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Structure and properties of the sodium, potassium and calcium salts of 2-(2,3-dimethylphenyl)aminobenzoic acid

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ABSTRACT

The mefenamic acid sodium, potassium, and calcium salts with general formulae $[Na(mef)(H_2O)_2]_n \cdot nH_2O$, $[K(mef)(H_2O)]_n$ and $[Ca(mef)_2(H_2O)_2]_n \cdot nH_2O$ have been synthesised, studied by X-ray crystallography, ¹H and ¹³C NMR and IR spectroscopy. The complex salts are air stable and soluble in water. During heating the Na and K complexes melt in the complexed water and next recrystallise in anhydrous form. In the solid state all salts create one-dimensional coordination polymers. The central atoms are five, six and seven coordinated, respectively, for Na, K and Ca complexes. In all structures exist O–H···O, N–H···O and C–H···O hydrogen bonds. The vibrational analysis has been carried out for mefenamic acid and its three coordination polymer compounds on the basis of experimental results as well as quantum mechanical calculations. The theoretical and experimental vibrational frequencies are similar and reveal characteristic vibrations for all IR active oscillators. In the IR spectra of salts exist strong bands at ca. 1365 and 1600 cm⁻¹ typical for carboxylate groups.

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1. Introduction

Mefenamic acid (2-(2,3-dimethylphenyl)aminobenzoic acid, Hmef) belongs to the fenamates family and is commonly used as non-steroidal anti-inflammatory, analgesic, and antipyretic agent [1,2]. It has been shown to affect various types of membrane channels [3,4]. The disadvantage of mefenamic acid is its low solubility in aqueous media that influences the bioavailability and pharmacokinetic behaviour [5,6]. Moreover, it can cause the side effects such as nausea, stomach upset, loss of appetite, headache, rash, etc. The variable bioavailability of mefenamic acid is related to pharmaceutical preparation process and in a consequence to variations in dissolution rate. It is known that the particle size distribution, crystal form, crystallinity and surface area of the drug are important parameters that influence its dissolution [7]. Thus it has been suggested that solubility is one of the main factors in determining bioavailability and reducing side effects. The search of mefenamic acid derivatives, possessing enlarged pharmacological activity, lower toxicity and higher solubility is continuously an active area of investigations. It has been shown that the stability and solubility of mefenamic acid can be enhanced, for example, by forming the inclusion complexes with cyclodextrins [8]. On the other hand the development and studying of coordination chemistry of hybrid frameworks and multinuclear assemblies originate from applications of these new functional materials [9,10]. The carboxylic acid anions exhibit a variety modes of binding to metal ions. Their complexes have been extensively studied due to their ability to coordinate in monodentate mode [11,12], form stable chelates [13,14], create di- and multinuclear species [15,16] and polymeric compounds with different topologies and dimensionality [17,18]. In addition, the carboxylate groups are excellent hydrogen bond acceptors and are used to create supramolecular assemblies [19].

In accordance to above mentioned findings, the studies on the coordination compounds of mefenamic acid with biologically important s block elements were carried out. It was previously claimed that sodium and calcium salts were obtained, characterised by IR spectroscopy and structurally studied [20,21], but these results are partially questionable and partially seem to be wrong (for detailed discussion see comment). Apart from mentioned s block elements, the mefenemates coordination compounds with p and d block elements were also studied and structurally characterised, namely bis(N-(2,3-dimethylphenyl)aniline-2-carboxylato)-bis(2-pyridylmethanol)-copper(II) [22], $bis((_3-oxo)-bis(\mu_2-2-(2,3-dimethylphenylamino)benzoato)-tetra$ methyl-di-tin(IV)) [23], $bis((\mu_3 - 0x0) - bis(\mu_2 - 2 - (2, 3 - dimethylpheny$ lamino)benzoato)-tetra-n-butyl-di-tin(IV)) [23], catena-(bis $(\mu_2$ -3-pyridylmethanol-*N*,*O*)-*bis*(2-(2,3-dimethylanilino)benzoato-0)-cadmium(II)) [24]. diagua-bis(2-((2,3-dimethylphenyl)) amino)benzoato-O)-bis(N',N'-diethylnicotinamide-N)-copper(II) [25],

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tetrakis(*N*-xylyl-anthraniloato-*O*,*O'*)-*bis*(dimethylformamide-*O*)-dicopper(II) [26,27], (2-[*bis*(2,3-dimethylphenyl)amino]benzoato)-triphenyl-tin [28], *bis*(*N*-(2,3-dimethylphenyl)aniline-2-carboxylato)-*bis*(methanol)-bis(pyridine)-copper(II) [22,29], tetrakis(μ_2 -*N*-(2,3-dimethylphenyl)anthranilato-*O*,*O'*)-*bis*(dimethylsulfoxide)-di-copper(II) [30], catena-((μ_2 -2-((2,3-dimethylphenyl)amino)benzoato-*O*,*O'*)-trimethyl-tin(IV)) [31].

2. Experimental

2.1. Synthesis

1.000 g (4.14 mmol) of mefenamic acid (Hmef, obtained from Sigma) was added to 0.226 g (4.18 mmol) of sodium methanolate (>99%, obtained from POCh) dissolved in 12 cm³ of methanol and

to 0.299 g (4.26 mmol) of potassium methanolate (>99%, obtained from POCh) dissolved in 25 cm³ of methanol. The solutions were stirred and left at room temperature. After a week the crystals of hydrated salts grew from the solutions with 74% and 69% yields, respectively, for $[Na(mef)(H_2O)_2]_n \cdot nH_2O$ (1) and $[K(mef)(H_2O)]_n$ (2). 0.182 g (4.28 mmol) of calcium hydride (99.9%, obtained from Aldrich) was added slowly to 15 cm³ of methanol and after reaction completing 1.000 g (4.14 mmol) of mefenamic acid was added. The mixture was stirred on the magnetic stirrer for 2 weeks, heated to boiling and filtered after cooling. The precipitate was mixed with methanol, the obtained suspension was boiled, cooled and filtered. Combined filtrates were left at room temperature. After a week the crystals of $[Ca(mef)_2(H_2O)_2]_n \cdot nH_2O$ (3) salt grew from solution with 51% yield. Elemental analysis (calculated/found): 1: C 56.78/56.54, H 6.35/6.42, N 4.41/4.40, O 25.21/25.29, Na 7.2/



Fig. 1. The comparison of recorded XRPD patterns (curves) and these ones calculated on the basis of single crystal measurements (bars) for compounds 1–3. Reflections of the standard were subtracted from the recorded XRPD patterns.

7.4; **2**: C 60.58/60.49, H 5.42/5.44, N 4.71/4.65, O 16.14/16.20, K 13.1/13.4; **3**: C 62.70/62.63, H 5.96/6.00, N 4.87/4.71, O 19.49/ 19.41, Ca 7.0/6.9. The comparison of recorded X-ray powder diffraction patterns and these ones calculated on the basis of single crystal measurements are presented in Fig. 1.

The salts **1**, **2**, and **3**, can be also obtained by direct acid–base reaction in water or in methanol media (as it was previously reported [20,21]), however, in all these cases the products were contaminated by metals hydroxides and carbonates as well as by unreacted Hmef. In the case of compound **3** over 70% of total amount of calcium occurs in form of inorganic salts. Nevertheless of salt creation, in all cases addition of base to the acid solution enlarges the Hmef solubility.

2.2. Crystal structure determination

Colourless needle shape crystals of 1, 2 and 3 were mounted in turn on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated MoKa radiation $(\lambda = 0.71073 \text{ Å})$ at temperature 291.0(3) K, with ω scan mode. A 20 s exposure time was used for each crystal. The unit cells parameters were determined from least-squares refinement of the setting angles of 4992, 4012 and 6883 the strongest reflections, respectively, for 1, 2 and 3. Details concerning crystal data and refinement are given in Table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed 0.00%, 0.04% and 0.78% loss of the intensity, respectively, for 1, 2 and 3. During the data reduction above decay correction coefficients were taken into account. Lorentz, polarization, and numerical absorption [32] corrections were applied. The structures were solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2 . All the hydrogen atoms were found from difference Fourier

Table 1

Crystal data and structure refinement details for 1, 2 and 3.

synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic displacement factor equal 1.2 times the value of equivalent displacement factor of the patent non-methyl carbon atoms and 1.5 times for patent methyl carbon, nitrogen and oxygen atoms. The carbon bonded hydrogen atom positions were idealised after each cycle of refinement. The methyl groups were allowed to rotate about their local threefold axis. At the end of compound 3 refinement, on the difference Fourier syntheses appears the 1.437 e $Å^{-3}$ peak at 0.3059 0.5120 0.4390 (1.08 Å from Ca1 atom). The next peak is distinctly smaller (0.810 e $Å^{-3}$) and comparable with the deepest hole (-0.868 e Å⁻³). This can suggest that absolute difference Fourier syntheses maximum may originate from the strong anisotropy of the electron density around calcium atom, as it was previously found, for example, for rhenium coordination compounds [33]. The SHELXS97. SHELXL97 and SHELXTL [34] programs were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in Table 2. The hydrogen bonds geometry is gathered in Table 3.

2.3. Other measurements

Elemental analyses were carried out using a Carbo-Erba C, H, N analyzer. Sodium and potassium content was determined by flame photometry and content of calcium was determined by complexometric titration with EDTA as a complexing agent [35]. IR spectra of complexes were recorded as KBr disc on a Bruker spectrometer over the range 4000–400 cm⁻¹. The thermal characteristics were determined on PerkinElmer Differential Scanning Calorimeter DSC4000. The X-ray powder diffraction (XRPD) patterns were measured in reflection mode on an XPert PRO X-ray powder diffraction system equipped with a Bragg–Brentano PW 3050/65 high resolution goniometer and PW 3011/20 proportional point detector. The

Compound	1	2	3		
Empirical formula	C ₁₅ H ₂₀ NNaO ₅	C ₁₅ H ₁₆ KNO ₃	C ₃₀ H ₃₄ CaN ₂ O ₇		
Formula weight	317.31	297.39	574.67		
Temperature [K]	291.0(3)				
Wavelength [Å]		λ (MoK α) = 0.710731			
Crystal system, space group		Triclinic, $P\bar{1}$			
Unit cell dimensions [Å, °]	a = 6.5387(2)	a = 6.9567(2)	a = 7.7226(2)		
	b = 6.8051(3)	b = 7.0650(2)	b = 10.8220(3)		
	c = 19.2000(9)	c = 16.3165(5)	c = 18.4199(5)		
	$\alpha = 81.615(4)$	$\alpha = 95.210(2)$	$\alpha = 97.231(2)$		
	$\beta = 89.757(3)$	$\beta = 94.715(2)$	$\beta = 91.459(2)$		
	$\gamma = 70.064(4)$	$\gamma = 114.279(3)$	$\gamma = 106.269(3)$		
Volume [Å ³]	793.60(6)	721.65(4)	1463.04(7)		
Z, Calculated density $[Mg/m^3]$	2, 1.328	2, 1.369	2, 1.304		
Absorption coefficient [mm ⁻¹]	0.122	0.374	0.263		
F(000)	336	312	608		
Crystal size [mm]	$0.117 \times 0.013 \times 0.010$	$0.203\times0.018\times0.017$	$0.154 \times 0.010 \times 0.009$		
θ range for data collection [°]	2.15-25.05	2.53-25.00	1.98-36.67		
Index ranges	$-7\leqslant h\leqslant 7$, $-8\leqslant k\leqslant 7$,	$-6\leqslant h\leqslant$ 8, $-8\leqslant k\leqslant$ 8,	$-12\leqslant h\leqslant 11$, $-17\leqslant k\leqslant 12$,		
	$-22\leqslant 1\leqslant 22$	$-19 \leqslant 1 \leqslant 19$	$-27\leqslant 1\leqslant 19$		
Reflections collected/unique	7892/2800	7396/2548	20342/10305		
	$[R_{(int)} = 0.0336]$	$[R_{(int)} = 0.0196]$	$[R_{(int)} = 0.0356]$		
Completeness to $2\theta = 50^{\circ}$ [%]	100.0	100.0	98.3		
Refinement method		Full-matrix least-squares on F ²			
Min. and max. transmission	0.996 and 1.000	0.990 and 0.999	0.994 and 1.000		
Data/restraints/parameters	2800/0/201	2548/0/183	10305/0/365		
Goodness-of-fit on F^2	1.091	1.078	1.015		
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0399,$	$R_1 = 0.0309,$	$R_1 = 0.0285,$		
	$wR_2 = 0.1118$	$wR_2 = 0.0867$	$wR_2 = 0.0638$		
R indices (all data)	$R_1 = 0.0471,$	$R_1 = 0.0393,$	$R_1 = 0.0570,$		
	$wR_2 = 0.1149$	$wR_2 = 0.0894$	$wR_2 = 0.1036$		
Largest diff. peak and hole [e $Å^{-3}$]	0.192 and -0.309	0.196 and -0.219	1.437 and –0.868		

 Table 2 (continued)

Table 2

Selected structural data for 1, 2 and 3	[Å, °].	Cg means aromatic C1-C6	i ring centroid
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Compound 1 Na103 Na104 Na104 Na104#2 C702 C701 Na1Na1#1 Na1Na1#2	2.3467(13) 2.3924(11) 2.4306(12) 2.4477(11) 2.5080(12) 1.2444(16) 1.2643(16) 3.5704(11) 3.7899(11)
$\begin{array}{l} 03\#1Na1-03\\ 03\#1Na1-04\\ 03Na1-04\\ 03\#1Na1-01\\ 03Na1-01\\ 03\#1Na1-01\\ 03\#1Na1-04\#2\\ 03Na1-04\#2\\ 03Na1-04\#2\\ 04Na1-04\#2\\ 01Na1-04\#2\\ 02C7-01\\ C701Na1\\ \end{array}$	$\begin{array}{c} 82.23(4)\\ 103.14(4)\\ 101.09(4)\\ 107.50(4)\\ 88.81(4)\\ 148.81(4)\\ 101.78(4)\\ 175.64(5)\\ 79.77(4)\\ 88.34(4)\\ 122.80(12)\\ 123.75(8)\end{array}$
Compound 2 K1-O1 K1-O3#3 K1-O3 K1-O1#2 K1-C1#4 K1-C2#4 K1-C2#4 K1-C3#4 K1-C3#4 K1-C4#4 K1-C5#4 K1-C6#4 K1-C6#4 K1-C6#4 K1-C6#4 K1-C6#4 K1-C7=0 C7-O1 C7-O2	2.6982(10) 2.7689(11) 2.7982(12) 2.8702(14) 3.4962(15) 3.552(2) 3.4322(19) 3.309(2) 3.2881(17) 3.112(2) 3.8570(9) 4.2189(9) 1.2550(18) 1.2441(17)
$\begin{array}{c} 01-K1-03\#3\\ 01-K1-03\\ 03\#3-K1-03\\ 01-K1-01\#2\\ 03\#3-K1-01\#2\\ 03-K1-01\#2\\ 03-K1-02\\ 03\#3-K1-02\\ 03\#3-K1-02\\ 03\#3-K1-02\\ 03-K1-02\\ 03-K1-02\\ 03-K1-Cg\#4\\ 03\#3-K1-Cg\#4\\ 01\#2-K1-Cg\#4\\ 01\#2-K1-Cg\#4\\ 01\#2-K1-Cg\#4\\ 02-K1-Cg\#4\\ C7-01-K1\\ C7-01-K1\#2\\ 02-C7-01\\ C7-02-K1\\ \end{array}$	$\begin{array}{c} 158.78(4)\\ 113.72(3)\\ 81.46(4)\\ 92.38(3)\\ 71.34(3)\\ 92.86(4)\\ 46.04(3)\\ 118.48(3)\\ 159.67(4)\\ 90.31(4)\\ 85.58(4)\\ 92.36(4)\\ 103.15(4)\\ 163.67(4)\\ 99.15(8)\\ 96.80(4)\\ 99.15(8)\\ 96.04(9)\\ 122.35(13)\\ 90.53(8)\end{array}$
Compound 3 Ca1 -021 Ca1 -01 Ca1 $-022#2$ Ca1 -041 Ca1 -042 Ca1 -042 Ca1 $-02#5$ Ca1 $-01#5$ Ca1 \cdots Ca1#5 Ca1 \cdots Ca1#5 Ca1 \cdots Ca1#2 O1 $-C7$ C7 -02 O21 $-C7$ C27 -022 O21 $-C27$ C27 -022 O21 $-Ca1-01$ O21 $-Ca1-022#2$ O1 $-Ca1-022#2$	2.250(9) 2.339(9) 2.351(8) 2.393(8) 2.508(10) 2.412(9) 2.670(9) 3.940(5) 4.838(5) 1.251(15) 1.251(15) 1.282(15) 1.250(14) 1.255(13) 93.7(3) 107.0(3) 88.0(3)

021–Ca1–O41	95.6(3)
01–Ca1–O41	81.4(3)
022#2-Ca1-041	155.6(3)
021—Ca1—02#5	138.9(3)
01-Ca1-02#5	127.3(3)
022#2-Ca1-02#5	80.7(3)
041—Ca1—02#5	88.3(3)
021–Ca1–042	70.2(4)
01–Ca1–O42	162.0(4)
022#2-Ca1-042	104.0(4)
041–Ca1–042	92.0(4)
02#5—Ca1—O42	68.8(3)
021-Ca1-01#5	168.5(3)
01-Ca1-01#5	76.4(3)
022#2-Ca1-01#5	79.0(3)
041-Ca1-01#5	77.2(3)
02#5—Ca1—O1#5	50.9(3)
042-Ca1-01#5	118.5(3)
C7—01—Ca1	167.2(9)
C7—O1—Ca1#5	88.8(8)
01	120.1(13)
C7—O2—Ca1#5	100.2(8)

Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y, -z + 1; #2 - x + 2, -y + 1, -z + 1; #3 - x + 3, -y + 1, -z + 1; #4x + 1, y, z; #5 - x + 1, -y + 1, -z + 1.

Table 3	
Hydrogen-bonds for 1, 2 and 3 [Å,	°].

D—H····A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdot}{\cdot}{\cdot}A)$	<(DHA)
Compound 1				
03—H30···02	0.89	1.78	2.6610(14)	168.5
O3—H3P…O99#1	0.88	1.91	2.7831(15)	169.9
04—H40· · · 099#2	0.96	1.83	2.7584(16)	161.9
04—H4P···01#2	0.91	2.01	2.9231(16)	177.8
N1—H1 N· · · O2	0.92	1.88	2.5883(16)	131.5
099—H990· · · 01#3	0.85	1.91	2.7315(14)	161.2
099—H99P…N1#4	0.93	2.27	3.158(2)	159.2
099—H99P…02#4	0.93	2.51	3.1267(17)	124.3
C6—H6···01	0.93	2.45	2.7743(18)	100.5
C14—H14A…N1	0.96	2.45	2.856(3)	105.4
Compound 2				
03 - H30 - 02 = 5	0.87	1.88	2,7397(17)	172.0
03—H3P…N1#2	0.90	2.21	3.083(2)	163.3
N1—H1 N····O1	0.88	1.87	2.6090(15)	140.3
C14—H14C ··· N1	0.96	2.46	2.865(3)	105.0
Common d 3				
Compound 3	0.92	2.22	2 020(12)	170 5
041—H410····022#6	0.82	2.22	3.038(12)	1/9.5
041—H41P099#6	0.89	2.38	3.15(2)	143.4
$042 - \pi 420 \cdots 099$	0.92	2.00	2.779(19) 2.780(12)	133.0
N1 U1 N O2	0.86	2.19	2.760(15)	123.9
$N1 = \Pi I N \cdots U2$	0.80	1.95	2.017(14) 2.702(14)	133.0
N21—H21 N···022	0.86	2.09	2.702(14)	127.5
099—H990···041#2	0.72	2.48	3.15(2)	154.2
099—H99P…042	0.78	2.04	2.779(19)	100.4
	0.93	2.43	2.757(15)	100.4
	0.93	2.40	5.279(10)	147.5
C14-0140···N1	0.90	2.40	2.023(17)	100.2
	(1 70)	7.40	6 7/11 191	111/0

Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y, -z + 1; #2x + 1, y, z; #3 - x + 1, -y + 1, -z + 1; #4 - x + 1, -y, -z + 1; #5x + 1, y + 1, z; #6x - 1, y, z.

CuK α_1 radiation was used. The patterns were measured at 291.0(2) K in the range 2–90° with the narrowest beam attenuator. A diamond powder was used as an internal reference. The samples were sprinkled onto the sample holders using a small sieve, to avoid a preferred orientation. The thicknesses of the samples were no more than 0.1 mm. During the measurements each specimen was spun in the specimen plane to improve particle statistics. ¹H NMR (250 MHz) and ¹³C NMR spectra were recorded with Bruker DPX-250 spectrometer with TMS as an internal standard. Signal

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	0		8	., 0		1 0 0,	0 1	,
Compound	H6	H5	H4	H3	H11	H12	H13	H ₃ (C14)/ H ₃ (C15)
Mefenamic acid [23] ^a 1	8.03 d 7.89 dd ${}^{3}J_{H3-H4} = 7.8$ ${}^{4}L_{H3}$ up = 1.7	6.69 dd 6.60 m ${}^{3}J_{H3-H4} = 7.8$ ${}^{3}J_{U4} = 8.3$	7.28 t 7.03 m ${}^{3}J_{H4-H5} \approx {}^{3}J_{H5-H6} = 8.3$ ${}^{4}J_{U2}$, $u_{7} = 1.7$	6.69 dd 6.59 d ${}^{3}J_{\rm H5-H6}$ = 8.3	7.10 m 6.73 d ${}^{3}J_{H4'-H5'} = 7.5$	7.10 m 6.94 t ${}^{3}J_{H4'-H5'} = {}^{3}J_{H5'-H6'} = 7.5$	7.10 m 7.08 d ${}^{3}J_{\rm H5'-H6'}$ = 7.5	2.18 s/2.34 s 2.13 s/2.06 s
2	$^{3}J_{H3-H5} = 1.7$ $^{3}J_{H3-H4} = 7.8$ $^{4}J_{H3-H5} = 1.7$	6.62 m ${}^{3}J_{H3-H4} = 7.8$ ${}^{3}J_{H4-H5} = 8.3$	7.09 m ${}^{3}J_{H4-H5} \approx {}^{3}J_{H5-H6} = 8.3$ ${}^{4}J_{H5-H3} = 1.7$	6.78 d ${}^{3}J_{H5-H6} = 8.3$	6.85 d ${}^{3}J_{H4'-H5'} = 7.6$	6.99 t ${}^{3}J_{H4'-H5'} = {}^{3}J_{H5'-H6'} = 7.6$	7.11 d ${}^{3}J_{H5'-H6'} = 7.6$	2.27 s/2.18 s
3	$^{3}J_{H3-H4} = 7.9$ $^{4}J_{H3-H5} = 1.7$	${}^{6.62 \text{ m}}_{{}^{3}J_{\text{H4-H5}}} \approx {}^{3}J_{\text{H3-H4}} = 7.9$ ${}^{4}J_{\text{H4-H6}} = 1.1$	7.18 m ${}^{3}J_{H4-H5} = 7.9$ ${}^{3}J_{H5-H6} = 8.4$ ${}^{4}J_{H3-H5} = 1.7$	${}^{3}J_{\rm H5-H6} = 8.4$	$^{3}J_{H4'-H5'} = 7.1$ $^{4}J_{H4'-H6'} = 2.3$	7.05t ${}^{3}J_{H4'-H5'} = {}^{3}J_{H5'-H6'} = 7.1$	$^{3}J_{H5'-H6'} = 7.1$ $^{4}J_{H4'-H6'} = 2.3$	2.30 s/2.14 s

¹H NMR data. Atom numbering scheme is as in the structural drawings. The chemical shifts (δ) are given in [ppm] and coupling constants (J) are given in [Hz].

^a spectrum was recorded in CDCl₃, coupling constants were not given.

assignments were accomplished *via* analysis of HMBC, HMQC and COSY experiments. The chemical shifts (δ) [ppm] and coupling constants (*J*) [Hz] were collected in Tables 4 and 5. All NMR spectra were recorded in CD₃OD.

2.4. Theoretical calculations

Table 4

Geometry optimisation and vibrational analysis were performed using the B3LYP functional [36,37] in conjunction with the 6-31++G(d,p) basis set, and GAUSSIAN03 [38] program package was used. Vibrational frequencies were calculated on the basis of energy second derivatives referenced to the mass-weighted coordinates obtained from transferring Cartesian nuclear coordinates. The geometric parameters of Hmef were employed from crystal structure data [39]. The optimised geometrical parameters were in good agreement with those found from X-ray measurement. A correction factor of 0.9613 [40] was applied to all frequencies.

3. Results and discussion

The complexes are air stable and soluble in water. The complexes **1** and **2** are stable up to 59.3 and 77.4 $^{\circ}$ C, respectively,

Table 5

¹³ C NMR data. Atom	numbering scher	me is as in the s	tructural drawings.
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and next they melt in complexed water. The recrystallisation of anhydrous compounds begins at 120 °C due to evaporation of water. The anhydrous salts melt with decomposition at 282-291 and 296-299 °C, respectively, for 1 and 2. The compound 3 loses its internal water within temperature range 66–106 °C without melting and anhydrous salt melt with decomposition at 180-188 °C. The elemental analyses of anhydrous compounds resemble well to the theoretical percentage amounts of the elements in M(mef) (where M = Na, K) and $Ca(mef)_2$ (calculated/found: 1: C 68.43/68.37, H 5.36/5.44, N 5.32/5.5.28, O 12.15/12.11, Na 8.7/ 8.9; 2: C 64.49/64.52, H 5.05/5.15, N 5.01/4.96, O 11.45/11.52, K 14.0/14.3; 3: C 69.21/69.16, H 5.42/5.49, N 5.38/5.43, O 12.29/ 12.35, Ca 7.7/7.6). The XRPD patterns of anhydrous compounds were different from these of Hmef what proofs that organic salts do not decompose to organic acid and inorganic salts. Heating the samples 1-3 at 120 °C until the weight is constant (about 4 h) shows 17.039%, 6.061%, 9.411% loss of mass what corresponds well to the amount of water in 1, 2 and 3, respectively, (theoretically 17.032%, 6.058%, 9.404%, respectively).

A perspective view of **1**, **2** and **3** monomers structures, together with the atom numbering scheme, is shown in Figs. 2–4. All atoms in studied compounds lie in general positions, but location of two inversion centres near central atoms of monomers expands com-

Compound	C7	C2	C1	C6	C5	C4	C3	C8	C9	C10	C11	C12	C13	C14/C15
Mefenamic acid [23] ^a	173.0	150.3	109.2	132.4	116.1	135.2	113.7	138.4	132.9	138.8	123.7	126.0	127.2	20.7/14.3
1	176.0	147.9	120.7	132.0	116.3	131.2	113.6	130.5	137.8	140.8	125.1	125.7	120.6	19.9/13.2
2	177.3	149.2	122.2	133.4	117.7	132.5	115.0	131.9	139.2	142.2	126.4	127.1	121.9	21.3/14.6
3	150.0	140.6	115.5	133.2	117.0	123.6	114.4	133.0	125.3	139.2	127.3	134.1	127.0	20.6/14.1



Fig. 2. The molecular conformation of compound **1** with atom numbering, plotted with 50% probability of displacement ellipsoids. The symmetry generated atoms and bonds are indicated by dashed lines (primed atoms are obtained by -x + 2, -y, -z + 1 symmetry transformation and double-primed by -x + 2, -y + 1, -z + 1 one).



Fig. 3. The molecular conformation of compound **2** with atom numbering, plotted with 50% probability of displacement ellipsoids. The symmetry generated atoms and bonds are indicated by dashed lines (primed atoms are obtained by -x + 2, -y + 1, -z + 1 symmetry transformation, double-primed by -x + 3, -y + 1, -z + 1, triple-primed by x + 1, y, z, quadruple x - 1, y, z and starred by -x + 3, -y + 1, -z + 1 one).

plex molecules to the one-dimensional polymers along crystallographic *b* axis (compound **1**, Fig. 5) and *a* axis (compounds **2** and **3**, Figs. 6 and 7). The outer coordination sphere water molecule in compound **3** shows symptoms of disorder what manifests in relatively large values of orthogonalised atomic displacement parameters (oADPs). The central atoms are five, six (the aromatic ring is considered as one point node coordinating *via* ring centroid) and seven coordinated, respectively, for sodium, potassium and calcium complexes and coordination polyhedra adopt, respectively, slightly distorted trigonal, tetragonal and pentagonal bipyramid (Fig. 8) [41–43]. The coordination sphere around central atom of



Fig. 4. The molecular conformation of compound **3** with atom numbering, plotted with 50% probability of displacement ellipsoids. The symmetry generated atoms and bonds are indicated by dashed lines (primed atoms are obtained by -x + 1, -y + 1, -z + 1 symmetry transformation and double-primed by -x + 2, -y + 1, -z + 1 one).

1 is composed from four bridging bidentate water molecules (three equatorial and one axial) and one monodentate carboxylate group (axial one) of mefenamate ion. In compound **2**, the potassium atom is coordinated by π electrons of aromatic ring (axial position), two bridging bidentate water molecules (equatorial ones) and three oxygen atoms from two tridentate chelating–bridging carboxylate groups (one group provides two oxygen atoms coordinating in chelating mode and occupying equatorial positions in polyhedron, and second one coordinates *via* bridging oxygen atom in axial position; this last atom participates in chelating of next metal atom in the polymer chain). The K1–C_(aromatic ring) distances (Table 2) lie in range of a conservative limit for K… π interactions [44,45], thus it can be supposed that these interactions are significant in con-



Fig. 5. The polymer chain of 1. The not involved into the polymer chain outer coordination sphere water molecule and mefenamate ion are omitted for clarity.



Fig. 6. The polymer chain of 2. The not involved into the polymer chain 1-amine-2,3-dimethylphenyl atoms of mefenamate ion are omitted for clarity.



Fig. 7. The polymer chain of 3. The not involved into polymer water molecules and 2-(2,3-dimethylphenyl)aminophenyl atoms of mefenamate ion are omitted for clarity.

struction of coordination sphere and in consequence in the creation of polymer chain. Noteworthy is the fact that each mefenamate ion coordinates three potassium cations, one *via* chelating carboxylate group, one by bridging oxygen atom and one *via* π electrons of aromatic ring. The central atom of compound **3** is coordinated by two monodentate water molecules (one axial and one equatorial) and five oxygen atoms from four carboxylate groups (two tridentate chelating-bridging and two bidentate bridging) of mefenamate ions. The one atom of bidentate bridging carboxylate group exists in axial position and all other carboxylate groups oxygen atoms occupy equatorial positions. In **3** (as in **2**) the tridentate chelating-bridging carboxylate group acts as bidentate chelating group toward one central atom and as monodentate group toward next metal atom in the polymer chain. Such coordination can be found in some *s* block coordination polymers, e.g. in catena-(*bis*(μ_2 -*N*-Phenylanthranilato-*O*,*O*,*O*')-*bis*(methanol)-calcium) [46], but the structure of polymer chains is different than in **2** or **3**. The planar within the experimental error aromatic rings are inclined at 64.11(5)°, 62.66(6)°, 48.4(4)° and 69.1(4)°, respectively, for compounds **1**, **2**, **3** (rings containing C1 and C8 atoms) and **3** (rings containing C21 and C28 atoms). The aromatic rings of benzoate moiety are inclined at 1.9(2)°, 12.8(2)°, 14.6(9)° and 20(1)° to carboxylate groups, for compounds, respectively, as above. All chelating carboxylate groups are asymmetrically bonded to the metal cations (Table 2). Noteworthy is the fact that one of carboxylate groups of **3** shows rare (close to linear) coordination mode to the metal, and observed C7–O1–Ca1 angle of 167.2(9)° lies far beyond preferred values of 93°, 119° and 127° [47] (Fig. 9). The polymer



Fig. 8. The central atom coordination polyhedra. (a) for compound **1** (symmetry transformations as in Fig. 1), (b) for compound **2** (symmetry transformations as in Fig. 2, Cg means aromatic C1^{''}-C6^{'''} ring centroid.) and (c) for compound **3** (symmetry transformations as in Fig. 3).

chains of compounds **1** and **2** are assembled *via* intermolecular $O-H\cdots O$ medium strength hydrogen bonds (Table 3) to the twodimensional net extending along crystallographic (0 0 1) and (0 1 0) planes, respectively, for **1** and **2**. Additionally, in the both structures can be found intramolecular medium strength N $-H\cdots O$, $O-H\cdots O$ and weak $C-H\cdots O$ hydrogen bonds (Table 3) [48,49] providing additional stabilisation to the structure. In the case of compound **3** the intermolecular hydrogen bonds do not lead to extend the structure to the second dimension because they link water molecules to the single polymer chain *via* two dihydrogen $O-H\cdots O$ bonds. As it is in **1** and **2**, in **3** the medium strength $N-H\cdots O$, $O-H\cdots O$ and weak $C-H\cdots O$ hydrogen bonds interlink the polymer chain. The face-to-face stacking interactions are not observed in the presented structures. Topacli and Ide [20] previously claimed that sodium and calcium salts were obtained, however, structural and diffraction results are in a disagreement with both now presented and previously reported data [39,50]. For example, Topacli and Ide found most intense diffraction peaks at 2θ equal to 38.2° and 38.4° [20], respectively, for Na and Ca salts, whereas these peaks in salts **1** and **3** exist at 4.65° and 4.87°. Additionally, Topacli and Ide observed strong diffraction peaks at 2θ about 38° and 45° in the salts and in the free acid, what is in a disagreement with both, currently presented and known data [39,51], because there is no significant diffraction beyond 2θ diffraction angle equal to 35° (in the free acid and in the respect salts). This strongly suggests that, even if Topacli and Ide obtained reported salts, these organic salts were largely contaminated by highly symmetrical (in crystalline phase) inorganic salts. Inorganic salts give relatively simple IR spectra (in comparison to organic compounds) thus above-mentioned impurity of complex salts does not influence the key features of the previously reported [20,21] IR spectra analyses. Topacli and Ide also assume that Hmef reacts with $Ca(OH)_2$ in ratio 1:1 with creation of hydride HCa(mef) which is rather senseless because even if 1:1 ratio will be retained in salt, the Ca(OH)(mef) will be created instead of mentioned hydride.

The ¹H and ¹³C NMR shifts of **1** and **2** recorded in CD_3OD are very similar to these ones of the free acid (Tables 4 and 5), what suggests

that the polymeric structure is not retained in CD_3OD solution. Typical differences exist in environment of carboxylic group due to its deprotonation in the salts. In the case of compound **3** some essential upfield and downfield shifts are observed in ¹³C NMR spectra (Table 5). Because in the single mef ion none of the aromatic rings can be placed over other ring, the interaction of ring currents should lead to deshielding of atoms of both rings. In the presented case only one ring is deshielded, and the second one is shielded, what suggests that a part of polymeric structure is maintained in solution and rings (containing C8-C13 atoms) of mef ion from one mer are



Fig. 9. Histogram showing preferred M-O-C angles in metal-carboxylate systems (according to Cambridge Structural Database [47]).



Fig. 10. The homosynthon motif observed in the crystal structure of Hmef.

Table 6							
Vibrational	frequencies	and	assignment	of Hmef	and	its	dimer

Hmef monomer			Hmef dimer				
	v _{exp.}	V _{theor} .	v _{theor} .	Assignment			
		3624	3430	v(OH)			
	3300 m	3351	3345	v(NH)			
		3053-3104	3053-3096	$v_{\rm s}(\rm CH)_{\rm aryl}, v_{\rm as}(\rm CH)_{\rm aryl}$			
	2760-			$v_{\rm s}(\rm CH)_{\rm aryl}, v_{\rm as}(\rm CH)_{\rm aryl}, v(\rm OH)$			
	-3250 b	2910-3013	2911-3010	$v_{as}(CH_3), v_s(CH_3)$			
	1650 s	1667	1634	$v(C=O), \delta(NH)$			
	1590 w, 1580 s	1591	1590	v(CC) _{aryl}			
		1560	1564	$v(CC)_{aryl}, \delta(NH)$			
	1510 s	1499	1500	$v(CC)_{aryl}, \delta(NH), \delta(CH)_{aryl}$			
	1460 w	1457	1452	$v(CC)_{aryl}, \delta(CH_3), \delta(CH)_{aryl}$			
	1445 s	1430	1430	$\delta(CH_3)$, $\delta(CH)_{aryl}$			
	1325 m	1342	1337	$v(CC)_{aryl}$, $v(C-COO)$, $\delta(OH)$			
		1305	1302	$\delta(NH)$, $\delta(CH)_{aryl}$			
	1235 s	1286	1284	$v(CN)$, $\delta(OH)$, $\delta(CH)_{aryl}$			
	1165 m	1153	1148	$\delta(OH)$, $\delta(CH)_{aryl}$			
		1140	1134	$\delta(OH)$, $\delta(CH)_{aryl}$			
	1095 w	1118	1116	$\delta(OH)$, $\delta(CH)_{aryl}$			
	1040 w	1051	1059	$\delta(CH_3)$, $\delta(CH)_{aryl}$			
		1036	1038	$\delta(CH_3)$, $\delta(CH)_{aryl}$			
	890 m	937	943	$\delta(CH_3)$			
	780 m	746	746	$\delta(CH)_{aryl}$			
	750 m	732	735	$\delta(CH)_{aryl}$			
	660 w	630	634	$\delta(NH)$			
		615	611	$\delta(OH), \delta(NH)$			
	540 w	552	550	$\delta(OH)$			

placed over second mer rings (containing C1—C6 atoms) similarly as it was found in the crystal structure of **3**.

The vibrational analysis was carried out for mefenamic acid and its three coordination polymer compounds in the solid state. The quantum mechanical calculations were performed for isolated mefenamic acid molecule to examine the proposed vibrational assignments and for dimer structure (Fig. 10) to check the position of absorption bands assigned to the vibrations of hydrogen bonded groups. All calculated frequencies are for gas-phase molecules. The characteristic frequencies are listed in Tables 6 and 7.

The theoretical and experimental vibrational frequencies of Hmef are close. The frequency differences are observed for the bending vibrations involving mainly the CH bonds. The experimental spectrum of monomer reveals characteristic NH stretching vibrations at 3300 cm⁻¹. The broad split absorption band in the frequency range 2760–3250 cm⁻¹ is attributed to the v(OH), v(CH) vibrations of methyl and aryl groups. The single band at 1650 cm⁻¹ is attributed to the overlapped C=O stretching vibrations and NH bending vibrations. The bands around 1580, 1510 and 1445 cm⁻¹ confirm the presence of aromatic CC bonds. The OH bending vibration appears as a band at 1325 cm⁻¹. The CN stretching mode is observed at 1255 cm⁻¹. The medium intensity bands at 750 and 780 cm⁻¹ correspond to vibrations of aryl CH bonds.

The most significant differences between experimental and calculated vibrational frequencies of Hmef were observed for OH and C=O stretching vibrations. They are caused by the presence of noncovalent interactions in the solid state. The calculated frequencies display remarkable bathochromic shift for dimer structure where OH and C=O bonds are involved in hydrogen bonding, similarly to the behaviour of hydrogen-bonded carboxylic group dimers [52]. Differences between the solid state and gas phase results indicate that the periodicity has a marked influence on the spectral characteristics of the Hmef molecule.

The IR spectra of **1–3** showed the additional strong bands at ca. 1365 and 1600 cm⁻¹, which can be assigned to the stretching vibrations of carboxylate groups, the $v_s(COO^-)$ and $v_{as}(COO^-)$, respectively. Since these bands are not split in the IR spectrum of

Table 7

Vibrational frequencies and assignment of Hmef coordination polymer compour	ıds.
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1	2	3	
Vexp.	v _{exp.}	v _{exp.}	Assignment
3085-3500	3000-3600	3000-3620	$v_{s}(CH)_{aryl}$, $v_{as}(CH)_{aryl}$, $v(OH)$, $v(NH)$
2743-3085	2850-2971	2830-2956	$v_{as}(CH_3), v_s(CH_3)$
1600	1603	1609	$v_{as}(COO^{-}), \delta(NH)$
1571	1571	1578	$v(CC)_{aryl}, \delta(NH)$
1535	1557	1545	$v(CC)_{aryl}, \delta(NH)$
1485	1486	1493	$v(CC)_{aryl}, \delta(NH), \delta(CH)_{aryl}$
1465	1443	1454	$v(CC)_{aryl}, \delta(CH_3), \delta(CH)_{aryl}$
1364	1367	1385	v _s (COO ⁻)
1278	1274	1280	$v(CN)$, $\delta(OH)$, $\delta(CH)_{aryl}$
1157	1150	1156	$\delta(OH), \delta(CH)_{aryl}$
1057	1057	1068	$\delta(CH_3), \delta(CH)_{aryl}$
1043	1028	1043	$\delta(CH_3), \delta(CH)_{aryl}$
835	844	858	$\delta(CH_3)$
778	769	812	$\delta(CH)_{aryl}$
750	750	760	$\delta(CH)_{aryl}$
700	700	705	$\delta(OH), \delta(NH)$
665	667	670	$\delta(NH)$
631			$\delta(OH), \delta(NH)$
		526	$\delta(OH)$
467	425	409	v(MO)

1 and 2, the carboxylate groups have the same coordination function in the particular compounds. Taking into account the presence of hydrogen bonds formed by the carboxylate groups it can be stated that these groups act in pentadentate fashion. The two different coordination functions of carboxylate groups - tridentate chelating-bridging and bidentate chelating - are confirmed for 3, since in the spectrum of this compound the bands of the carboxylate stretching vibrations have more complex structure. Such a disappearance of the band (at 1650 cm^{-1}) corresponding to C=O stretching vibrations of COOH group and an appearance of two bands corresponding to carboxylate ion stretching vibrations have been previously observed for Na and Ca salts of mefenamic acid [20,21]. The NH group of mefenamate ion is involved in the intramolecular N-H···O hydrogen bonds in both Hmef and its three coordination polymer compounds, but the band corresponding to NH bending vibrations is red-shifted for 1-3. The bands at 467, 425 and 410 cm⁻¹ are attributed to the v(Na=0), v(K=0) and v(Ca–O), respectively.

4. Supplementary data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No CCDC740723, CCDC740724, and CCDC740725, respectively, for compounds **1**, **2** and **3**.

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