



Synthesis and characterization of a new noncentrosymmetric organic-inorganic hybrid material $C_7H_7N_2 \cdot NO_3$

S. Riahi¹, M. L. Mrad¹, E. Jeanneau², F. Lefebvre³ and C. Ben Nasr^{1*}

¹Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 - Zarzouna - Bizerte Tunisie.

²Centre de Diffractométrie Henri Longchambon, Université Claude Bernard Lyon 1, Villeurbanne Cedex, France.

³Université de Lyon, Institut de Chimie de Lyon, UMR C2P2, LCOMS ; Bâtiment CPE Curien; 43 Boulevard du 11 Novembre 1918; F-69616, Villeurbanne, France.

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ABSTRACT

The crystal structure of the title organic-inorganic hybrid material $C_7H_7N_2 \cdot NO_3$ has been determined by single crystal X-ray diffraction. The compound crystallizes in the noncentrosymmetric orthorhombic space group $Pca2_1$ with the lattice parameters $a = 15.824$ (1), $b = 6.5461$ (4), $c = 16.215$ (1) (6) Å, $V = 1679.64$ (18) Å³, and $Z = 8$. The framework is built upon layers parallel to (0 0 1) made up from the nitrate anions and the ammonium groups associated by N---H...O and N---H...N hydrogen bonds. The organic entities are interconnected via weak C-H...N hydrogen bonds involving the nitrogen atoms of the nitrile groups, leading to an infinite one-dimensional chains running along the a-axis. These chains are located alternatively on either side of the ionic layers. Results from solid state ¹H, ¹³C and ¹⁵N spectroscopy are in good agreement with the X-ray structure. Density functional theory calculations allowed for the assignment of some carbon and nitrogen peaks to the independent crystallographic sites. The IR spectrum is dominated by the antisymmetric stretching mode of NO₃⁻, which splits into two components indicating that the symmetry of the nitrate anion is lowered by interaction with the ammonium group.

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Introduction

Organic-inorganic hybrid materials with noncentrosymmetric structures are interesting for their application in various fields such as e.g. quadratic non-linear optical materials research [1]. Their abilities to combine the properties of organic and inorganic entities within one single molecular scale leads to interesting crystal structures [2]. Among these materials, salts of amine attracted more attention for their potential importance in constructing sophisticated assemblies from discrete ionic and molecular building blocks characterized by their strength and directionality [3, 4]. The interesting structural diversity of this kind of compounds is mainly governed by hydrogen bonds [5], whose crystal pattern seems to be strongly influenced by the nature of the anion [6]. As a contribution to the investigation of the above materials, we report here the synthesis and the characterization of a new organic-inorganic hybrid material $C_7H_7N_2 \cdot NO_3$ including the 2-cyanoaniline, a chromophore which could be efficient in the blue-UV wavelength region.. This compound could exhibit a richness of interesting physical properties such as ferroelectricity and nonlinear optic phenomena like second harmonic generation.

Experimental

Chemical preparation

The commercial 2-cyanoaniline (3 mmol) was dissolved in water/nitric acid (50:1 v/v) solution. Colorless single crystals of the title compound, suitable for X-ray analysis, were obtained after slowly evaporation of the solvent at room temperature. The crystals are stable for months in normal conditions of temperature and humidity.

Investigation techniques

The characterization of the salt was carried out using X-ray diffraction, solid state NMR spectroscopy, DFT calculations, and infrared spectroscopy.

X-ray diffraction

A single crystal was carefully selected under a microscope in order to perform its structural analysis by X-ray diffraction. The intensity data were collected on a Bruker AXS S Xcalibur, Atlas, Gemini ultra diffractometer using omega scan technique with MoK α radiation ($\lambda = 0.7107$ Å). The structure was solved with direct methods using the SIR97 [7] and refined with full-matrix least-squares techniques using CRYSTALS [8]. The drawings were made with Diamond [9]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

NMR spectroscopy

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 MHz for ¹H, 30.30 MHz for ¹⁵N and 75.49 MHz for ¹³C, with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ¹³C and ¹H NMR chemical shifts are given relative to tetramethylsilane, while the ¹⁵N ones are given relative to glycine (at 30.0 ppm, external reference precision 0.5 ppm). The proton spectrum was recorded under classical MAS conditions, while the carbon and nitrogen ones were recorded by use of cross-polarization from protons (contact time 5 ms). A 2D HETCOR ¹³C-¹H NMR spectrum was obtained with a classical sequence and a 200 μ s contact time to ensure mainly a transfer of protons to carbons directly linked to them.

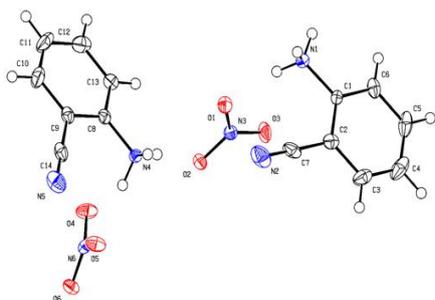
IR Spectroscopy

The spectrum was recorded in the range 4000 - 400 cm^{-1} with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet.

Results and discussion

X-ray diffraction study

The title organic-inorganic material crystallizes in a non-centrosymmetric setting in the chiral orthorhombic space group $Pca2_1$. Its structure consists of two nitrate anions and two crystallographically independent 2-cyanoanilinium cations (Fig. 1). The nitrogen atoms of the amino groups are protonated, thus indicating a positive charge, while the N atoms of the nitrile groups are not protonated. The NO_3^- anions are showing a negative charge to make the charge balance.



(3) and $C14\equiv N5 = 1.147$ (3 Å), are within the normal range. These geometrical characteristics are consistent with that observed for 3-cyano-N-(2-hydroxybenzyl)anilinium nitrate for which the mean corresponding C-C and C-N distance are 1.382 and 1.143 (5) Å, respectively [13]. The aromatic ring and the nitrile group are essentially coplanar as previously described [14].

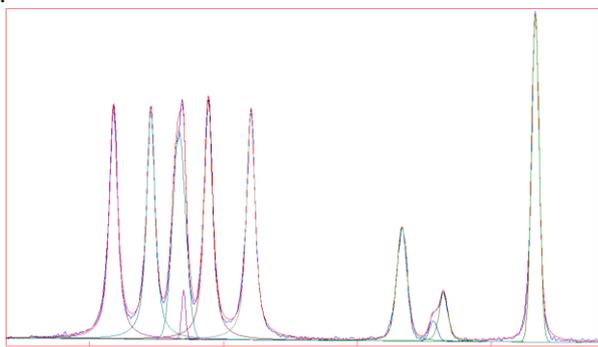


Fig. 6. Simulated and experimental ^{13}C CP-MAS-NMR spectra of $C_7H_7N_2 \cdot NO_3$.

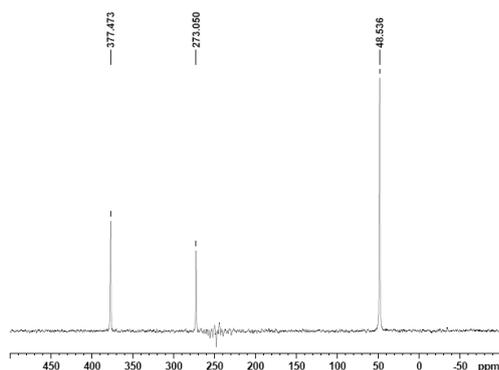


Fig. 7. ^{15}N CP-MAS-NMR spectrum of $C_7H_7N_2 \cdot NO_3$.

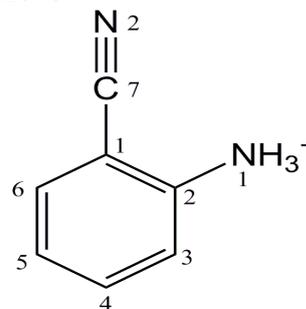
Refining the structure in the asymmetric space group gives a value of 0.29 (18) for the Flack parameter [15]. This value shows that the atomic arrangement corresponds to the correct absolute structure.

NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of the title compound is shown in Fig. 6. Since the 2-cyanoanilinium cation contains 7 carbon atoms, the presence of 8 well-defined resonances in the spectrum shows that the asymmetric unit cell should contain two crystallographically independent organic entities, which is in good agreement with the X-ray results. Figure 7 shows the ^{15}N CP-MAS NMR spectrum of the studied materials. It displays 3 well-resolved peaks, proving that there is only three nitrogen environments for the two different cations. The peak having the highest chemical shift, at 377.5 ppm, corresponds to the nitrogen atoms of the two nitrate anions. The 2D ^{13}C - 1H spectrum of $C_7H_7N_2 \cdot NO_3$, recorded with a short contact time, shows only the resonances of the carbons directly bonded to protons. Thus, the signals absent at 113.6, 116.6 and 133.0 correspond to the C1, C2 or C7 carbon atoms. The other four peaks have the same intensity, so they correspond to each time to the two ligands. The two shoulders on the peaks at 133 and 113 ppm correspond to impurities due to their very low intensities (about 1%).

Density functional theory (DFT) calculations were undertaken in order to assign the NMR resonances to the different crystallographically inequivalent carbon and nitrogen atoms of the unit cell. These calculations were made at the B3LYP/6-311++G** level using the GAUSSIAN 09 program.

Three different calculations were made on the organic cation and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane or glycine) calculated at the same level of theory: (i) calculation of the NMR chemical shifts (with the GIAO method) by taking the positions of atoms obtained by X-ray diffraction; (ii) optimization of the positions of the protons in the above molecule and calculation of the NMR chemical shifts in this semi-optimized geometry. Indeed X-ray diffraction leads always to underestimated X-H bond lengths, due to the fact that it is sensitive to the electronic cloud and does not see the nuclei; (iii) full optimization of all atoms and calculation of the corresponding NMR chemical shifts. This calculation, compared to the above one will give indications on the steric hindrance around the organic cation and on the positions where it is the strongest. Carbon and nitrogen atoms are depicted as follows:



The results, listed in Table 4, show that there is a relatively good agreement between the experimental and theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals to the various carbon and nitrogen atoms of the structure.

IR spectroscopy

The IR spectrum of crystalline $C_7H_7N_2 \cdot NO_3$ is shown in Figure 5. The most representative and characteristic vibrational modes of this compound can be compared to those of similar complexes [16, 17]. Some aspects of the performed assignments are briefly commented.

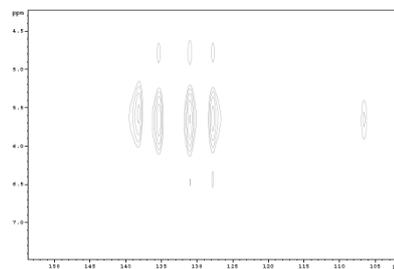


Fig. 8. Two-dimensional ^{13}C -H CP-MAS-NMR spectrum of $C_7H_7N_2 \cdot NO_3$.

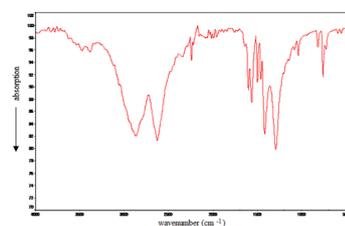


Fig. 9. IR spectrum of $C_7H_7N_2 \cdot NO_3$.

Table 1. Crystal data, experimental parameters used for the intensity data collection, strategy, and final results of the structure determination of C₇H₇N₂·NO₃

Empirical Formula	C ₇ H ₇ N ₂ ·NO ₃
Formula weight	181.151
Crystal system	Orthorhombic
Space group	<i>Pca</i> 2 ₁
a	15.824(1) Å
b	6.5461(4) Å
c	16.215(1) Å
Z	8
V	1679.64(18) Å ³
ρ _{cal.}	1.433 g cm ⁻³
F(000)	752
μ(CuK _α)	0.98 (mm ⁻¹)
Crystal size [mm]	0.34 x 0.17 x 0.13
Theta range	3°/66°
h, k, l range	-18/18, -7/7, -19/19
Reflections measured	23414
Independent reflections	2942
Unique reflections included (<i>I</i> > 2σ <i>I</i>)	2849
Refined parameters	237
Δρ _{max} /Δρ _{min} (e/Å ³)	-0.21/0.21
R	0.0408
R(<i>w</i>)	0.1120
Largest shift/error	0.97

Table 2. Hydrogen-bond geometry (Å, °) in C₇H₇N₂·NO₃

D - H...A	D - H (Å)	H...A (Å)	D...A (Å)	D - H...A (°)
C6—H1...N2i	0.95	2.49	3.376 (3)	155 (1)
N1—H7...O1	0.92	1.90	2.804 (3)	167
N1—H6...N3ii	0.90	2.57	3.375 (3)	150 (1)
N1—H6...O2ii	0.90	1.88	2.782 (3)	178 (1)
N1—H5...N6iii	0.93	2.52	3.385 (3)	154 (1)
N1—H5...O5iii	0.93	2.40	3.042 (3)	126 (1)
N1—H5...O6iii	0.93	1.91	2.835 (3)	172 (1)
C13—H11...N5iii	0.91	2.52	3.364 (3)	153 (1)
C12—H10...O3iv	0.96	2.57	3.429 (3)	150 (1)
N4—H14...O6ii	0.90	1.90	2.782 (3)	166 (1)
N4—H13...N6	0.91	2.58	3.386 (3)	149
N4—H13...O5	0.91	1.86	2.766 (3)	176
N4—H12...O1	0.88	2.49	3.164 (3)	134
N4—H12...N3	0.88	2.59	3.438 (3)	162
N4—H12...O2	0.88	1.96	2.831 (3)	169

Symmetry codes : (i) x+1/2, -y+2, z; (ii) x, y+1, z; (iii) x+1/2, -y+1, z; (iv) -x+3/2, y, z-1/2.

For the organic cation, the broad bands in the high-frequency region, between 3600 and 2500 cm^{-1} , correspond to the valence vibrations of C-H and N-H groups interconnected by a system of hydrogen bonds in the crystal [18]. The observed bands in the 1620-1200 cm^{-1} region can be attributed to the bending vibrations of N-H groups and to the valence vibrations of C=C, C-C and C-N groups [19]. The CN group is characterized by one or more sharp absorption bands in the region 2000- 2260 cm^{-1} . The sharp band at 2245 cm^{-1} is characterized of the nitrile functional group. The bands between 1000 and 700 cm^{-1} are assigned to out of plane bending modes $\gamma(\text{C}_{\text{ary}}\text{-H})$ and $\gamma(\text{C}_{\text{ary}}\text{-C})$ [20].

For the nitrate group, the free ionic state, which having a D_{3h} symmetry (A_3), predicts two bending and two stretching modes, of which two are doubly degenerate [21]. The symmetric stretching vibration ν_1 is not infrared-active, while the degenerate ν_3 antisymmetric stretching vibration is infrared-active. If the symmetry of the ion is lowered by interaction with the ammonium group, a splitting of the degenerate ν_3 and

ν_4 fundamentals should occur. The extent of the splitting will then depend on the point-group symmetry of the ion in its bonded state [22]. Thus, the pair of intense peaks centered around 1356 cm^{-1} corresponds to the antisymmetric NO_3^- stretching mode ν_3 and the doublet at 762 and 730 cm^{-1} is assigned to in-plane deformation $\delta(\text{NO}_3)$ mode (ν_4). The weak IR band at 821 cm^{-1} is attributed to out-of-plane deformation mode $\gamma(\text{NO}_3)(\nu_2)$ [23].

Supplementary material

Crystallographic data for the title compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 881211). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; mailto: deposit@ccdc.cam.ac.uk).

Table 3. Main interatomic distances (\AA) and bond angles ($^\circ$) in $\text{C}_7\text{H}_7\text{N}_2\text{NO}_3$

O1—N3	1.251 (2)	C3—C2	1.389 (3)
N3—O2	1.273 (2)	C2—C7	1.446 (3)
N3—O3	1.231 (2)	C7—N2	1.151 (3)
O4—N6	1.228 (2)	N4—C8	1.451 (3)
N6—O5	1.257 (2)	C8—C9	1.401 (3)
N6—O6	1.267 (2)	C8—C13	1.369 (3)
N1—C1	1.468 (3)	C9—C14	1.435 (3)
C1—C6	1.378 (3)	C9—C10	1.397 (3)
C1—C2	1.385 (3)	C14—N5	1.147 (3)
C6—C5	1.400 (4)	C10—C11	1.368 (4)
C5—C4	1.378 (4)	C11—C12	1.390 (4)
C4—C3	1.386 (4)	C12—C13	1.382 (3)
O1—N3—O2	118.26 (15)	C3—C2—C7	119.8 (2)
O1—N3—O3	121.80 (15)	C1—C2—C7	120.27 (19)
O2—N3—O3	119.94 (15)	C2—C7—N2	178.9 (2)
O4—N6—O5	121.70 (15)	N4—C8—C9	118.52 (19)
O4—N6—O6	120.78 (15)	N4—C8—C13	120.6 (2)
O5—N6—O6	117.52 (14)	C9—C8—C13	120.85 (19)
N1—C1—C6	119.27 (19)	C8—C9—C14	120.40 (17)
N1—C1—C2	119.32 (18)	C8—C9—C10	119.0 (2)
C6—C1—C2	121.4 (2)	C14—C9—C10	120.55 (18)
C1—C6—C5	118.3 (2)	C9—C14—N5	178.9 (2)
C6—C5—C4	120.6 (2)	C9—C10—C11	119.7 (2)
C5—C4—C3	120.6 (2)	C10—C11—C12	120.6 (2)
C4—C3—C2	119.1 (2)	C11—C12—C13	120.1 (2)
C3—C2—C1	119.9 (2)	C12—C13—C8	119.6 (2)

Table 4. Calculated and experimental carbon-13 and nitrogen-15 chemical shifts for in $\text{C}_7\text{H}_7\text{N}_2\text{NO}_3$.

Atom	X-ray (ppm)	Full optimization	Optimization of proton positions (ppm)	Experimental (ppm)
C1	112.1	113.8	112.4	106.7
	114.1		114.4	
C2	126.2	133.9	127.3	133.0
	126.4		126.9	
C3	123.2	127.3	127.6	127.9
	119.6		124.7	
C4	136.7	144.3	142.7	
	136.4		142.0	
C5	139.1	143.8	141.8	
	135.9		141.1	
C6	139.3	142.4	143.4	
	138.8		142.4	
C7	115.1	116.9	116.0	116.6
	114.5		115.3	
N1	42	69	68	48.6
	34		67	
N2	343	344	340	273.0
	344		341	

Conclusion

$C_7H_7N_2NO_3$ was prepared as single crystals at room temperature and characterized by various physico-chemical methods. On the structural level, the framework is built upon layers parallel to (0 0 1) made up from the nitrate anions and the ammonium groups associated by N-H...O and N---H...N hydrogen bonds. The organic entities are interconnected via weak C-H...N hydrogen bonds involving the nitrogen atoms of the nitrile groups, leading to infinite one-dimensional chains running along the a-axis. The numbers of solid state ^{15}N and ^{13}C CP-MAS-NMR components are in full agreement with the X-ray structure. The presence of two pairs of infrared peaks centered around 1356 and 746 cm^{-1} corresponding, respectively, to the NO_3^- antisymmetric stretching and in-plane deformation modes, proves that the symmetry of the nitrate anion is lowered by interaction with the ammonium group.

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