



L-Arginine nitrates

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Abstract

In the L-Arg + HNO₃ + H₂O system, where Arg stands for arginine (⁺(H₂N)₂CNH(CH₂)₃CH(NH₂)COO⁻), crystals of 2(L-Arg·HNO₃)·H₂O (or formal L-Arg·HNO₃·0.5H₂O) (I) and L-Arg·2HNO₃ (II) compounds have been produced. The structures of both compounds were solved by X-ray crystallography. The asymmetric part of the triclinic unit cell (space group *P*1) of the (I) compound contains two monocharged arginine cations (Arg⁺), two nitrate ions and a water molecule interacting through hydrogen bonds. The monoclinic unit cell of the (II) compound (space group *P*2₁) is composed of two crystallographically independent nitrate ions and one doubly charged arginine cation hydrogen bonded to nitrate groups. The Arg⁺ cations are hydrogen bonded to each other, while the Arg²⁺ cations do not interact. In addition the crystal of compound (II) emits phase matched second harmonic generation signal of a Nd:YAG laser. © 2003 Elsevier B.V. All rights reserved.

Keywords: Semiorganic NLO crystals; L-arginine nitrate; L-arginine dinitrate; Crystal structure

1. Introduction

The discovery of promising nonlinear optical properties in L-arginine phosphate monohydrate (L-Arg·H₃PO₄·H₂O, LAP) [1] and in its deuterated analog [2,3] stimulated a strong interest in the crystals of this family. In order to widen the understanding of LAP properties and to discover crystals with better nonlinear, mechanical and thermal properties, investigations on LAP analogs are in progress. The widest search for such crystals with interesting results were performed by Monaco et al. [4], who investigated known crystalline salts of L-arginine (L-Arg·HCl, L-Arg·HCl·H₂O and L-Arg·HBr·H₂O) and as well prepared some new ones (L-Arg·HF, L-Arg·HClO₄, L-Arg·HBF₄, L-Arg·malate, L-Arg·2H₃AsO₄). In addition and independently from Suresh and Vijayan [5] L-Arg·CH₃COOH was synthesized and investigated. In Ref. [4] the compounds were prepared by evaporation at ambient temperature of aqueous solutions containing equimolar quantities of L-arginine and corresponding acids. Together with these

compounds obtained in crystalline form, they synthesized five other compounds in a form of noncrystalline fine powder (L-Arg-iodate, L-Arg-nitrate, L-Arg-formate, L-Arg-glutamate, L-Arg-aspartate). The authors did not clarify whether the glutamic and aspartic acids were in optically active form, or they exist as a racemate. In slightly different conditions (slow diffusion of different precipitants into aqueous solutions of arginine and acids), Vijayan with co-workers grew crystals of L-Arg-L-glutamate·H₂O [6], L-Arg-D-glutamate·3H₂O [7], L-Arg-D-glutamate·H₂O [8], L-Arg-L-aspartate [9] and L-Arg-D-aspartate [7]. From three other compounds obtained by Monaco et al. [4] as powders, crystals of L-Arg·2HIO₃ and L-Arg·2HNO₃ [10,11] were grown for iodate and nitrate salts of arginine. In the attempts to grow crystals of the same composition for formate from solutions of L-Arg + *n* HCOOH with *n* ≥ 2, crystals of L-Arg·HCOOH in space group *P*₂₁2₁2₁ were obtained [11]. Previously [12] another modification of L-Arg·HCOOH in space group *P*₂₁ from the aqueous solution of arginine and formic acid by slow diffusion of acetonitril was prepared. This raised hopes that from aqueous solutions of L-Arg + *n* HNO₃ with 1 < *n* < 2 crystals of nitrate of arginine could be grown and indeed they were justified. This paper describes crystal structures of two L-arginine nitrate compounds grown by us.

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2. Experimental

Crystals of nitrate and dinitrate salts of arginine were grown by evaporation of aqueous solutions. Phases were identified by IR spectra that were recorded by the method of suspension in nujol. Thermal properties were measured on a Paulik–Paulik–Erdey derivatograph and on a Boëtius type microscope equipped with a heated table. A Q-switched

Nd:YAG laser was used to detect existence of second harmonic generation signals. Room temperature X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer. Statistics on the data are given in Table 1. The structures were solved and refined employing program suites SHELXS-97 and SHELXL-97 [13,14]. The positions of all hydrogen atoms were determined from difference Fourier maps and were refined with isotropic thermal parameters.

Table 1
Crystal data and structure refinement for 2(L-Arg-HNO₃)·H₂O and L-Arg·2HNO₃

Chemical formula	C ₁₂ H ₃₂ N ₁₀ O ₁₁	C ₆ H ₁₆ N ₆ O ₈
Chemical formula weight	492.48	300.25
Cell setting	Triclinic	Monoclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁
<i>a</i> (Å)	5.142(1)	7.754(2)
<i>b</i> (Å)	10.439(2)	7.286(1)
<i>c</i> (Å)	10.557(2)	11.673(2)
α (°)	88.43(3)	90.
β (°)	79.57(3)	92.60(3)
γ (°)	81.28(3)	90.
Volume (Å ³), <i>Z</i>	550.9(2), 1	658.8(2), 2
Density (calculated)	1.485 mg/m ³	1.514 mg/m ³
Density (measured)	Not measured	1.514(3) mg/m ³
Radiation type	Mo K α	Mo K α
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	24	24
θ range (°)	14–16	14–16
μ (mm ⁻¹)	0.129	0.139
Temperature (K)	293	293
Crystal form	Needle	Platy
Crystal size	0.22 × 0.15 × 0.15	0.21 × 0.21 × 0.12
Crystal color	Colorless	Colorless
Data Collection		
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Data collection method	$\omega - 2\theta$ scans	$\omega - 2\theta$ scans
Absorption correction	None	None
No. of measured reflections	2960	1750
No. of independent reflections	2960	1575 ($R_{\text{int}} = 0.0155$)
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{max} (°)	27.96	24.97
Range of <i>h</i> , <i>k</i> , <i>l</i>	$0 \leq h \leq 6, -13 \leq k \leq 13, -13 \leq l \leq 13$	$-7 \leq h \leq 9, -8 \leq k \leq 8, -8 \leq l \leq 13$
No. of standard reflections	3	3
Frequency of standard reflections	Every 60 min	Every 60 min
Intensity decay (%)	None	None
Refinement		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2960/3/395	1575/1/230
<i>S</i>	1.054	1.104
R [$F^2 > 2\sigma(F^2)$]	0.0338	0.0308
wR [$F^2 > 2\sigma(F^2)$]	0.0715	0.0844
R [F_{all}^2]	0.0619	0.0329
wR (F_{all}^2)	0.0789	0.0864
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.186	0.168
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.158	-0.159
Absolute structure parameter	-0.3(11)	-0.4(13)
Extinction method	SHELXL97	SHELXL97
Extinction coefficient	0.044(5)	0.008(6)
Computer programs, data collection, cell refinement and data reduction	CAD-4 Software (Enraf-Nonius, 1988) SHELXL97	

3. Results and discussion

From the aqueous solution containing equimolar quantities of L-arginine and nitric acid only an apparently noncrystalline powder could be obtained. Needle like crystals were grown from aqueous solution containing L-arginine and HNO₃ in 1:1.25 ratio. It is important to mention that the IR absorption spectra of these crystals and the powder were identical. Thermal analysis showed that above 90 °C, a sample mass loss of about 2.5% takes place accompanied by an endothermic effect. Further heating results in decomposition of the sample above 200 °C. From this, an assumption could be made that the sample was a hydrocrystal. The mass loss of 2.5% corresponds to $n = 0.4$ water molecules. But comparison of IR spectra of initial and heated at 130 °C samples (see Fig. 1) did not show any absorption band above 3000 cm⁻¹ that disappears during heating. Thus IR spectra and thermal analysis did not allow us to identify with confidence the existence and quantity of crystallization water molecules. Nevertheless the crystal structure determination revealed that nitrate of L-arginine is a hydrocrystal of 2(L-Arg·HNO₃)·H₂O (or formally L-Arg·HNO₃·0.5H₂O) composition.

Growth conditions and preliminary data on L-Arg·2HNO₃ were represented in Ref. [11]. In Table 1, the crystallographic data and details of structure determination and refinement for 2(L-Arg·HNO₃)·H₂O (I) and L-Arg·2HNO₃ (II) are represented. Further tables with even numbers correspond to structure (I), while those with odd numbers correspond to structure (II). Coordinates of atoms are represented in Tables 2 and 3. In Fig. 2 asymmetric unit cells and numbering of atoms for both structures are illustrated. Bond lengths and angles are collected in Tables 4 and 5, while Tables 6 and 7 represent hydrogen bond parameters. In the selection of intermolecular hydrogen bonds we followed the recommendations of Zefirov [15]

declaring that for N–H···O and O–H···O type bonds the H···O distances of strongest van der Waals and weakest hydrogen bonds lie in the range 2.45–2.15 Å.

The unit cell of (I) contains one formula unit composed of two ions of NO₃⁻, two cations of L-Arg⁺ and one crystallization water molecule. The bond lengths for C–O are typical for negatively charged carboxylate groups. The guanidyl and α-amino groups are protonated, as is usual for L-Arg⁺. The bond lengths in cations are typical as well, except for C(6B)–N(3B), which is shorter than the expected value of 1.32 Å. A characteristic feature of L-arginine cations is their interaction with each other through hydrogen bonds, as they contain a negatively charged carboxylate group and positively charged protonated guanidyl and α-amino groups. The hydrogen bonds between α-amino groups and oxygen atoms of corresponding carboxylate groups N(1A)–H(1A)···O(1A) and N(1B)–H(1B)···O(1B) are strong, while weaker ones connect guanidyl groups N(3A) and N(3B) with atoms O(2A) and O(2B), respectively. A water molecule acting as an acceptor, binds to both cations by hydrogen bonds (N(1A)–H(3A)···O(1W) and N(4B)–H(14B)···O(1W)) and as a donor to two symmetrically equivalent cations of second type through O(1W)–H(2W)···O(1B) and O(1W)–H(1W)···O(2B). In addition the O(2A) oxygen atom of the first cation is hydrogen bonded to α-amino group of the second cation. The rest of hydrogen bonds (quite weak) connect cations with NO₃⁻ ions. Two of these hydrogen bonds (N(4A)–H(15A)···O(3B) and N(3B)–H(12B)···O(3A)) have H···O distances almost at the edge of above mentioned range and their angles significantly differ from 180°. Corresponding N–O bonds were expected to be shorter but that is true only for the N(5A)–O(3A) bond. The data on hydrogen bonds allows estimation of the range of the frequencies for stretching vibrations $\nu(\text{O–H})$ and $\nu(\text{N–H})$. Vibration frequencies for water molecules $\nu(\text{O–H})$ in

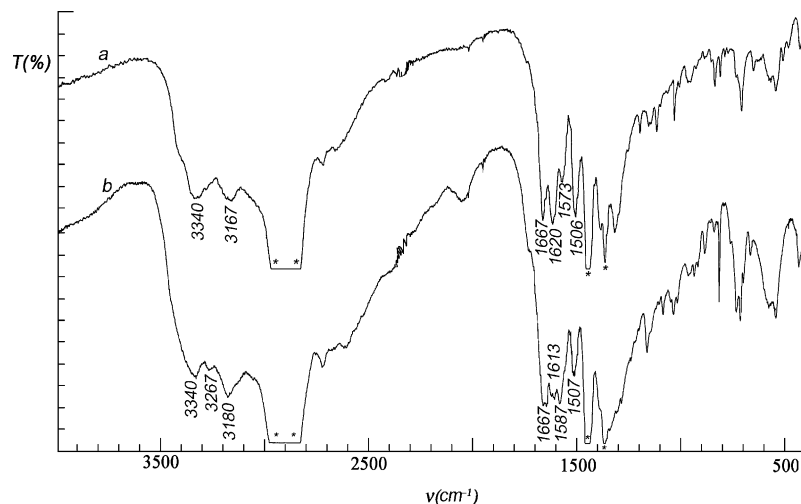


Fig. 1. The IR spectra of 2(L-Arg·HNO₃)·H₂O: (a) at room temperature and (b) at 130 °C. The absorption bands of nujol are marked with asterisks.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2(L-Arg-HNO₃)·H₂O

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
O1W	9107(6)	322(2)	764(2)	50(1)
O1A	2877(4)	6659(2)	−1115(2)	39(1)
O2A	7311(4)	6150(2)	−1684(2)	37(1)
O3A	6487(7)	3560(4)	1834(3)	106(1)
O4A	9304(5)	4752(2)	2131(2)	53(1)
O5A	6701(6)	4046(3)	3742(2)	73(1)
N1A	8145(5)	8488(2)	−947(2)	33(1)
N2A	1200(5)	6367(2)	3854(2)	39(1)
N3A	−1297(6)	5529(3)	5609(3)	51(1)
N4A	1640(7)	6895(3)	5894(3)	50(1)
N5A	7489(6)	4112(2)	2569(3)	50(1)
C1A	5221(5)	6848(2)	−1131(2)	28(1)
C2A	5615(5)	8003(2)	−356(2)	29(1)
C3A	5747(6)	7653(3)	1052(2)	35(1)
C4A	3308(6)	7135(3)	1777(3)	39(1)
C5A	3324(6)	7064(3)	3210(3)	37(1)
C6A	513(6)	6278(3)	5120(2)	37(1)
O1B	7046(4)	2135(2)	9160(2)	50(1)
O2B	3087(4)	1757(2)	10,194(2)	47(1)
O3B	4042(6)	8882(3)	7066(3)	80(1)
O4B	5881(6)	8928(3)	5073(2)	73(1)
O5B	7670(5)	9681(2)	6532(2)	60(1)
N1B	467(5)	3981(3)	9399(2)	38(1)
N2B	1240(5)	1404(2)	5049(2)	42(1)
N3B	2621(6)	1873(3)	2934(3)	55(1)
N4B	−261(7)	405(3)	3476(3)	57(1)
N5B	5861(6)	9156(2)	6216(2)	50(1)
C1B	4570(6)	2391(3)	9446(2)	34(1)
C2B	3351(5)	3609(3)	8817(2)	31(1)
C3B	3668(6)	3451(3)	7357(2)	35(1)
C4B	2263(6)	2400(3)	6942(2)	37(1)
C5B	2844(6)	2275(3)	5491(2)	38(1)
C6B	1214(6)	1234(3)	3817(3)	40(1)
H1W	1021(8)	65(4)	49(4)	60
H2W	784(8)	92(4)	56(4)	60
H1A	951(7)	779(3)	−104(3)	50
H2A	807(7)	891(3)	−173(3)	50
H3A	846(7)	914(3)	−42(3)	50
H4A	424(7)	866(3)	−42(3)	50
H5A	601(7)	842(3)	146(3)	50
H6A	724(7)	698(3)	109(3)	50
H7A	329(7)	636(4)	150(3)	50
H8A	165(7)	769(3)	165(3)	50
H9A	308(7)	791(3)	357(3)	50
H10A	508(7)	665(3)	337(3)	50
H11A	61(7)	584(3)	338(3)	50
H12A	−192(7)	518(4)	510(4)	50
H13A	−192(7)	565(3)	641(3)	50
H14A	114(7)	680(3)	662(4)	50
H15A	250(7)	753(3)	566(3)	50
H1B	−53(7)	334(3)	929(3)	50
H2B	20(7)	422(3)	1026(3)	50
H3B	−19(7)	473(3)	904(3)	50
H4B	432(7)	433(3)	898(3)	50
H5B	300(7)	430(3)	699(3)	50
H6B	556(7)	327(3)	705(3)	50
H7B	35(7)	261(3)	726(3)	50
H8B	287(7)	155(3)	732(3)	50
H9B	251(7)	309(3)	507(3)	50
H10B	482(7)	196(3)	515(3)	50
H11B	34(7)	89(3)	561(3)	50

Table 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
H12B	354(8)	231(4)	313(3)	50
H13B	261(7)	179(3)	219(4)	50
H14B	−32(7)	39(3)	269(4)	50
H15B	−129(8)	3(3)	401(3)	50

U(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

accordance with the correlation between the O···O distance and $\nu(\text{O-H})$ [16,17] belong to region 3200 cm^{−1}, while the frequencies for $\nu(\text{N-H})$, because of a large dispersion in hydrogen bond lengths, occupy a wide range of frequencies (3050–3500 cm^{−1}), overlapping with the $\nu(\text{O-H})$ frequency range of the water molecule. It is possible that

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for L-Arg-2HNO₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
O1	5855(2)	4987(3)	3651(1)	58(1)
O2	8650(2)	4204(3)	3817(2)	52(1)
O3	8517(2)	621(2)	8011(1)	43(1)
O4	11,201(2)	−67(3)	8405(1)	50(1)
O5	9728(2)	1330(4)	9645(2)	66(1)
O6	3167(3)	5650(3)	6724(2)	65(1)
O7	1472(4)	3661(4)	7433(2)	90(1)
O8	1545(2)	3983(3)	5608(2)	54(1)
N1	8281(3)	2270(3)	5704(2)	40(1)
N2	6601(2)	6230(3)	9401(2)	42(1)
N3	5010(3)	6074(4)	11,002(2)	50(1)
N4	3639(3)	6304(4)	9237(2)	50(1)
N5	9805(2)	636(3)	8694(2)	38(1)
N6	2064(3)	4421(3)	6605(2)	45(1)
C1	7072(3)	4351(4)	4195(2)	44(1)
C2	6968(3)	3707(3)	5415(2)	39(1)
C3	7203(3)	5338(3)	6230(2)	40(1)
C4	6981(4)	4857(3)	7483(2)	39(1)
C5	6885(4)	6573(4)	8204(2)	42(1)
C6	5092(3)	6189(3)	9879(2)	36(1)
H1	880(4)	448(5)	309(3)	55
H2	817(4)	129(5)	526(3)	55
H3	597(5)	284(5)	560(3)	55
H4	830(4)	186(4)	643(3)	55
H5	587(4)	321(5)	553(3)	55
H6	834(5)	585(5)	613(3)	55
H7	639(4)	623(5)	600(2)	55
H8	789(4)	413(5)	782(3)	55
H9	597(4)	420(5)	756(2)	55
H10	794(4)	718(5)	816(3)	55
H11	605(4)	734(5)	792(3)	55
H12	741(4)	605(5)	988(3)	55
H13	581(4)	612(5)	1142(3)	55
H14	410(5)	596(5)	1129(3)	55
H15	276(5)	622(5)	956(3)	55
H16	359(4)	631(5)	849(3)	55

U(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

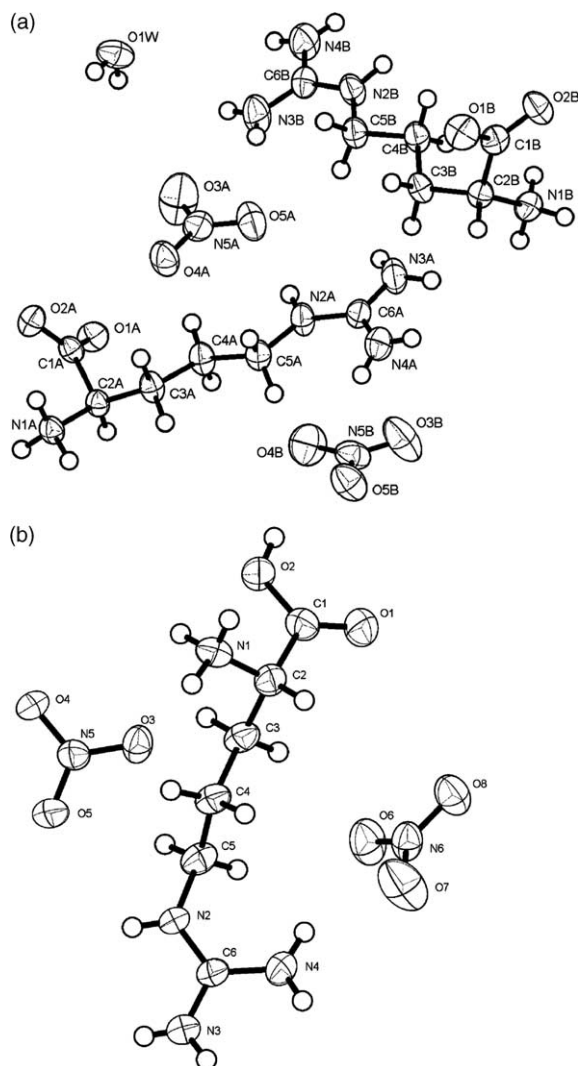


Fig. 2. Asymmetric unit cells of (a) 2(L-Arg-HNO₃)·H₂O and (b) L-Arg·2HNO₃.

the difficulty in the determination of $\nu(\text{O}-\text{H})$ for water from IR spectra of L-Arg-HNO₃·0.5H₂O and L-Arg-HNO₃ (see Fig. 1) was caused by this phenomenon. The packing of molecules in the structure of 2(L-Arg-HNO₃)·H₂O is shown in Fig. 3a.

In the second structure, L-Arg·2HNO₃, the asymmetric unit cell contains doubly charged cation of arginine (L-Arg²⁺) and two NO₃⁻ ions. The difference between cations L-Arg²⁺ and L-Arg⁺ is that, in the case of L-Arg²⁺, as a result of additional protonation of carboxylate group, there is an uncharged carboxylic group. α -Amino and guanidyl groups similar to the case of L-Arg⁺, are protonated. The existence of a doubly charged cation L-Arg²⁺ was first discovered by Seely [18] in L-Arg·2HI. The presence of neutral carboxylic group results in significant differences between hydrogen bonding in salts of L-Arg⁺ and L-Arg²⁺, particularly (I) and (II). One of the NO₃⁻ ions is bonded to cation of L-Arg²⁺

Table 4

Bond lengths (Å) and angles (°) for 2(L-Arg-HNO₃)·H₂O

O1A–C1A	1.248(3)	C6A–N2A–C5A	124.0(3)
O2A–C1A	1.259(3)	O3A–N5A–O5A	120.1(3)
O3A–N5A	1.208(4)	O3A–N5A–O4A	119.3(3)
O4A–N5A	1.243(3)	O5A–N5A–O4A	120.6(3)
O5A–N5A	1.235(4)	O1A–C1A–O2A	126.2(2)
N1A–C2A	1.492(3)	O1A–C1A–C2A	117.2(2)
N2A–C6A	1.324(3)	O2A–C1A–C2A	116.5(2)
N2A–C5A	1.458(4)	N1A–C2A–C3A	108.4(2)
N3A–C6A	1.330(4)	N1A–C2A–C1A	109.8(2)
N4A–C6A	1.316(4)	C3A–C2A–C1A	112.4(2)
C1A–C2A	1.533(3)	C4A–C3A–C2A	114.4(2)
C2A–C3A	1.532(3)	C3A–C4A–C5A	111.4(2)
C3A–C4A	1.512(4)	N2A–C5A–C4A	110.0(2)
C4A–C5A	1.515(4)	N4A–C6A–N2A	120.9(3)
O1B–C1B	1.243(3)	N4A–C6A–N3A	119.9(3)
O2B–C1B	1.245(3)	N2A–C6A–N3A	119.2(3)
O3B–N5B	1.235(4)	C6B–N2B–C5B	122.6(2)
O4B–N5B	1.235(3)	O3B–N5B–O4B	120.9(3)
O5B–N5B	1.246(3)	O3B–N5B–O5B	118.7(3)
N1B–C2B	1.496(4)	O4B–N5B–O5B	120.4(3)
N2B–C6B	1.320(3)	O1B–C1B–O2B	125.8(3)
N2B–C5B	1.454(4)	O1B–C1B–C2B	114.7(2)
N3B–C6B	1.306(4)	O2B–C1B–C2B	119.4(3)
N4B–C6B	1.330(4)	N1B–C2B–C1B	111.0(2)
C1B–C2B	1.521(4)	N1B–C2B–C3B	110.2(2)
C2B–C3B	1.531(3)	C1B–C2B–C3B	111.8(2)
C3B–C4B	1.517(4)	C4B–C3B–C2B	114.6(2)
C4B–C5B	1.512(4)	C5B–C4B–C3B	110.1(2)
		N2B–C5B–C4B	111.5(2)
		N3B–C6B–N2B	120.6(3)
		N3B–C6B–N4B	119.9(3)
		N2B–C6B–N4B	119.6(3)

through hydrogen bond O(2)–H(1)···O(4). The second ion NO₃⁻ is connected to α -amino group through hydrogen bonds N(1)–H(3)···O(8) and N(1)–H(2)···O(8). The hydrogen bonds established by

Table 5

Bond lengths (Å) and angles (°) for L-Arg·2HNO₃

O1–C1	1.205(3)	C1–O2–H1	117.8(2)
O2–C1	1.324(3)	C6–N2–C5	126.1(2)
O3–N5	1.250(2)	O5–N5–O3	120.8(2)
O4–N5	1.257(3)	O5–N5–O4	119.3(2)
O5–N5	1.224(3)	O3–N5–O4	119.9(2)
O6–N6	1.242(3)	O7–N6–O6	121.3(2)
O7–N6	1.222(3)	O7–N6–O8	120.1(2)
O8–N6	1.255(3)	O6–N6–O8	118.5(2)
N1–C2	1.488(3)	O1–C1–O2	124.7(2)
N2–C6	1.320(4)	O1–C1–C2	122.9(2)
N2–C5	1.446(4)	O2–C1–C2	112.3(2)
N3–C6	1.318(4)	N1–C2–C1	111.6(2)
N4–C6	1.327(3)	N1–C2–C3	110.2(2)
C1–C2	1.505(4)	C1–C2–C3	109.7(2)
C2–C3	1.527(3)	C5–C4–C3	110.8(2)
C3–C4	1.522(4)	N2–C5–C4	114.1(2)
C4–C5	1.511(3)	N3–C6–N2	120.4(2)
		N3–C6–N4	119.2(3)
		N2–C6–N4	120.4(2)

Table 6
The geometric parameters of H-bonds in 2(L-Arg-HNO₃)·H₂O

D-H···A	Symmetry code of A	D···A (Å)	D-H (Å)	H···A (Å)	D-H-A (°)
O1W-H1W···O2B	$x + 1, y, z - 1$	2.688	0.72	1.99	165.5
O1W-H2W···O1B	$x, y, z - 1$	2.727	0.88	1.98	141.4
N1A-H1A···O1A	$x + 1, y, z$	2.837	0.93	1.93	165.2
N1A-H2A···O5B	$x, y, z - 1$	2.941	0.93	2.02	174.0
N1A-H3A···O1W	$x, y + 1, z$	2.824	0.94	1.88	174.0
N2A-H11A···O4A	$x - 1, y, z$	2.900	0.87	2.03	174.4
N3A-H12A···O5A	$x - 1, y, z$	2.954	0.80	2.16	173.6
N3A-H13A···O2A	$x - 1, y, z + 1$	2.884	0.86	2.04	167.2
N4A-H15A···O3B	x, y, z	2.972	0.86	2.39	125.4
N4A-H15A···O4B	x, y, z	3.260	0.86	2.42	165.4
N1B-H1B···O1B	$x - 1, y, z$	2.844	0.92	1.93	173.7
N1B-H3B···O2A	$x - 1, y, z + 1$	2.913	0.91	2.03	162.1
N2B-H11B···O5B	$x - 1, y - 1, z$	2.978	0.90	2.10	164.8
N3B-H12B···O3A	x, y, z	2.918	0.76	2.37	129.8
N3B-H13B···O2B	$x, y, z - 1$	2.864	0.79	2.08	170.5
N4B-H14B···O1W	$x - 1, y, z$	2.945	0.83	2.12	174.2
N4B-H15B···O4B	$x - 1, y - 1, z$	2.954	0.84	2.13	169.2

the guanidyl group are significantly weaker. The bond lengths for some of them are close to the upper edge of the range and N(3)–H(13) do not form any hydrogen bond. Among the bonds in the nitrate ions, the shortest is the bond N(5)–O(5) because of the weakness of hydrogen bonds established by the O(5) atom, as well as the bond N(6)–O(7). Here oxygen O(7) does not have hydrogen bonds. The strongest hydrogen bonds O(2)–H(1)···O(4) and N(1)–H(3)···O(8) slightly elongate the corresponding bonds N(5)–O(4) and N(6)–O(8). The important difference between structures (I) and (II) is that L-Arg⁺ cations interact with each other via hydrogen bonds while L-Arg²⁺ do not. This peculiarity, which apparently is general for salts of L-Arg²⁺ with oxygen containing anions, was mentioned in Ref. [19] for L-Arg·2H₃PO₄ and for isotypical L-Arg·2H₃AsO₄. On the basis of the data on hydrogen bonds in L-Arg·2HNO₃, correspondence between high frequency absorption bands in the IR spectrum of L-Arg·2HNO₃ [11] and its groups could be

refined. For example, the absorption band $\nu(\text{O-H})$ proceeding from correlation between the $\nu(\text{O-H})$ and O···O distance is in the 3000 cm⁻¹ region, while absorption bands of $\nu(\text{N-H})$ occupy the 3100–3500 cm⁻¹ range. The highest frequency bands must be related to vibrations of the N(3)H₂ group, in which bond N(3)–H(13) is free and does not form hydrogen bonds. Fig. 3b displays the crystal packing for L-Arg·2HNO₃ showing only strongest hydrogen bonds. Heating of L-Arg·2HNO₃ causes melting of the sample around 130 °C (DTA peak at 135 °C) and its decomposition with exothermal effect at temperatures above 160 °C. Our first crystals of L-Arg·2HNO₃ had the shape of thin plates. Later we grew optical quality crystals of 33 × 10 × 5 mm³ size, in which phase matched second harmonic generation of Nd:YAG laser was obtained.

After publication of our preliminary data [11] on the L-Arg·2HNO₃ crystal structure, Ramaswamy et al. [20] also determined the structure of L-Arg·2HNO₃,

Table 7
The geometric parameters of H-bonds in L-Arg·2HNO₃

D-H···A	Symmetry code of A	D···A (Å)	D-H (Å)	H···A (Å)	D-H-A (°)
O2-H1···O4	$-x + 2, y + 1/2, -z + 1$	2.655	0.88	1.78	171.9
N1-H2···O8	$-x + 1, y - 1/2, -z + 1$	2.850	0.89	1.98	166.9
N1-H3···O8	$x + 1, y, z$	2.829	0.96	1.88	172.5
N1-H4···O3	x, y, z	2.946	0.90	2.05	171.9
N2-H12···O5	$-x + 2, y + 1/2, -z + 2$	3.010	0.83	2.27	148.5
N2-H12···O4	$-x + 2, y + 1/2, -z + 2$	3.157	0.83	2.38	156.6
N3-H14···O3	$-x + 1, y + 1/2, -z + 2$	3.034	0.80	2.24	176.9
N4-H15···O5	$-x + 1, y + 1/2, -z + 2$	2.972	0.80	2.18	172.8
N4-H16···O6	x, y, z	2.978	0.87	2.13	165.2

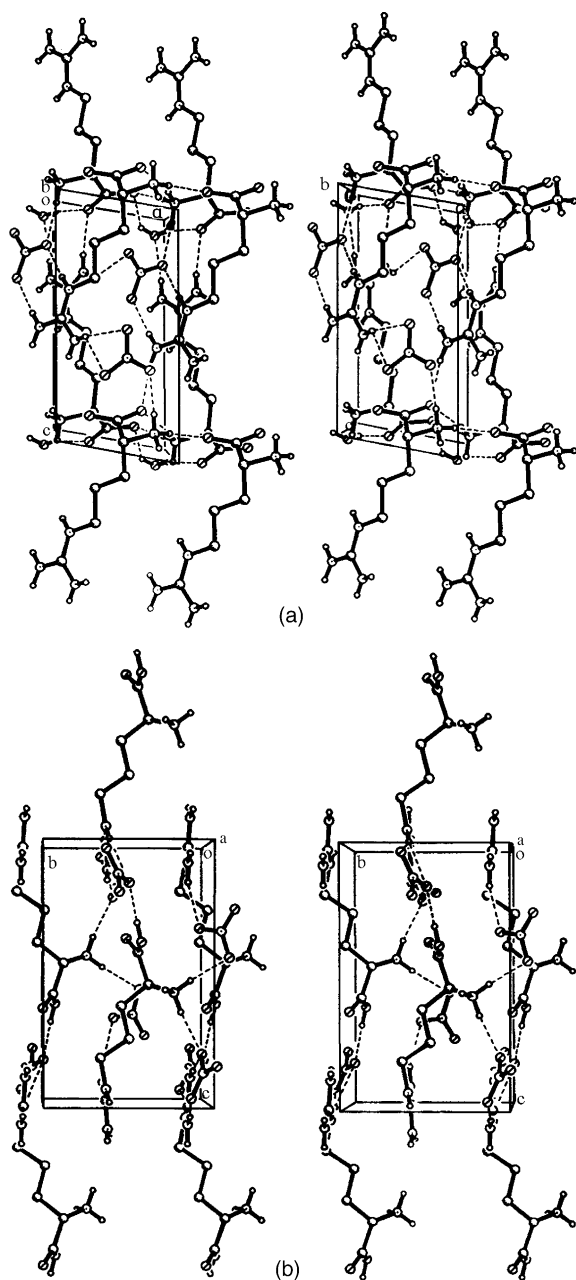


Fig. 3. A stereoview of the crystal packing in (a) $2(\text{L-Arg-HNO}_3)\cdot\text{H}_2\text{O}$ and (b) $\text{L-Arg}\cdot 2\text{HNO}_3$. Hydrogen bonds are shown by dashed lines. In structure of $\text{L-Arg}\cdot 2\text{HNO}_3$ only strongest hydrogen bonds are shown.

In spite of difference in R -factors (0.031 and 0.070, respectively) (with the exception of one C–N bond length in guanidyl group) results are in good accordance.

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