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Synthesis and crystal structure of the pyridinium acid nitrate $[(PyH)_2(NO_3)][H_2(NO_3)_3]$ containing a dihydrogen trinitrate anion

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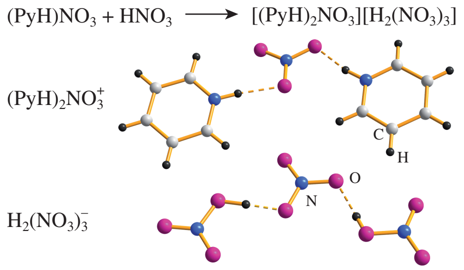
A new protic room-temperature ionic liquid (T_c = 14 ± 1 °C) – pyridinium hydrogen dinitrate – was obtained from a solution of pyridinium nitrate in anhydrous nitric acid in a desiccator with P_2O_5. According to single crystal X-ray diffraction data, the solid state structure of $[(PyH)_2(NO_3)][H_2(NO_3)_3]$ consists of hydrogen bonded cations $[(PyH)_2(NO_3)]^+$ and anions $[(NO_3)(HNO_3)_2]^-$ with a previously unknown configuration containing two HNO_3 molecules linked *via* hydrogen bonds to the central NO_3^- anion by the *sin–anti* type.



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The molecules of monobasic acids and the parent anions can form dimers, trimers, and larger associates *via* hydrogen bonds, for example, $[H_{n-1}F_n]^-$ (n = 1–7)[1,2] in the case of hydrofluoric acid. Nitric acid demonstrates interesting examples of such anions. The salts $M[H(NO_3)_2]$, where M can be an inorganic (K, Rb, Cs, NH_4, or Tl),[3–5] organic (Ph_4As[6] or nitrogen-containing aromatic heterocyclic cations),[7–9] or complex cation, as in *trans*-$[XPy_4Cl_2]$ (X = Ru,[8] Rh[10]), are known. The $[H(NO_3)_2]^-$ anion consists of two nitrate groups linked by a very strong hydrogen bond O–H–O with short O···O distances of 2.44–2.46 Å.[11] The planes of nitrate groups can be fixed at different angles to one another from 0° (Ph_4As[6] and 9-cyano-10-methylacridinium[9]) to nearly 90° (Cs[5] and *trans*-$[RhPy_4Cl_2]$[10]) [Figures 1(*a*),(*b*)]. As far as we know, only one compound with the dihydrotrinitrate anion $[H_2(NO_3)_3]^-$, *viz.* $NH_4[H_2(NO_3)_3]$, has been studied structurally.[3,4,12] The IR and Raman spectra of the salts $M[H_2(NO_3)_3]$ (M = K, Rb, Cs, Tl)[3,4] made it possible to conclude that the geometry of the $[H_2(NO_3)_3]^-$ anion in these salts is close to that in ammonium salt [Figure 1(*c*)].

Here, we report the synthesis and crystal structure of a new salt **1** with the $[(PyH)_2NO_3]^+[H_2(NO_3)_3]^-$ crystallographic formula. The precursors (pyridinium nitrate and anhydrous nitric acid) were synthesized according to published procedures.[13,14] Compound **1** was obtained as a hydroscopic viscous liquid by the slow evaporation of a pyridinium nitrate (2.27 g) solution in anhydrous nitric acid (1.51 g, 1.00 ml) at a molar ratio of 1 : 1.5 in a vacuum desiccator with P_2O_5. After 10 days, the weight of the reaction mixture corresponded to the formula $(C_5H_5N)\cdot(HNO_3)_2$ to indicate the end of the removal of excess nitric acid. Compound **1** melts at 14 ± 1 °C; thus, it can be considered as a protic ionic liquid,[15] which can probably be used as a catalyst in the nitration of aromatic compounds.[16]

The interaction of pyridinium nitrate with an excess of nitric acid in a vacuum desiccator was the first step of the synthesis of pyridinium nitratometalates $(PyH)_n[M(NO_3)_m(H_2O)_l]$ (M is a *d*-element). The interaction of HNO_3 vapor with P_2O_5 resulted in not only the removal of HNO_3 but also the formation of volatile N_2O_5, which is a strong dehydrating agent. As a result of this process, compound **1** was formed. Along with dehydration, other processes can occur under these conditions with the formation of nitronium and nitrosonium salts,[17,18] but they were not observed in this system.

According to the X-ray diffraction data, the four pyridinium cations ($C_5H_5NH^+$ or PyH^+) and eight nitrate groups in **1**[†] are crystallographically independent and form two $[(PyH)_2NO_3]^+$ cations and two $[H_2(NO_3)_3]^-$ anions. The nitrate anion NO_3^- in $[H_2(NO_3)_3]^-$ connects two nitric acid molecules through *sin–anti* type O–H···O hydrogen bonds with the formation of the planar trimer $[(NO_3)(HNO_3)_2]^-$ [Figure 1(*d*)].

The distances between O atoms connected by a hydrogen bond in these anions range from 2.525(2) to 2.580(2) Å, which correspond to medium-strength hydrogen bonds.[19] In contrast, dimeric $[H(NO_3)_2]^-$ anions, in which the H atom is located in the

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[†] *Crystal data for* **1**. $C_5H_7N_3O_6$, M_r = 205.14, triclinic, $P\bar{1}$, a = 3.5956(2), b = 21.8431(12) and c = 21.8991(12) Å, α = 92.822(4), β = 91.750(5) and γ = 92.377(4)°, V = 1715.46(16) Å^3, Z = 8, μ = 0.147 mm^{-1}. X-ray diffraction data were collected at 100 K using an image plate diffractometer IPDS (Stoe) with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The melt of compound **1** was placed in a thin-walled glass capillary. The crystals of **1** were grown by slowly cooling (1 K min^{-1}) the capillary below the crystallization point (14 ± 1 °C). A single crystal could not be grown even after multiple cycles of cooling/heating. Instead, an intergrowth of two larger crystals was obtained. The set of low-temperature diffraction data could be divided into two subsets, which were integrated separately and gave similar final structure solutions. The crystal structure was solved with SHELXD and refined anisotropically for all non-hydrogen atoms with SHELXL. The positions of hydrogen atoms at donor O and N atoms were determined and refined isotropically, whereas H atoms at the pyridinium carbon atoms were placed in geometrically calculated positions and refined in a riding mode. A refinement with 9131 reflections and 538 parameters converged to wR_2 = 0.150 and R_1 = 0.061 for 6024 reflections with $I > 2\sigma(I)$.

CCDC 2056974 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

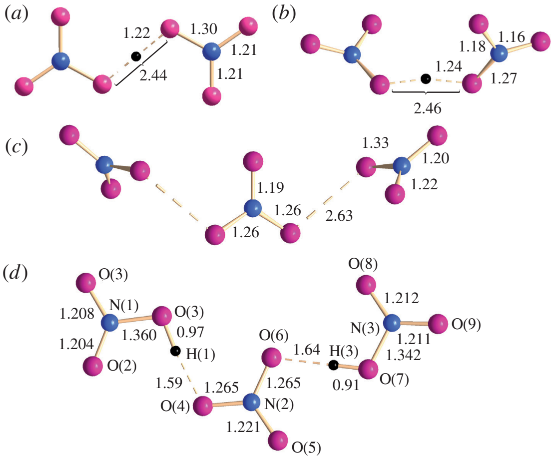

Figure 1 Acidic nitrate anions: (*a*) centrosymmetric $H(NO_3)_2^-$ anion in the structure of $[C_{15}H_{11}N_2]H(NO_3)_2$[9] (CSD-AFUZAC); (*b*) $H(NO_3)_2^-$ anion in the structure of $[RhPy_4Cl_2]H(NO_3)_2$,[10] (CSD-TPYRRH01), twofold symmetry axis exists, the dihedral angle between the planes of the two NO_3 groups is 96(3)°; (*c*) $[H_2(NO_3)_3]^-$ anion in the structure of $NH_4[H_2(NO_3)_3]$[12] (ICSD-30637), H atom is not determined, twofold symmetry axis exists; and (*d*) $[H_2(NO_3)_3]^-$ anion in the structure of **1**. Distances are given in Å.

middle of the O···O distance[5,9,10] or is slightly displaced to one of the O atoms,[7,11] are characterized by very strong O–H–O hydrogen bonds with an O···O distance of 2.43–2.47 Å [see Figures 1(*a*),(*b*)]. A decrease in the H-bond strength on going from the dimer to the trimer was noted earlier,[20] and it correlates with a shift of the H atom to one of the O atoms.[19]

Similarly to **1**, the previously known anion $[(NO_3)(HNO_3)_2]^-$, present in $NH_4[H_2(NO_3)_3]$ (**2**), consists of two HNO_3 molecules forming medium-strength O–H···O hydrogen bonds with the central NO_3^- anion [Figure 1(*c*)].[12] The difference is that the *anti–anti*-type bonding of the central nitrate group is observed in the trimer anion $[(NO_3)(HNO_3)_2]^-$ in **2** in contrast to **1**.[12] The two-fold axis passes through this NO_3^- group and the angle between the planes of the terminal nitrate groups is 83°, while the trimeric anion $[(NO_3)(HNO_3)_2]^-$ in **1** is nearly flat [see Figure 1(*d*)]. Moreover, the hydrogen bonds in **2** are noticeably weaker: for example, the average distances between hydrogen bonded O atoms in **1** and **2** are 2.55 and 2.63 Å, respectively.

The distortion of the terminal HNO_3 units that make up trimers is typical of HNO_3 molecules [Table 1, Figure 1(*d*)]: the N–O distance with the O atom acting as an H donor is 1.34–1.36 Å and significantly exceeds the other distances (1.20–1.22 Å). A similar distortion was detected in the previously investigated $[(NO_3)(HNO_3)_2]^-$ trimer in **2** [see Figure 1(*c*)].[12] Moreover, a similar distortion was observed in HNO_3 molecules forming infinite chains $(\cdots O–NO–OH\cdots)_n$ in the crystal structure of nitric acid.[21] The longest N–O distance (1.32–1.36 Å) corresponds to the O atom acting as an H donor, the shortest one (1.19–1.20 Å), to the terminal atom, and the intermediate one (1.22–1.25 Å), to the O atom that acts as an H acceptor in the hydrogen bond. The geometry of the central nitrate anion in both trimers also reveals a similar pattern: two O atoms accepting H bonds are farther from the nitrogen atom than the terminal O atom (Tables 1, 2), which is typical of bidentate coordinated nitrate groups.

Note that the average N–O distance to the O donor atom (1.36 Å) is significantly shorter than the corresponding distance in an isolated nitric acid molecule (1.41 Å)[20] but noticeably longer than the N–O bond in monodentate coordinated nitrate groups in the nitratometalates. For example, one of the longest N–O bonds (1.31 Å) with the participation of the coordinated O atom is observed in the $[Au(NO_3)_4]^-$ anions.[22]

Table 1 Bond lengths in anions $[(HNO_3)_2(N(2)O_3)]^-$ and $[(HNO_3)_2(N(5)O_3)]^-$.

$[(HNO_3)_2(\mathbf{N(2)}O_3)]^-$			$[(HNO_3)_2(\mathbf{N(5)}O_3)]^-$		
	Bond	Length/Å		Bond	Length/Å
HNO_3	N(1)–O(1)	1.359(2)	HNO_3	N(4)–O(10)	1.345(2)
	N(1)–O(2)	1.205(2)		N(4)–O(11)	1.216(2)
	N(1)–O(3)	1.209(2)		N(4)–O(12)	1.201(2)
NO_3^-	N(2)–O(4)	1.265(2)	NO_3^-	N(5)–O(13)	1.282(2)
	N(2)–O(5)	1.220(2)		N(5)–O(14)	1.261(2)
	N(2)–O(6)	1.265(2)		N(5)–O(15)	1.217(2)
HNO_3	N(3)–O(7)	1.343(2)	HNO_3	N(6)–O(16)	1.354(2)
	N(3)–O(8)	1.212(2)		N(6)–O(17)	1.212(2)
	N(3)–O(9)	1.211(2)		N(6)–O(18)	1.207(2)

Table 2 Geometry of hydrogen bond in **1**.

D–H···A	D–H/Å	H···A/Å	D···A/Å	∠D–H–A/°
O(1)–H(1)···O(4)	0.97(4)	1.59(3)	2.553(2)	175(3)
O(7)–H(3)···O(6)	0.91(4)	1.63(4)	2.540(2)	178(4)
O(10)–H(4)···O(13)	1.06(3)	1.47(3)	2.525(2)	174(3)
O(16)–H(6)···O(14)	0.84(3)	1.74(3)	2.580(2)	178(4)
N(9)–H(9)···O(22)	0.99(3)	1.86(3)	2.836(3)	169(3)
N(10)–H(10)···O(24)	0.91(3)	1.81(3)	2.712(2)	170(3)
N(11)–H(11)···O(20)	0.93(3)	1.83(3)	2.756(2)	174(3)
N(12)–H(12)···O(21)	0.96(3)	1.79(3)	2.729(2)	168(3)

The cations $[(PyH)_2NO_3]^+$ consist of two pyridinium cations, which are pairwise linked to the NO_3^- anion by N–H···O hydrogen bonds. Both cations are almost planar and differ in that the $N(7)O_3^-$ and $N(8)O_3^-$ anions are bound to the PyH^+ cations by the *sin–anti* and *anti–anti* types, respectively (Figure 2).

The participation of two O atoms of the nitrate group in the formation of hydrogen bonds with the pyridinium nitrogen atom leads to an elongation of the corresponding N–O distances, which is typical of the bidentate coordinated NO_3 group (see Table 1).[22] The N–H···O hydrogen bonds in two $[(PyH)_2NO_3]^+$ cations are of medium strength (see Table 2),[19] and they are only slightly weaker than the H-bonds N–H···O in the structure of $(PyH)NO_3$.[13]

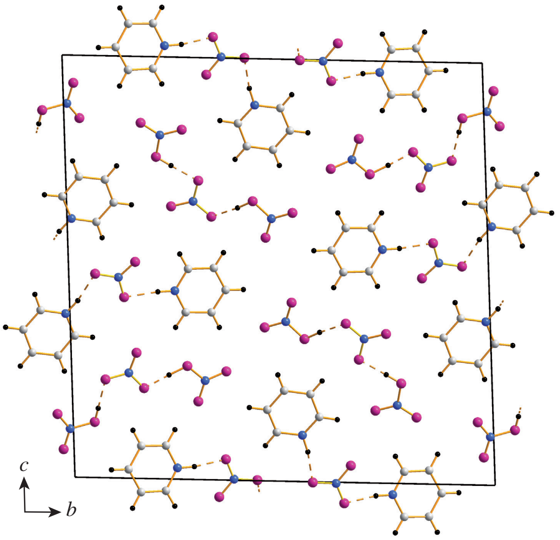

Figure 2 Projection of a unit cell along the *a* axis.

The cations and anions are stacked into columns along the *a* axis (Figure 2). The packing of pyridinium cations in parallel layers is due to the interaction of the π systems of aromatic rings (stacking effect). Interplane stacking distances of four pyridinium rings are in a range of 3.30–3.35 Å, which is typical of such systems. Cations and anions are connected with each other through weak C–H···O hydrogen bonds: the C···O distances range from 3.140 to 3.352 Å, in comparison with 3.076–3.272 Å in pyridinium nitrate.[13]

Thus, the crystal structure of acidic pyridinium nitrate **1** contains a dihydrotrinitrate anion in a previously unknown configuration, which significantly differs from the only known structure of an anion of similar composition in compound **2**. Apparently, the planar conformer of **1** occurs due to the parallel arrangement of pyridinium cations with the formation of a layered structure.

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