Interaction of lysine with iodic acid

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Abstract

A new compound in the Lys–HIO_3–H_2O system (where Lys = lysine), lysine–iodic acid (1/3), $C_6H_{14}N_2O_2.3HIO_3$, has been discovered. Its crystals display nonlinear optical properties. They were investigated by X-ray analysis, IR spectroscopy and NQR methods. The parameters of the unit cell are a = 8.360 (2), b = 6.330 (1), c = 14.750 (3) Å, β = 92.86 (3)°, D_x = 2.87 Mg m^{-3}, space group $P2_1$, Z = 2. The three iodate groups in the structure have different roles. Interaction of lysine and iodic acid results in a compound containing a doubly protonated lysine cation and two counterions, IO_3^- and $I_2O_5OH^-$.

1. Introduction

Among nonlinear optical crystals, organic salts occupy an intermediate position between molecular organic compounds with covalent bonds and inorganic compounds with mainly ionic bonds (Koreneva *et al.*, 1985; Nicoud & Twieg, 1987). The salts of protonated amino acids are representatives of an important class of such compounds, interest in which has recently increased following the discovery of promising nonlinear optical properties in crystals of L-arginine phosphate monohydrate (LAP) (Xu & Jiang, 1988; Eimerl *et al.*, 1989; Yokotani *et al.*, 1990; Andreev *et al.*, 1990; Dhanaraj *et al.*, 1991). The active search for nonlinear optical crystals of LAP analogues with improved properties continues. One possible class of organic salts of protonated amino acids are iodates (Monaco *et al.*, 1987; Suzuki & Matsuoka, 1991). We have discovered that, besides the iodates of arginine and lysine, a bis(hydrogeniodate) of arginine, $Arg.2HIO_3$, and a tris(hydrogeniodate) of lysine, $Lys.3HIO_3$, also display nonlinear optical properties. The results of the investigation of $Arg.2HIO_3$ will be described elsewhere. This work describes the investigation of $Lys.3HIO_3$.

2. Results and discussion

2.1. *Growth, IR and NQR spectra*

As L-lysine [Lys or α,ε-diaminocaproic acid, $H_2N(CH_2)_4CH(NH_2)COOH$] has two amino groups it is able to form salts with, for example, hydrochloric acid in a 1:1 and 1:2 ratio. We have tried to prepare corresponding salts of iodic acid. Besides salts in the ratios 1:1 and 1:2, crystals with the composition 1:3, *i.e.* $Lys.3HIO_3$, were formed (Petrosyan *et al.*, 1995). These crystals are colourless elongated plates and their IR spectrum, recorded on a Specord 75 IR spectrophotometer, is shown in Fig. 1. The absorption band at 3300–3500 cm^{-1}, typical for stretching vibrations of NH_2 groups, is absent. This means that both amino groups are protonated and two NH_3^+ groups are formed (Bellamy, 1963). The band at 1713 cm^{-1} could be related to the COOH carboxylic group. The split band near 1600 cm^{-1} (1606 and 1593 cm^{-1}) can be assigned to bending vibrations of NH_3^+ groups (Bellamy, 1963). In the range for the stretching vibrations of the I—O bonds there is an intense band with frequency 613 cm^{-1} which could be related to the ν(I—OH) vibration (Petrosyan *et al.*, 1986, 1990; Petrosyan & Shishkin, 1996). Hence two of the three HIO_3 molecules are present as IO_3^- ions while the third is present as an HIO_3 molecule. Taking into account the value of ν(I—OH), one can conclude that the HIO_3 group is significantly distorted.

The crystals of $Lys.3HIO_3$ were also investigated by iodine-127 nuclear quadrupole resonance (NQR). NQR frequencies at liquid-nitrogen temperature were measured on an ISSH-2-13 pulsed spectrometer. In Table 1 the values of the resonance frequencies of the (1/2–3/2) (ν_1) and (3/2–5/2) (ν_2) transitions and, calculated from them, values of the electric field gradient tensor asymmetry parameter (η) and the quadrupole coupling constant (eQq_{zz}) are given. Three lines for each of the transitions illustrate the existence of three nonequivalent I atoms in the unit cell of the $Lys.3HIO_3$ crystals. One of the I atoms, with asymmetry parameter η = 0.0561, is in a less distorted and quite isolated IO_3 group. The second I atom, with η = 0.1240, is also in an IO_3 group but is significantly distorted. The third I atom, with η = 0.5488, is undoubtedly in an HIO_3 group. The distortion of the second IO_3 group can be explained by a hydrogen bond or a strong O$\cdots$I bond from the second coordination sphere of the I atom (Petrosyan & Shishkin, 1996). However, a hydrogen bond between this IO_3 group and an HIO_3 group is unlikely since this would cause a corresponding decrease in the distortion of the HIO_3 group with an associated decrease of η.

Table 1. *Iodine-127 NQR data for Lys.3HIO₃ at 77 K*

ν_1 (MHz)	ν_2 (MHz)	η	eQq_{zz} (MHz)
152.67	304.10	0.0561	1014.32
155.69	305.33	0.1240	1020.93
216.66	320.33	0.5488	1123.99

Remaining possibilities include a hydrogen bond with a COOH group or a strong $O \cdots I$ bond. In the latter case the strongest $O \cdots I$ bond could be realized with the I atom of the HIO₃ group (Petrosyan *et al.*, 1986).

2.2. *The crystal structure of Lys.3HIO₃*

In order to investigate the relationship of the spectral and nonlinear optical properties to the symmetry and structure, an X-ray structure investigation of Lys.3HIO₃ was undertaken. Data were collected in the range $2 \leq \theta \leq 30°$. The structure was solved by direct methods and refined by the full-matrix least-squares technique with anisotropic displacement parameters for non-H atoms using *SHELXL*93 (Sheldrick, 1993). Because the H atoms could not be found from a difference Fourier synthesis their positions were determined on the basis of spectral data and analysis of the geometry of the non-H atoms. The absolute configuration was determined by refinement of the Flack parameter (Flack, 1983) and its value is 0.02 (5). Further details are given in Table 2. Fig. 2 and Fig. 3 depict the structure and crystal packing, respectively. The coordinates of non-H atoms are given in Table 3 and bond lengths and valence angles are given in Table 4.†

Comparison of the C1—O1 and C1—O2 bond lengths with the standard values for a COOH carboxylic group (Allen *et al.*, 1987) shows that this group is not ionized and the H atom is bonded to O2. This conclusion confirms the inference drawn from the spectral data about the existence of a COOH group. The three iodate groups in the structure of Lys.3HIO₃ have different roles. I1 forms an iodate group which may be considered as an isolated IO_3^- ion. In addition to three short I—O bonds in the first coordination sphere, I1 also has three other neighbouring O atoms (see Table 4), which are usually in the range 2.6–3.2 Å for iodates (Ilyukhin & Kalinin, 1980). This is obviously the group that has the smallest asymmetry parameter in Table 1 ($\eta = 0.0561$). I2 has one rather long bond to O22 [1.914 (6) Å], which undoubtedly indicates that O22 is bonded to a proton and, consequently, I2 forms an HIO₃ group. It is apparent that this is the group with the largest asymmetry parameter, $\eta = 0.5488$. O22 forms a hydrogen bond with the O21[vi] atom of a symmetry-related HI2O₃ group (see Table 4 and Fig. 2), resulting in an infinite zigzag chain along the *b* axis. I3 differs from the other

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0540). Services for accessing these data are described at the back of the journal.

Table 2. *Experimental details*

Crystal data	
Chemical formula	$C_6H_{16}N_2O_2^{2+}.HI_2O_6^-.IO_3^-$
Chemical formula weight	673.92
Cell setting	Monoclinic
Space group	$P2_1$
a (Å)	8.360 (2)
b (Å)	6.330 (1)
c (Å)	14.750 (3)
β (°)	92.86 (3)
V (Å³)	779.6 (3)
Z	2
D_x (Mg m⁻³)	2.87
Radiation type	Mo *Kα*
Wavelength (Å)	0.71073
No. of reflections for cell parameters	24
θ range (°)	14–16
μ (mm⁻¹)	6.072
Temperature (K)	293 (2)
Crystal form	Plate
Crystal size (mm)	$0.6 \times 0.2 \times 0.1$
Crystal colour	Colourless
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω–2θ scans
Absorption correction	ψ scans
No. of measured reflections	2601
No. of independent reflections	2452
No. of observed reflections	2443
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.1171
θ_{max} (°)	29.98
Range of *h*, *k*, *l*	$0 \rightarrow h \rightarrow 11$
	$0 \rightarrow k \rightarrow 8$
	$-20 \rightarrow l \rightarrow 20$
No. of standard reflections	3
Frequency of standard reflections	Every 60 min
Intensity decay (%)	10
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0338
$wR(F^2)$	0.0918
S	1.071
No. of reflections used in refinement	2452
No. of parameters used	200
H-atom treatment	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 1.2606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.21
$\Delta\rho_{max}$ (e Å⁻³)	3.061
$\Delta\rho_{min}$ (e Å⁻³)	−1.963
Extinction method	*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient	0.010 (1)
Source of atomic scattering factors	*International Tables for Crystallography* (Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Data collection, cell refinement and data reduction	*CAD*-4 *Software* (Enraf–Nonius, 1988)
Structure solution	*SHELXS*86 (Sheldrick, 1990)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I1	0.72398 (4)	0.38284 (7)	0.87423 (3)	0.01554 (13)
O11	0.6527 (8)	0.1946 (11)	0.7880 (4)	0.0259 (12)
O12	0.6660 (8)	0.6270 (11)	0.8169 (4)	0.0262 (12)
O13	0.9336 (5)	0.3776 (14)	0.8507 (4)	0.0279 (13)
I2	0.22512 (4)	0.35791 (7)	0.93412 (3)	0.01528 (13)
O21	0.1524 (7)	0.1153 (11)	0.9821 (5)	0.0277 (12)
O22	0.1510 (7)	0.5336 (13)	1.0289 (4)	0.0272 (14)
O23	0.4277 (6)	0.3537 (11)	0.9774 (4)	0.0238 (11)
I3	0.43204 (5)	−0.08631 (7)	0.81957 (2)	0.01402 (13)
O31	0.2990 (7)	0.1453 (10)	0.8057 (4)	0.0230 (11)
O32	0.4450 (7)	−0.1352 (12)	0.7001 (3)	0.0224 (11)
O33	0.2810 (7)	−0.2824 (10)	0.8399 (4)	0.0248 (12)
O1	0.5864 (7)	0.4468 (14)	0.5196 (4)	0.032 (2)
O2	0.3679 (7)	0.4472 (15)	0.4265 (4)	0.033 (2)
C1	0.4459 (9)	0.4389 (14)	0.5065 (4)	0.0206 (13)
C2	0.3304 (8)	0.4029 (15)	0.5828 (4)	0.0212 (13)
C3	0.1906 (9)	0.5578 (15)	0.5788 (5)	0.0225 (14)
C4	0.0650 (10)	0.5108 (17)	0.6487 (6)	0.028 (2)
C5	−0.0709 (10)	0.6730 (17)	0.6432 (6)	0.030 (2)
C6	−0.0343 (9)	0.8843 (19)	0.6861 (5)	0.029 (2)
N7	−0.0361 (8)	0.8759 (15)	0.7870 (4)	0.0260 (14)
N8	0.4238 (8)	0.4192 (13)	0.6700 (4)	0.0222 (12)

two. Bond-length analysis shows that I3 forms an iodate group which, unlike I1O$_3$, is quite distorted and cannot be considered as isolated. On the contrary, the short O31—I2 bond of 2.429 (6) Å could be considered as intermediate between the first and second coordination spheres (Ilyukhin & Kalinin, 1980; Petrosyan & Shishkin, 1996) This short bond causes lengthening of the I3—O31 bond and significant distortion of the I3O$_3$ group. As was suggested by Ilyukhin & Kalinin (1980), the HI2O$_3$.I3O$_3$ combination could be thought of as a united I$_2$O$_5$OH$^-$ complex. Therefore, interaction of lysine with iodic acid forms a compound containing a doubly protonated lysine cation [$^+$H$_3$N(CH$_2$)$_4$-CH(NH$_3$$^+$)COOH] and two counterions: IO$_3^-$ and I$_2$O$_5$OH$^-$. The O32 atom of the I3O$_3$ group has a short contact to the O2 atom of the carboxylic group, indicating that they participate in a hydrogen bond of length 2.549 (8) Å. Besides the hydrogen bonds mentioned above between O atoms, there are also hydrogen bonds between the protonated amino groups of the lysine cation and the O atoms of the iodate groups (see Table 4 and Fig. 2).

Good correspondence between the structural data obtained at room temperature and the NQR data obtained at 77 K shows that the structure of Lys.3HIO$_3$ does not change in this temperature range.

2.3. *Nonlinear optical properties and symmetry*

Optically active organic molecular compounds crystallize in non-centrosymmetric space groups, mainly in $P2_12_12_1$ and $P2_1$ (Koreneva *et al.*, 1985). Almost half of the ten LAP analogues investigated by Monaco *et al.* (1987) are in $P2_12_12_1$ and the others are in $P2_1$. Monaco *et al.* (1987) pointed out that the crystals with $P2_1$
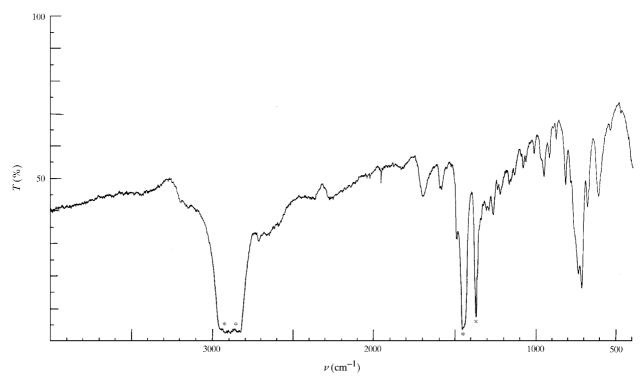

Fig. 1. The IR spectrum of Lys.3HIO$_3$. The absorption bands of vaseline oil are marked with asterisks.

symmetry gave considerably more intense second harmonic generation (SHG) signals than those with $P2_12_12_1$ symmetry, but they did not offer an explanation. We believe that the cause of this phenomenon could, in general, be connected with the influence of crystal symmetry on the optimum contribution of the molecular microscopic nonlinearity of the molecules to the macroscopic nonlinear susceptibility of the crystals (see Shigorin & Shipulo, 1974; Zyss & Oudar, 1982; Nicoud & Twieg, 1987). The space group $P2_1$ allows the maximum possible contribution of a molecule's non-linearity (38%), while the $P2_12_12_1$ group allows only the minimum of 19%. Hence, from this point of view, the crystals of Lys.3HIO$_3$ belong to an auspicious symmetry group.

The single crystals of Lys.3HIO$_3$ were investigated by an SHG method (a Q-switched YAG:Nd laser was used

Table 4. *Selected geometric parameters (Å, °)*

I1—O11	1.821 (6)	I1···O21^i	2.740 (7)
I1—O12	1.816 (7)	I1···O22^{ii}	2.805 (7)
I1—O13	1.804 (5)	I1···O23	2.977 (5)
I2—O21	1.809 (7)	I2···O13^{iii}	2.677 (5)
I2—O22	1.914 (6)	I2···O31	2.429 (6)
I2—O23	1.780 (5)	I2···O33^{iv}	2.720 (6)
I3—O31	1.845 (6)	I3···O11	2.620 (7)
I3—O32	1.798 (5)	I3···O12^v	2.670 (7)
I3—O33	1.806 (6)	I3···O23^{ii}	3.184 (6)
O1—C1	1.182 (9)	C1···O2	1.320 (9)
C2—C1	1.537 (10)	C2···C3	1.524 (11)
C2—N8	1.474 (9)	C3···C4	1.538 (11)
C5—C4	1.531 (13)	C5···C6	1.50 (2)
N7—C6	1.491 (10)		

O12—I1—O11	99.3 (3)	O23—I2—O21	100.3 (3)
O13—I1—O11	98.1 (3)	O23—I2—O22	94.8 (3)
O13—I1—O12	99.5 (3)	O21—I2—O22	94.6 (4)
O32—I3—O33	97.0 (3)	O1—C1—O2	126.0 (7)
O32—I3—O31	95.4 (3)	O1—C1—C2	122.8 (7)
O33—I3—O31	98.1 (3)	O2—C1—C2	111.1 (6)
N8—C2—C3	111.2 (6)	C4—C3—C2	113.4 (7)
N8—C2—C1	107.7 (6)	C5—C4—C3	111.4 (8)
C3—C2—C1	112.6 (7)	C6—C5—C4	116.0 (7)
N7—C6—C5	112.1 (9)		

O22···O21^{vi}	2.586 (8)	O2···O32^{vii}	2.549 (8)
N8···O11	2.895 (10)	N7···O33^{iv}	2.903 (10)
N8···O31	2.883 (9)	N7···O12^{iii}	2.998 (10)
N8···O32^{iv}	2.859 (11)		

Symmetry codes: (i) $1-x, \frac{1}{2}+y, 2-z$; (ii) $1-x, y-\frac{1}{2}, 2-z$; (iii) $x-1, y, z$; (iv) $x, 1+y, z$; (v) $x, y-1, z$; (vi) $-x, \frac{1}{2}+y, 2-z$; (vii) $1-x, \frac{1}{2}+y, 1-z$.
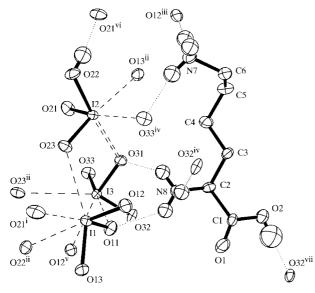

Fig. 2. A general view of Lys.3HIO$_3$. H atoms derived from the experimental results are shown. Hydrogen bonds are shown as dotted lines, the bond of intermediate length between the first and second coordination spheres of I2 is shown by a double dashed line and bonds between I atoms and O atoms of the second coordination sphere are shown by dashed lines. Symmetry codes are given in Table 4.
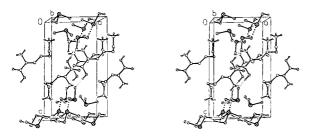
as a source). Phase matching was observed and a strong signal was found. During NQR investigation of Lys.3HIO$_3$ strong piezoresonances were discovered.

The results reported here show that crystals of Lys.3HIO$_3$ could be important for nonlinear optics, and detailed investigation of its linear and nonlinear characteristics and development of methods for the growth of large crystals are justified.

Fig. 3. A stereoview of the crystal packing in Lys.3HIO$_3$. Hydrogen bonds are shown by dashed lines and the intermediate I—O bond is shown as in Fig. 2.

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