NQR in Alanine and Lysine Iodates

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Z. Naturforsch. **55a,** 199–206 (2000); received October 13, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25–30, 1999.

The structure of iodates of α- and β-alanine (Ala) ($2(\beta\text{-Ala} \cdot HIO_3) \cdot H_2O$, β-Ala-$2HIO_3$, DL-Ala $\cdot$ $HIO_3 \cdot 2H_2O$, L-Ala $\cdot$ HIO_3) and L-lysine (L-Lys) (L-Lys $\cdot$ HIO_3, L-Lys $\cdot$ $2HIO_3$, L-Lys $\cdot$ $3HIO_3$, L-Lys $\cdot$ $6HIO_3$) have been investigated by means of iodine-127 NQR, IR spectroscopy and X-ray diffraction.

Introduction

Organic salts, which result from reaction of amino acids with various acids, are an important class of nonlinear optical crystals [1–4]. Simple and/or acid iodates may be formed in reaction of iodic acid with various amino acids [5]. Useful information on the structure and chemical bonding of these compounds may be obtained by iodine-127 NQR, IR spectroscopic and X-ray diffraction investigation [6]. In the present work the results on α and β alanine and L-lysine with iodic acid are reported. The following compounds with alanine were synthesized: L-Ala $\cdot$ HIO_3, DL-Ala $\cdot$ $HIO_3 \cdot 2H_2O$, β-Ala $\cdot$ $HIO_3 \cdot 0.5H_2O$, and β-Ala $\cdot$ $2HIO_3$. From these compounds, β-Ala $\cdot$ $HIO_3 \cdot 0.5H_2O$ and DL-Ala $\cdot$ $HIO_3 \cdot 2H_2O$ could be crystallized and investigated by NQR and X-ray diffraction.

According to our previous results [5] the reaction of lysine with iodic acid leads to the formation of Lys $\cdot$ $nHIO_3$ with $n > 3$ in addition to Lys $\cdot$ HIO_3, Lys $\cdot$ $2HIO_3$ and Lys $\cdot$ $3HIO_3$. We succeeded in obtaining this crystal, determined its composition (Lys $\cdot$ $6HIO_3$) and investigated it by NQR, IR spectroscopy and X-ray diffraction. From the point of view of structural peculiarities and chemical bonds, the most interesting crystal is L-Lys $\cdot$ $6HIO_3$.

Experimental

The reaction of amino acids (alanine and lysine) with iodic acid was carried out by mixing aqueous solutions of amino acids and HIO_3 in appropriate mole ratios and subsequent evaporation at room temperature. L-α-alanine (L-Ala) and β-alanine (β-Ala) were obtained from Reanal (Hungary), and DL-α-alanine (DL-Ala) from Yerevan Factory of Chemical Reagents. L-lysine (L-Lys) was synthesized at the Institute of Biotechnology (Yerevan). The iodic acid HIO_3 was used after recrystallization of the commercial reagent.

The determination of iodine was performed by iodometric titration with sodium thiosulphate in presence of starch.

IR spectra were registered on a Specord 75 IR spectrophotometer at room temperature using nujol mull. NQR frequencies were measured on an ISSh-2-13 pulsed spectrometer at 77 K.

Thermal properties were studied using a 3427-904 type Derivatograph (MOM, Hungary) and a Boëtius type microscope with heating table.

The X-ray data were collected on an automatic diffractometer ENRAF-NONIUS CAD-4 (Mo K_α radiation, graphite monochromator) at room temperature by the $\omega/2\theta$-scan technique in the range of $1.5° \leq \theta \leq 30°$. The structures were solved by the direct method and refined by the full-matrix least-squares technique with anisotropic thermal parameters for nonhydrogen atoms using the SHELXL-93 program [7]. Because of presence of heavy iodine atoms in the structure, the positional parameters of the hydrogen atoms were calculated geometrically and were refined using restraints.

The crystals of $2(\beta\text{-Ala} \cdot HIO_3) \cdot H_2O$ (empirical formula: $C_6H_{18}N_2O_{11}I_2$) are monoclinic: $a = 10.324(2)$ Å, $b = 7.1610(14)$ Å, $c = 21.78(4)$ Å, $\beta = 101.11(3)°$,

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Table 1. Atomic coordinates [×10^4] and equivalent isotropic displacement parameters (Å^2×10^3) of 2 (β-Ala · HIO_3) · H_2O **U**(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	**U** (eq)	Atom	*x*	*y*	*z*	**U** (eq)
I (1)	7366 (1)	5845 (1)	2373 (1)	21 (1)	C (2)	4003 (6)	8087 (10)	4507 (3)	39 (1)
I (2)	3771 (1)	3062 (1)	2609 (1)	21 (1)	C (3)	4392 (7)	9160 (8)	3959 (3)	38 (1)
O (11)	5715 (3)	5567 (5)	2502 (2)	32 (1)	O (1A)	7725 (9)	3222 (13)	334 (4)	33 (2)
O (12)	7478 (4)	3911 (5)	1825 (2)	32 (1)	O (1A′)	7489 (13)	3913 (20)	274 (6)	60 (3)
O (13)	7025 (4)	7766 (5)	1799 (2)	29 (1)	O (2A)	5922 (10)	2718 (16)	757 (5)	38 (2)
O (21)	4079 (4)	3836 (6)	3427 (2)	36 (1)	O (2A′)	5864 (10)	3315 (16)	712 (5)	37 (2)
O (22)	4883 (4)	1101 (5)	2643 (2)	32 (1)	N (1A)	5787 (4)	1646 (6)	–1495 (2)	29 (1)
O (23)	2223 (4)	1860 (5)	2608 (2)	32 (1)	C (1A)	6499 (6)	3080 (9)	252 (3)	39 (1)
O (1)	2089 (4)	7026 (6)	3782 (2)	38 (1)	C (2A)	5634 (6)	2492 (9)	–380 (3)	35 (1)
O (2)	2383 (5)	6002 (8)	4772 (2)	53 (1)	C (3A)	6311 (6)	2855 (9)	–941 (3)	35 (1)
N (1)	4905 (5)	7956 (7)	3506 (2)	34 (1)	O (W)	3501 (8)	5870 (14)	5928 (4)	33 (2)
C (1)	2746 (6)	7003 (8)	4320 (3)	31 (1)	O (W′)	3499 (10)	6700 (15)	5897 (5)	42 (2)

Table 2. Atomic coordinates [×10^4] and equivalent isotropic displacement parameters (Å^2×10^3) of DL-Ala · HIO_3 · 2 H_2O.

Atom	*x*	*y*	*z*	**U** (eq)
I (1)	226.8 (2)	2544.3 (4)	7418.8 (3)	18 (1)
O (11)	89 (4)	2660 (6)	5479 (5)	33 (1)
O (12)	1116 (3)	4378 (6)	7881 (4)	28 (1)
O (13)	1046 (3)	576 (6)	7757 (4)	26 (1)
O (1)	–3498 (4)	747 (9)	7190 (5)	50 (2)
O (2)	–4497 (4)	–1324 (10)	8000 (6)	54 (2)
O (W1)	–5816 (4)	–892 (13)	5768 (6)	70 (2)
O (W2)	–2124 (4)	4390 (7)	9422 (5)	37 (1)
C (1)	–3691 (5)	–343 (11)	8082 (7)	33 (1)
C (2)	–2972 (5)	–751 (1)	9461 (7)	32 (1)
C (3)	–2062 (4)	382 (9)	9487 (5)	19 (1)
N (1)	–3444 (6)	–424 (15)	10820 (8)	73 (3)

V= 1536.4 (5) Å^3, Z=4 . [2 (β-Ala · HIO_3) · H_2O], space group $P2_1/n$, ϱ_c=2.368 g/cm^3. The refinement was carried out using 3884 independent reflections with $I \geq 2\,\sigma\,(I)$. The final discrepancy factor and goodness of fit were $R1 = 0.0360$ and $S = 1.190$, respectively. The coordinates of non-hydrogen atoms are listed in Table 1.

The crystals of DL-Ala · HIO_3 · 2 H_2O (empirical formula: $C_3H_{12}NO_7I$) are monoclinic: a = 13.536 (3) Å, b=7.3240(15) Å, c=9.312(2) Å, β =98.52(3)°, V= 913.0(3) Å^3, Z=4, ϱ_c=2.189 g/cm^3, space group $P2_1/c$. The final discrepancy factor and goodness of fit were $R1 = 0.0475$ and $S = 1.101$, respectively (1939 independent reflections with $I \geq 2\,\sigma\,(I)$). The coordinates of non-hydrogen atoms are listed in Table 2.

The crystals of L-Lys · 6 HIO_3 (empirical formula: $C_6H_{20}N_2O_{20}I_6$) are orthorhombic: a = 7.3657 (15) Å, b= 14.400(3) Å, c=22.171 (4) Å, V=2351.7(8) Å^3, Z=4, ϱ_c=3.394 g/cm^3, space group $P2_12_12_1$. The final discrepancy factor and goodness of fit were $R1 = 0.0433$ and S=1.065, respectively (6516 independent reflections with $I \geq 2\,\sigma\,(I)$). The coordinates of non-hydrogen atoms are listed in Table 3.

Results and Discussion

Alanine Iodates

β-Alanine (β-Ala), $NH_2CH_2CH_2COOH$ does not contain an asymmetric carbon atom and hence is not optically active. One may expect the protonation of the amino group $NH_3^+CH_2CH_2COOH \cdot IO_3^-$, by the proton of HIO_3. The IR spectrum contains a strong and wide absorption band near 700 cm^{-1} (peaks at 693; 720; 733; 753; 787 cm^{-1}) which is characteristic for the IO_3^- ion. The band at 1687 cm^{-1} indicates the presence of a carboxylic group COOH. The content of HIO_3 is 64.0± 0.2%, which indicates the composition β-Ala · HIO_3 · 0.5 H_2O, i.e. 2 (β-Ala · HIO_3) · H_2O (calculated value is 64.20%).

The NQR spectrum (Table 4) shows two lines for each of the transitions ν_1 (±1/2 → ±3/2) and ν_2 (±3/2 → ±5/2). This spectrum allows to conclude that there are two differently distorted iodate groups. One may expect similar bond lengths for the iodate group with small asymmetry parameter (η = 0.0226) and a significant difference in bond lengths for the second group with η = 0.1799. The reason for such difference may be in the hydrogen bonding. An X-ray structure investigation was undertaken in order to compare the conclusions from NQR with structural data. Selected bond lengths and angles are given in Table 5. The asymmetric unit (Fig. 1) contains two molecules of β-alanine (the atoms of the second molecule are designated as A), two iodate groups and a water molecule. Thus the formula 2 (β-Ala · HIO_3) · H_2O was con-

Table 3. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) of L-Lys · 6HIO_3.

Atom	x	y	z	**U** (eq)	Atom	x	y	z	**U** (eq)
I (1)	6718.5 (6)	2351.4 (3)	–10.8 (2)	17 (1)	O (51)	11036 (10)	300 (5)	1744 (3)	36 (2)
O (11)	8396 (9)	2078 (4)	–580 (3)	26 (1)	O (52)	11046 (9)	1059 (5)	610 (3)	30 (1)
O (12)	4689 (9)	1955 (5)	–420 (3)	29 (1)	O (53)	8520 (10)	–248 (5)	958 (3)	32 (1)
O (13)	6996 (9)	1334 (5)	461 (3)	28 (1)	I (6)	15374.2 (8)	232.7 (4)	2412.1 (3)	25 (1)
I (2)	3945.6 (7)	4978.5 (3)	787.9 (2)	20 (1)	O (61)	17654 (11)	638 (6)	2384 (4)	42 (2)
O (21)	4448 (12)	5815 (5)	139 (3)	38 (2)	O (62)	15587 (14)	–823 (5)	1956 (3)	42 (2)
O (22)	4371 (9)	5866 (4)	1329 (3)	25 (1)	O (63)	14387 (12)	894 (5)	1806 (3)	38 (2)
O (23)	1536 (9)	5028 (5)	762 (3)	31 (1)	O (2)	7051 (10)	–2949 (5)	1236 (3)	33 (2)
I (3)	9054.0 (7)	3856.4 (3)	1343.0 (2)	21 (1)	N (7)	14321 (15)	–136 (6)	346 (6)	53 (3)
O (31)	8516 (12)	4281 (5)	2154 (3)	42 (2)	C (6)	14983 (12)	–1114 (7)	424 (5)	30 (2)
O (32)	7645 (10)	4613 (5)	909 (4)	36 (2)	C (5)	13375 (13)	–1807 (6)	445 (4)	26 (2)
O (33)	7568 (9)	2883 (5)	1472 (4)	35 (2)	C (4)	12450 (13)	–1794 (7)	1067 (4)	28 (2)
I (4)	13918.3 (7)	2717.6 (3)	1735.9 (2)	19 (1)	C (3)	10863 (12)	–2456 (6)	1070 (4)	27 (2)
O (41)	13733 (10)	3992 (4)	1708 (3)	29 (1)	C (2)	9754 (12)	–2420 (6)	1658 (4)	26 (2)
O (42)	14657 (10)	2651 (4)	2522 (3)	29 (1)	C (1)	8237 (12)	–3139 (6)	1649 (5)	26 (2)
O (43)	11526 (8)	2459 (5)	1822 (3)	27 (1)	N (8)	10902 (11)	–2623 (6)	2200 (4)	32 (2)
I (5)	9411.6 (8)	852.7 (4)	1187.3 (2)	23 (1)	O (1)	8221 (10)	–3788 (5)	2000 (3)	33 (1)

Table 4. Iodine-127 NQR frequencies ν_1 (1/2–3/2), ν_2(3/2–5/2), asymmetry parameters (η) and quadrupole coupling constants (eQq_{zz}) of some alanine and lysine iodates at 77 K.

Compounds	ν_1, MHz	ν_2, MHz	η	eQq_{zz}, MHz
2(β-Ala · HIO_3) · H_2O	151.715	303.23	0.0226	1010.87
	164.905	316.69	0.1799	1062.47
DL-Ala · HIO_3 · H_2O	161.27	311.05	0.1698	1042.82
L-Lys · 2HIO_3	152.148	300.059	0.1247	1001.64
	152.245	303.82	0.0996	1010.75
L-Lys · 3HIO_3	152.67	304.10	0.0561	1014.32
	155.69	305.33	0.1240	1020.93
	216.656	320.33	0.5488	1123.99
L-Lys · 6HIO_3	156.547	297.68	0.2015	1000.28
	163.362	313.101	0.1850	1050.73
	166.151	316.531	0.1976	1063.06
	208.825	316.826	0.5206	1106.21
	211.935	317.767	0.5370	1111.38
	230.86	322.218	0.6084	1161.07

firmed. The water molecule and the oxygen atoms of the carboxylic group of one β-alanine molecule (A) are disordered at room temperature (see Figure 1). Bond lengths C(1)–O(1) and C(1)–O(2) in each molecule indicate the presence of a COOH group. The hydroxyls are O(2) and O(2A). Both iodate groups are IO_3^- ions. This means that the amino groups in each molecule are protonated. The group I(1)O_3 has longer I(1)–O(12) and I(1)–O(13) than I(1)–O(11) bonds, which is caused by the presence of the hydrogen bonds O(12)···H–O(2A) [O(2A′)] and O(13)···O(W) [O(W′)] with distances 2.651 (2.646 Å) and 2.786 (2.689 Å), respectively. The water molecule forms strong hydrogen bonds with one alanine molecule. The hydrogen bond length of O(2)–H···O(W) is 2.499 Å and that of O(2)–H···O(W′) 2.489 Å. The iodate groups form hydrogen bonds with the protonated amino groups N(1)H_3^+ and N(1A)H_3^+ as

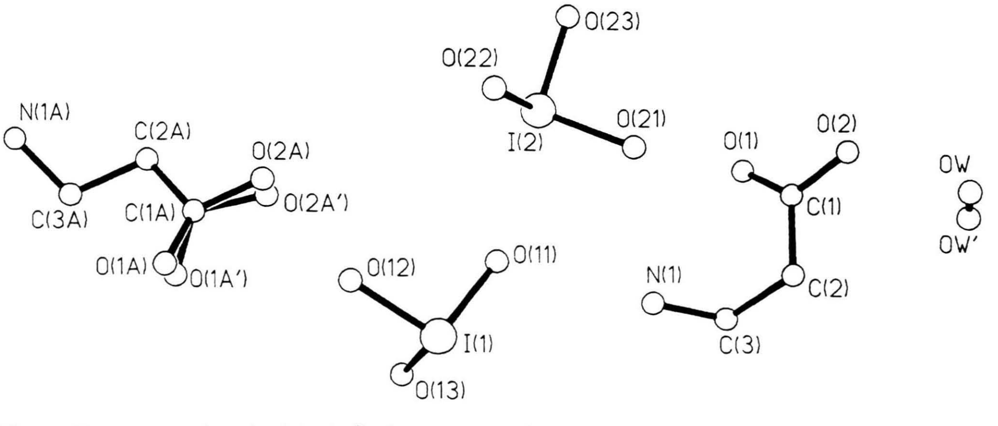

Fig. 1. The asymmetric unit of the 2(β-Ala · HIO_3) · H_2O unit cell.

Table 5. Bond lengths [Å] and angles [°] of $2(\beta\text{-Ala} \cdot HIO_3) \cdot H_2O$.

I (1)–O (11)	1.788 (3)	I (2)–O (21)	1.787 (4)
I (1)–O (12)	1.825 (4)	I (2)–O (22)	1.807 (4)
I (1)–O (13)	1.824 (4)	I (2)–O (23)	1.815 (4)
I (1)···O (12)^{i}	2.762 (4)	I (2)···O (11)	2.734 (3)
I (1)···O (13)^{ii}	2.812 (4)	I (2)···O (23)^{iii}	2.911 (4)
I (1)···O (22)^{i}	2.852 (4)	I (2)···O (1)^{iv}	3.003 (4)
C (1)–O (1)	1.208 (7)	C (1)–O (2)	1.306 (7)
C (3)–N (1)	1.463 (7)	C (1)–C (2)	1.499 (8)
C (2)–C (3)	1.508 (8)	O (1A)–O (1A′)	0.555 (14)
C (1A)–O (1A)	1.249 (11)	C (1A)–O (1A′)	1.177 (14)
C (1A)–O (2A)	1.345 (12)	C (1A)–O (2A′)	1.285 (12)
C (3A)–N (1A)	1.474 (7)	C (1A)–C (2A)	1.518 (8)
C (2A)–C (3A)	1.514 (8)	O (W)–O (W′)	0.598 (11)

O (11)–I (1)–O (13)	96.8 (2)	O (21)–I (2)–O (23)	98.1 (2)
O (13)–I (1)–O (12)	100.1 (2)	O (21)–I (2)–O (22)	102.1 (2)
O (11)–I (1)–O (12)	101.1 (2)	O (22)–I (2)–O (23)	100.6 (2)
O (1)–C (1)–O (2)	120.6 (5)	O (1)–C (1)–C (2)	122.8 (5)
O (2)–C (1)–C (2)	116.6 (5)	C (1)–C (2)–C (3)	114.0 (5)
N (1)–C (3)–C (2)	112.8 (5)	O (1A′)–O (1A)–C (1A)	70 (2)
O (1A)–O (1A′)–C (1A)	84 (2)	O (1A′)–C (1A)–O (1A)	26.3 (7)
O (1A′)–C (1A)–O (1A′)	118.0 (9)	O (1A)–C (1A)–O (2A′)	122.4 (8)
O (1A′)–C (1A)–O (2A)	125.5 (9)	O (1A)–C (1A)–O (2A)	119.9 (8)
O (2A′)–C (1A)–O (2A)	19.1 (6)	O (1A′)–C (1A)–C (2A)	122.2 (8)
O (1A)–C (1A)–C (2A)	123.5 (6)	O (2A′)–C (1A)–C (2A)	113.9 (7)
O (2A)–C (1A)–C (2A)	111.8 (7)	C (3A)–C (2A)–C (1A)	111.3 (5)
N (1A)–C (3A)–C (2A)	111.7 (5)		

Symmetry codes:
(i) 1.5−*x*; 0.5+*y*; 0.5−*z*;
(ii) 1.5−*x*; *y*−0.5; 0.5−*z*;
(iii) 0.5−*x*; 0.5+*y*; 0.5−*z*;
(iv) 0.5−*x*; *y*−0.5; 0.5−*z*.

well. The shortest bond from these is N(1A)–H ··· O(23) with distance 2.835 Å. There is a short distance O(W) [O(W′)] ··· O(21) equal to 2.615 (2.659) Å (possibly a hydrogen bond), which, however, does not affect the I(2)–O(21) bond length.

β-Ala · $2HIO_3$ was synthesized from solutions containing β-Ala and HIO_3 in mole ratios 1 : 1,5 ÷ 2. In addition to the absorption band of IO_3^- (700–800 cm^{-1}) the spectrum contains also a band at 600 cm^{-1}, which indicates the presence of HIO_3 group. The spectrum contains also a band near 1700 cm^{-1} (with peaks at 1673; 1687; 1707 cm^{-1}) which indicates the presence of COOH group. From this we may conclude the formation of acid iodate β-Ala · $2HIO_3$ with structure $NH_3^+CH_2COOH \cdot IO_3^- \cdot HIO_3$.

On heating, $2(\beta\text{-Ala} \cdot HIO_3) \cdot H_2O$ and β-Ala · $2HIO_3$ melt at 95 °C and 100 °C, respectively, and then decompose with exothermal effect.

α-Alanine $CH_3CH(NH_2)COOH$ contains an asymmetric carbon atom and may display optical activity. Reaction of aqueous solutions of equimolar quantities of racemic DL-Ala and HIO_3 leads to formation of crystals with composition DL-Ala · HIO_3 · $2H_2O$ according to chemical and thermogravimetric analysis. The IR spectrum DL-Ala · HIO_3 · $2H_2O$ contains a strong absorption band in the 700–800 cm^{-1} region, which is characteristic for the IO_3^- ion. A band at 1713 cm^{-3} shows a COOH group, and a wide absorption band near 3420 cm^{-1} represents the stretching ν (OH) vibration of a water molecule.

Table 6. Bond lengths [Å] and angles [°] of DL-Ala · HIO_3 · $2H_2O$.

I (1)–O (11)	1.790 (4)	O (1)–I (1)–O (2)	99.8 (2)
I (1)–O (12)	1.812 (4)	O (1)–I (1)–O (3)	100.5 (2)
I (1)–O (13)	1.817 (4)	O (2)–I (1)–O (3)	100.4 (2)
C (1)–O (1)	1.208 (9)	C (1)–C (2)–N (1)	110.4 (6)
C (1)–O (2)	1.299 (9)	C (1)–C (2)–C (3)	109.3 (5)
C (1)–C (2)	1.521 (9)	N (1)–C (2)–C (3)	112.2 (6)
C (2)–N (1)	1.518 (9)	O (4)–C (3)–O (5)	126.2 (6)
C (2)–C (3)	1.483 (9)	O (4)–C (3)–C (2)	122.2 (6)
		O (5)–C (3)–C (2)	111.5 (6)

The NQR spectrum contains one line for each transition. An asymmetry parameter of 0.1698 (Table 4) may indicate the participation of hydrogen bonds from water molecules and carboxylic groups in the distortion of the IO_3^- group. Availability of single crystals allowed the crystal structure determination at room temperature. Selected bond lengths and angles are given in Table 6. The bond lengths of C(1)–O(1) and C(1)–O(2) show that O(1) forms a carbonyl group C=O, and O(2) forms a hydroxyl group O–H. The I–O bond lengths of the iodate group show that it is an IO_3^- ion. This means that the amino group is protonated. The hydroxyl group forms a strong hydrogen bond with the O(W1) water molecule

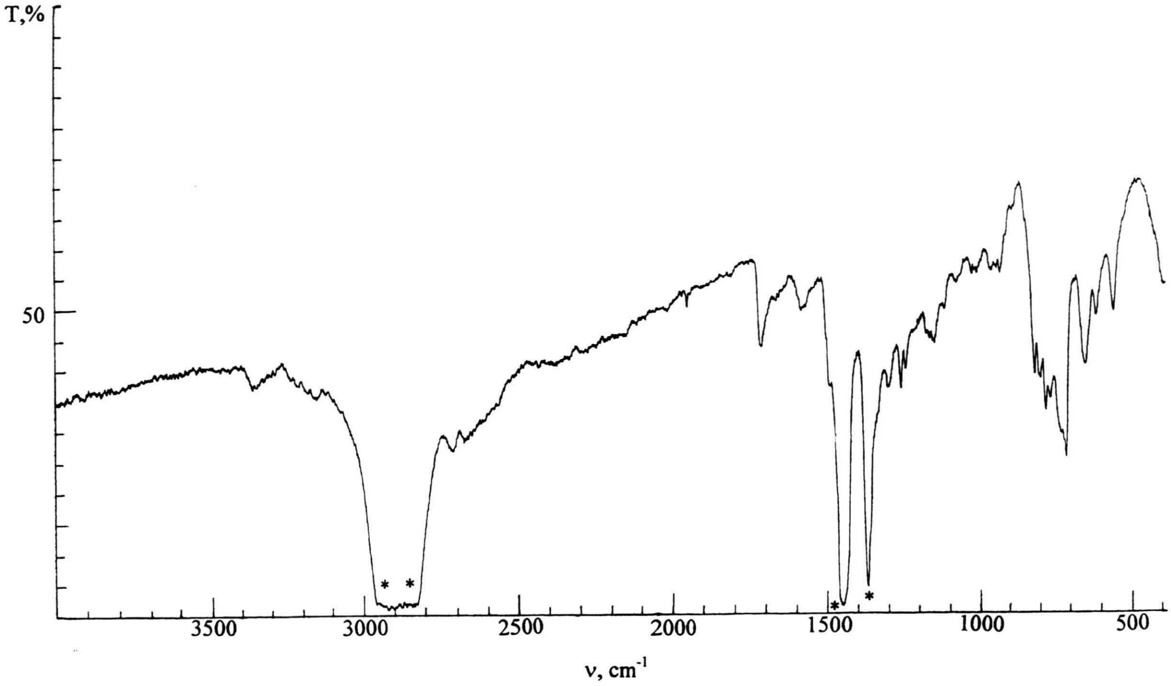

Fig. 2. The IR spectrum of L-Lys · 6 HIO_3. The absorption bands of vaseline oil are marked with asterisks.

O(2)–H ··· O(W1) of 2.552 Å. The second water molecule to all appearances forms a hydrogen bond with the iodate group O(W2)–H ··· O(13) of 2.806 Å, which may be the cause of some lengthening of I(1)–O(13). However, this difference in the I–O bond lengths of the iodate group does not explain the value of the asymmetry parameter at 77 K. This may indicate structural variations between 77 K and room temperature.

On heating, DL-Ala · HIO_3 · 2 H_2O melts at 60 °C. At 108 °C the compound loses water and decomposes at above 110 °C with exothermic effect. In addition to β-alanine and racemic DL-α-Ala we also examined the L-α-Ala. The optically active compound can form salts with acentric symmetry. Colorless crystals are deposited from a saturated aqueous solution containing L-Ala and HIO_3 in the ratio 1 : 1. The IR spectrum contains an IO_3^- ion absorption band at 700–800 cm^{-1} (with peaks at 720; 733; 773; 787 cm^{-1}), and a band near 1700 cm^{-1} (with peaks at 1687 and 1707 cm^{-1}) from a COOH group. On this basis one may suppose the formation of L-Ala · HIO_3 with structure $CH_3CH(NH_3^+)COOH \cdot IO_3^-$. The compound is not stable and on standing becomes pink.

Our efforts to synthesize acid iodates of both DL and L-alanine failed.

Lysine Iodates

In contrast to alanine, the lysine molecule $NH_2(CH_2)_4CH(NH_2)COOH$ has two amino groups. We did not find NQR signals for the compound L-Lys · HIO_3 which was obtained as a powder. However, on the basis of the IR spectrum [5], namely, the absence of bands characteristic for HIO_3 and COOH groups, its structure may be represented as $NH_3^+(CH_2)_4CH(NH_3^+)COO^- \cdot IO_3^-$. For the L-Lys · 2 HIO_3 two possible forms could be expected: $NH_3^+(CH_2)_4CH(NH_3^+)COO^- \cdot IO_3^- \cdot HIO_3$ and $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot 2IO_3^-$. The IR spectrum [5] and NQR data (Table 4) allowed us to reject the first form. The NQR spectrum contains two lines ν_1 and ν_2 with η and eQq_{zz} values characteristic for a IO_3^- group. The NQR data of L-Lys · 3 HIO_3 are quoted in Table 4 for comparison. L-Lys · 3 HIO_3 has the structure $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot IO_3^- \cdot (IO_3 \cdots IO_3H)^-$. A detailed consideration of NQR data, IR spectrum and structure has been published in [5, 8].

There is one more compound [5] in the system Lys + HIO_3 + H_2O, in addition to the above mentioned compounds. A poorly crystallizing compound is formed at ratio Lys: $HIO_3 \geq 4$. The content of HIO_3 in this compound amounts to 88.0±0.5%, which corresponds to the composition L-Lys · 6HIO_3 (calculated 87.83%). The crystallization of α-HIO_3 starts at the ratios 1 : 7 and 1 : 8 after precipitation of L-Lys · 6HIO_3. The structure $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot 2IO_3^- \cdot 4HIO_3$ could be expected for L-Lys · 6HIO_3. However, the NQR data (Table 4) and IR spectrum (Fig. 2) do not permit such an interpretation. Three atoms from six crystallographically independent iodine atoms have high values of the asymmetry parameter (0.5206; 0.5370; 0.6084) and exist undoubtedly in HIO_3 groups. There are three bands in the region of ν(I-OH) (556; 610; 647 cm^{-1}) (Fig. 2), which also indicate the presence of three distinct HIO_3 groups. There is also a band at 1710 cm^{-1} related to a COOH group. From this, one may conclude that both amino groups are protonated by two protons of six HIO_3 groups. However, from the remaining three iodine atoms it is difficult to choose two, which may form slightly distorted IO_3^- groups. On the contrary, rather high values of η (0.2015; 0.1850; 0.1976) allow to suppose the presence of rather strong bonds with IO_3^- groups, which lead to their distortion. Such bonds may be [6] so called intermediate between first and second coordination spheres with O···I distance ≤2.5 Å and strong hydrogen bonds between HIO_3 and IO_3^- groups. It was thus necessary to determine the crystal structure for the interpretation of the NQR and IR spectra and in order to know the details of the above mentioned bonds.

Selected geometric parameters are given in Table 7. As in the case of L-Lys · 3HIO_3 [5, 8] the bond lengths of C(1)–O(2) (1.295 Å) and C(1)–O(1) (1.216 Å) indicate the presence of a carboxylic group and confirm the conclusion made on the basis of the IR spectrum. The length of the other bonds in the doubly protonated lysinium cation are close to that of L-Lys · 3HIO_3. Consideration of the nearest environment of the iodine atoms sort out the three atoms I(5), I(2), and I(3) which form bonds with length 1.894; 1.913; and 1.941 Å, respectively. These bond lengths indicate that oxygen atoms O(51), O(21) and O(31) form hydroxyl groups, and hence the mentioned atoms enter in HIO_3 groups. We think that these are the same iodine atoms which became apparent in NQR and IR spectra and have η values equal to 0.5206; 0.5370; 0.6084 and ν(I-OH) values equal to 647; 610; 556 cm^{-1}, respectively.

Table 7. Bond lengths [Å] and angles [°] of L-Lys · 6HIO_3.

I (1)–O (11)	1.809 (6)	I (1)···O (11)^{i}	2.894 (6)
I (1)–O (12)	1.839 (6)	I (1)···O (12)^{ii}	2.588 (6)
I (1)–O (13)	1.811 (6)	I (1)···O (52)^{i}	2.692 (7)
I (2)–O (23)	1.777 (7)	I (2)···O (11)^{i}	3.024 (7)
I (2)–O (22)	1.780 (6)	I (2)···O (32)	2.789 (7)
I (2)–O (21)	1.913 (7)	I (2)···O (41)^{iii}	2.491 (6)
I (3)–O (31)	1.941 (7)	I (3)···O (12)^{ii}	2.403 (6)
I (3)–O (32)	1.785 (7)	I (3)···O (23)^{iv}	2.801 (6)
I (3)–O (33)	1.801 (6)	I (3)···O (43)	2.914 (6)
I (4)–O (41)	1.841 (6)	I (4)···O (11)^{ii}	2.609 (6)
I (4)–O (42)	1.829 (6)	I (4)···O (33)^{iv}	2.761 (6)
I (4)–O (43)	1.811 (6)	I (4)···O (63)	2.654 (6)
I (5)–O (51)	1.894 (7)	I (5)···O (13)	2.498 (6)
I (5)–O (52)	1.783 (7)	I (5)···O (43)	3.123 (6)
I (5)–O (53)	1.789 (7)	I (5)···O (61)^{iii}	2.969 (6)
I (6)–O (61)	1.779 (8)	I (6)···O (22)^{v}	2.943 (6)
I (6)–O (62)	1.833 (7)	I (6)···O (41)^{vi}	2.726 (6)
I (6)–O (63)	1.799 (7)	O (2)···O (22)^{viii}	2.608 (7)
C (1)–O (1)	1.216 (12)	O (21)···O (53)^{i}	2.654 (7)
C (1)–C (2)	1.524 (12)	O (31)···O (1)^{vii}	2.812 (7)
C (2)–N (8)	1.498 (12)	O (51)···O (63)	2.620 (7)
C (4)–C (5)	1.540 (12)	O (62)···O (42)^{vi}	2.482 (7)
C (1)–O (2)	1.295 (12)	N (7)···O (13)^{iv}	2.901 (7)
C (2)–C (3)	1.541 (12)	N (7)···O (23)^{ix}	2.951 (7)
C (3)–C (4)	1.509 (12)	N (8)···O (43)^{v}	2.806 (7)
C (5)–C (6)	1.549 (13)	N (8)···O (61)^{vi}	2.872 (7)
C (6)–N (7)	1.501 (13)		
O (11)–I (1)–O (13)	98.6 (3)	O (23)–I (2)–O (22)	99.7 (3)
O (11)–I (1)–O (12)	98.3 (3)	O (23)–I (2)–O (21)	98.3 (3)
O (13)–I (1)–O (12)	97.2 (3)	O (22)–I (2)–O (21)	91.2 (3)
O (32)–I (3)–O (33)	101.9 (4)	O (43)–I (4)–O (42)	100.3 (3)
O (32)–I (3)–O (31)	100.9 (4)	O (43)–I (4)–O (41)	97.8 (3)
O (33)–I (3)–O (31)	88.5 (3)	O (42)–I (4)–O (41)	96.1 (3)
O (52)–I (5)–O (53)	101.0 (3)	O (61)–I (6)–O (63)	100.5 (4)
O (52)–I (5)–O (51)	96.4 (3)	O (61)–I (6)–O (62)	99.9 (4)
O (53)–I (5)–O (51)	92.6 (3)	O (63)–I (6)–O (62)	93.5 (3)
O (1)–C (1)–O (2)	127.5 (9)	N (8)–C (2)–C (1)	107.0 (7)
O (1)–C (1)–C (2)	121.3 (9)	N (8)–C (2)–C (3)	111.9 (7)
O (2)–C (1)–C (2)	111.1 (8)	C (1)–C (2)–C (3)	110.8 (8)
C (3)–C (4)–C (5)	109.7 (7)	N (7)–C (6)–C (5)	111.1 (8)
C (4)–C (3)–C (2)	113.1 (7)	C (4)–C (5)–C (6)	110.9 (8)

Symmetry codes: (i) $x-0.5$; $0.5-y$; $-z$; (ii) $0.5+x$; $0.5-y$; $-z$; (iii) $x-1$; y; z; (iv) $x+1$; y; z; (v) $2-x$; $y-0.5$; $0.5-z$; (vi) $3-x$; $y-0.5$; $0.5-z$; (vii) x; $y+1$; z; (viii) x; $y-1$; z; (ix) $1.5+x$; $0.5-y$; $-z$.

The remaining three iodine atoms I(1), I(4) and I(6) form rather distorted iodate groups, the longest bond lengths of which correspond to that expected on the basis of correlation [6]. The iodine atom I(1) has a lengthened bond I(1)–O(12) (1.839 Å). This lengthening is caused by the very short distance of O(12) with the nearest I(3) at 2.403 Å, which may be considered as intermediate between first (<2 Å) and second (>2.6 Å) coordination spheres. One more iodine atom which has a lengthened bond and two shorter bonds is I(6) with I(6)–O(62) distance equal to 1.833 Å. However, in contrast to O(12), oxygen atom O(62) does not show a short O(62)···I bond, which may lengthen the bond I(6)–O(62). There is the O(42) atom in the vicinity of O(62) at a short O(62)···O(42) distance equal to 2.482 Å. In addition, the bond I(4)–O(42) is also longer (1,829 Å). This allows to conclude that the O(62)···O(42) contact is a hydrogen bond. By that the problem of the fourth HIO_3 group, which does not appear in the IR spectrum and

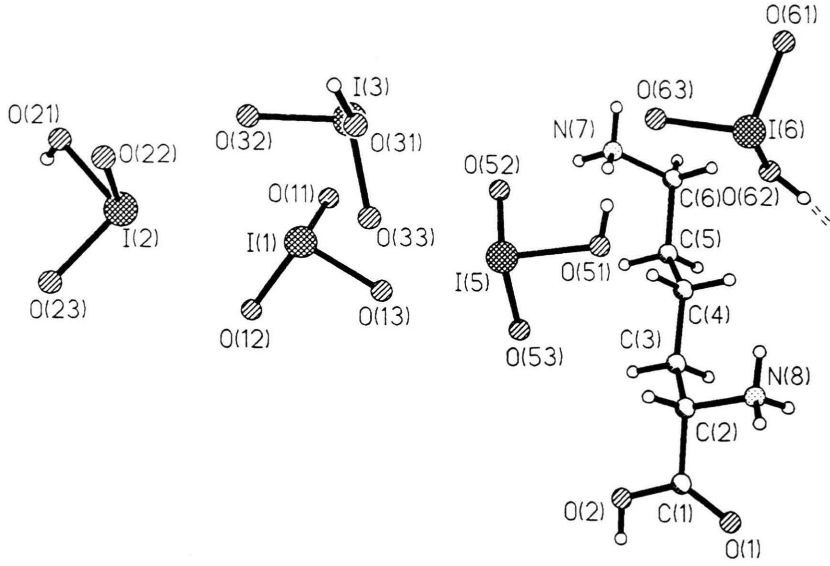

Fig. 3. The asymmetric unit of the L-Lys · 6 HIO_3 unit cell.

about which it was difficult to conclude definitely on the basis of NQR data only, is solved. The assignment of NQR frequencies to these three iodine atoms I(1), I(4) and I(6) is difficult on the basis of the asymmetry parameters only for their similarity. However, on the basis of $eQq = 1000.28$ MHz, which is characteristic for the IO_3^- group [6], one may conclude that the value $\eta = 0.2015$ and the corresponding frequencies relate to the $I(1)O_3^-$ group.

For the assignment of the remaining frequencies to I(6) and I(4) it is necessary to examine the O(62) ··· O(42) hydrogen bond more closely. The hydrogen bonds O ··· O with length –2.5 Å may be both symmetric and asymmetric [9]. On the basis of the apex angles of the $I(6)O_3$ and $I(4)O_3$ iodate groups, one may conclude that the I(6)–O(62) ··· H ··· O(42)–I(4) hydrogen bond is not exactly central. The consideration of numerous structures of simple and acid iodates shows that the apex angles of the IO_3^- group are 99±3°, and in case of the HIO_3 group one of these angles as a rule is smaller and roughly equal to 90±3°. On this basis we think that the I(62)– I(6)–O(63) angle being equal to 93.5° indicates that O(62) is a donor in a hydrogen bond. Hence we may assign the higher value of $eQq_{zz} = 1063.06$ MHz to I(6) and the value $eQq_{zz} = 1050.73$ MHz to I(4). From the correlation between O–H bond length vs. O ··· O distance for asymmetric hydrogen bonds [9] we can estimate for O(62) ··· O(42) with length 2.482 Å an O–H bond length of 1.11 Å. This means that the proton is shifted from the center by 0.13 Å. However, the grouping $O_2I(6)O \cdots H \cdots OI(4)O_2$ with an almost central hydrogen bond is not singular. On the contrary, there is a rather strong $O(41) \cdots I(2)O_3H$ bond with O(41) ··· I(2) distance equal to 2.491 Å, which leads to a corresponding lengthening of the I(4)–O(41) bond up to 1.841 Å. This allows to consider the more complicated complex $[I(6)O_3 \cdots H \cdots O_2I(4)O \cdots I(2)O_3H]^-$ as a second counter-ion of the doubly charged lysinium cation in addition to $[I(1)O_3 \cdots I(3)O_3H]^-$. To the best of our knowledge the $[O_2IO \cdots H \cdots OIO_2 \cdots IO_3H]^-$ type of complex, in which instead of IO_3^- the biiodate $H(IO_3)_2^-$ ion appears, has not been discovered before. These complex anions are held together by hydrogen bonds. The $[I(1)O_3 \cdots I(3)O_3H]^-$ group is attached to the carbonyl oxygen atom of lysinium through an O(31)–H ··· O(1) hydrogen bond with length 2.812 Å. The $HI(2)O_3$ group of the second complex acts both as donor and acceptor in a hydrogen bond. Through a hydrogen bond O(22) ··· H–O(2) with length 2.608 Å it is linked with the carboxylic group of lysinium and through a hydrogen bond O(21)–H ··· O(53) of 2.654 Å length with the remaining $HI(5)O_3$ group, which in turn forms a hydrogen bond O(51)–H ··· O(63) with length 2.620 Å. The protonated nitrogen atoms $N(7)H_3^+$ and $N(8)H_3^+$ have oxygen atoms at N(7) ··· O(13) of

2.901 Å, N(7)··· O(23) of 2.951 Å, N(8)···O(43) of 2.806 Å, and N(8)···O(61) of 2.872 Å in their environment, with hydrogen bonds probably occurring.

There are channels in the direction [100] in the structure of L-Lys · 6 HIO_3 constructed from iodine-oxygen polyhedrons. The lysine molecules lie in these channels attached to the iodate groups through hydrogen bonds.

On heating, L-Lys · 6 HIO_3 decomposes above 130 °C with exothermic effect and forms I_2O_5, which in turn decomposes above 350 °C with endothermic effect.

Summary

Investigation of alanine and lysine iodates using NQR, IR spectroscopic and X-ray diffraction methods allows to suggest the following structural formulas for these compounds:

1. $2(NH_3^+CH_2CH_2COOH \cdot IO_3^-) \cdot H_2O$ for $2(\beta\text{-Ala} \cdot HIO_3) \cdot H_2O$,
2. $NH_3^+CH_2CH_2COOH \cdot IO_3^- \cdot HIO_3$ for $\beta\text{-Ala} \cdot 2HIO_3$,
3. $CH_3CH(NH_3^+)COOH \cdot IO_3^- \cdot 2H_2O$ for $\text{DL-Ala} \cdot HIO_3 \cdot 2H_2O$,
4. $CH_3CH(NH_3^+)COOH \cdot IO_3^-$ for $\text{L-Ala} \cdot HIO_3$,
5. $NH_3^+(CH_2)_4CH(NH_3^+)COO^- \cdot IO_3^-$ for $\text{L-Lys} \cdot HIO_3$,
6. $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot 2IO_3^-$ for $\text{L-Lys} \cdot 2HIO_3$,
7. $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot (IO_3 \cdots IO_3H)^-$ for $\text{L-Lys} \cdot 3HIO_3$,
8. $NH_3^+(CH_2)_4CH(NH_3^+)COOH \cdot (IO_3 \cdots IO_3H)^- \cdot (O_2IO \cdots H \cdots O\,IO_2 \cdots IO_3H)^- \cdot HIO_3$ for $\text{L-Lys} \cdot 6HIO_3$.

Acknowledgements

The authors thank Dr. A. E. Aghajanyan for the synthesis and purification of L-lysine. The research described in this publication was made possible in part by award No. ACH-009-98 of the National Foundation of Science and Advanced Technologies and No. AB2-958 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF).

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