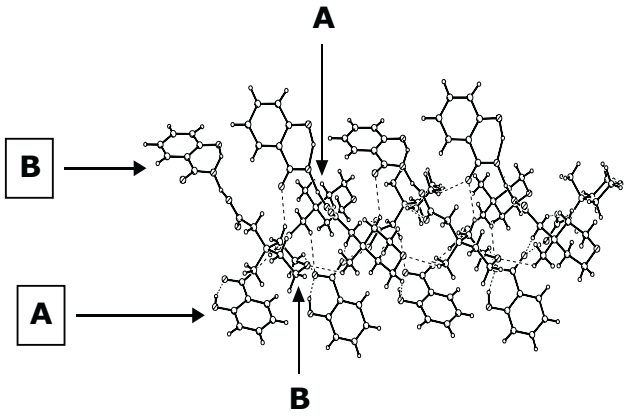

Figure 3. C–H···O hydrogen bonds interconnecting complexes **A** and **B**. The salicylate labels are boxed, the betaine labels – unboxed. The [010] direction runs across the page, as in Fig. 2.

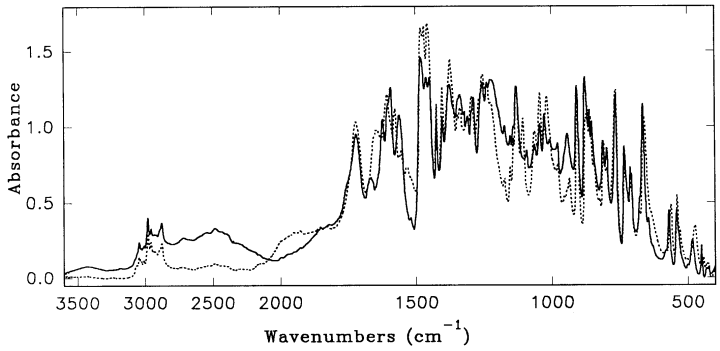

Figure 4. FTIR spectra of *N*-methylmorpholine betaine complex with salicylic acid (—) and its deuterated analogue (·····).

intensity decreases, while its position remains largely unchanged. Similar absorption was observed in type A acid salts of carboxylic acids [14], 2:1 complexes of heterocyclic N-oxides with mineral acids [15], and 2:1 complexes of betaines with mineral acids [16].

In the FTIR spectrum of salicylic acid, the νOH mode, due to the intramolecular hydrogen bond, appears at 3240 cm^{-1}, while that due to the intermolecular one at 2600 cm^{-1}. The νC=O band is observed at 1660 cm^{-1} [17]. In the FTIR spectrum of $MMB^+ \cdot SAL^-$ in the carbonyl/carboxyl region there are several bands. The band at 1721 cm^{-1} is attributed to the νC=O stretching vibration in the protonated molecule of *N*-methylmorpholine betaine. In the spectrum of MMBH· Cl, the νC=O band is at 1728 cm^{-1} [18]. The bands at 1667, 1623 and 1593 cm^{-1} are probably attributed to the ν_{as}COO mode of the different carboxylate groups in complexes **A** and **B**. A weak band at 1660 cm^{-1} is observed in the spectrum of sodium salicylate [17]. The in-plane (δOHO) and out-of-plane (γOHO) modes of medium and strong hydrogen bonds are usually observed in the 1600–1450 and 1285–1000 cm^{-1} regions, respectively

[14,19,20]. Unfortunately, we failed to localize the deformation modes because they are covered by the νOHO vibration.

^{1}H and ^{13}C NMR spectra: Proton and carbon chemical shifts are given in the experimental section. The proton chemical shifts assignments were based on 2D (COSY) experiments, in which the proton-proton connectivities are observed through the off-diagonal peaks in the contour plot. The carbon chemical shift assignments were based on the heteronuclear correlation ^{1}H-^{13}C (HETCOR) experiments. The ^{13}C chemical shifts of the phenyl ring carbon atoms were interpreted by use of the chemical shift parameters [21,22]. Two separate multiplets observed for the axial and equatorial α protons (C(2)H and C(6)H) in the morpholine ring are similar to those found in the spectra of complexes of *N*-methylmorpholine betaine with mineral acids [10] and phenols [18]. The chemical shifts of the protons (4.16 ppm) and the carbon atom (62.58 ppm) of the methylene group in the $N^{+}CH_2COOH$ moiety confirm that the proton is transferred from salicylic acid to the betaine molecule. The chemical shifts of these protons are sensitive to the protonation of the COO group and to the hydrogen bond strength [23].

CONCLUSIONS

N-Methylmorpholine betaine and salicylic acid form a 1:1 complex, in which the acidic proton is transferred from the acid to the betaine molecule. In the crystal structure of the complex there are two independent cation···anion units (**A** and **B**), each formed by a short intermolecular hydrogen bond between the carboxylic group of the betaine moiety and the carboxylate group of the salicylate anion. The O–H···O bond in complex **A** is longer than in complex **B**. The salicylate anion in both complexes is stabilized by a short intramolecular O–H···O hydrogen bond, which is shorter in complex **A**. The donors in those intramolecular interactions are the phenolic OH groups, which are not involved in any other hydrogen bonds. An important difference between the two cation···anion units is that in complex **B** the two O–H···O bonds are accepted by one carboxylate oxygen atom of the salicylate anion, while in complex **A** the inter- and intramolecular O–H···O bonds are accepted by different salicylate O atoms.

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