2-Amino-3-nitropyridinium hydrogensulfate hydrate: a nonlinear optical crystal engineered with a two-dimensional hyperpolarisable chromophore

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A new nonlinear optical crystal, 2-amino-3-nitropyridinium hydrogensulfate hydrate, has been engineered following a strategy which induces the formation of herringbone motifs of chromophores. The crystal packing of such motifs is non-centrosymmetric, with a $P2_12_12_1$ space group. The crystal stability is lowered by the presence of water molecules in the host matrix. The second harmonic generation signal at 530 nm of a powder sample is slightly lower than that of 3-methyl-4-nitropyridine *N*-oxide.

Hydrogénosulfate hydrate de 2-amino-3-nitropyridinium: un sel organique non-linéaire construit autour d'un chromophore bidimensionnel. Un cristal optiquement non linéaire, le sulfate acide monohydraté de 2-amino-3-nitropyridinium a été préparé suivant une stratégie d'ingénierie cristalline qui a pour but la formation de motifs herringbone organo-minéraux. De tels motifs s'empilent de façon non centrosymétrique ($P2_12_12_1$). La capture d'une molécule d'eau fragilise la matrice anionique à laquelle s'accrochent les chromophores. La réponse en génération de second harmonique d'un échantillon de poudre à 530nm est plus faible que celle observée sur une référence de 3-methyl-4-nitropyridine *N*-oxyde.

Among traditional engineering routes of nonlinear optical (NLO) crystals based on polar molecules, such as nitroaniline and stilbene derivatives,[1] new directions in molecular and crystal design have appeared over the past five years.[2,3] The challenge was to enhance the off-diagonal hyperpolarisability tensor components β_{ijj} and to favour their constructive addition in the crystal cell in order to gain high values of macroscopic susceptibilities (χ^2). Answering these questions the concept of octupolar chromophores for quadratic nonlinear optics emerged recently.[4–6] This concept, which was developed from group theory considerations, was illustrated experimentally in a triaminotrinitrobenzene crystal,[7] crystal violet,[8] barium trimetaborate [9,10] and ruthenium tris-bipyridine derivatives.[11] The two dimensional (2D) hyperpolarisable chromophores have received particular attention for new NLO materials:[2,12,13] original molecular building blocks such as zigzag donor–acceptor phenylethynylbenzene,[14] bis(donor–acceptor) tetraphenylethynylethene[15] or 1,3,5-trisubstituted phenylethynylbenzene[16] derivatives have been specifically synthesised with that aim and characterised. These chromophores are supposed to lead to enhanced transparency compared to classical one-dimensional dipolar structures as well as increased stability of polar order in poled polymers or Langmuir–Blodgett films.[12] However none of these sophisticated chromophores has been used in the molecular engineering of NLO crystals. Lately, some success was achieved by using NLO crystals including the two-dimensional 2-amino-5-nitropyridinium chromophore ($2A5NP^+$),[17,18] which suggested the use of the 2-amino-3-nitropyridinium isomer cation ($2A3NP^+$) as a new two-dimensional chromophore. Actually these cations possess two electron-accepting centres, NO_2 and NH^+, and one donor amino group leading to two-dimensional charge-transfer entities. An engineering strategy using organic salts in which an organic ionic chromophore is associated with an inorganic counter ion aims at improving the mechanical and thermal stabilities of the crystal packing. Such a strategy, namely the use of 'organic–inorganic hybrid materials', is justified by the double role played by the inorganic host matrix (anionic in our case). The main point is to favour a strong anchorage of NLO chromophores onto the inorganic matrix through a 3D hydrogen-bond network. The second point is the influence of the charge of the inorganic network on the molecular hyperpolarisabilities of the chromophores packed in the crystal. 2-Amino-3-nitropyridinium chloride (2A3NPCl), a remarkable non-centrosymmetric layered structure (Fig. 1), exemplifies precisely this double role played by the Cl^- inorganic matrix:[19] the packing is achieved through a 2D network of short hydrogen bonds (Fig. 2) and the favourable effect of anion charge on the cation hyperpolarisabilities has been suggested from calculations using the semi-empirical AM1 parameters and the Finite Field method available in MOPAC 6.[20] The same cation $2A3NP^+$ could be combined with weak conjugated bases able to induce 2D or 3D hydrogen-bond connections. We report the chemical preparation and the $P2_12_12_1$ crystal structure of 2-amino-3-nitropyridinium hydrogensulfate hydrate ($C_6H_6O_2N_3^+ \cdot HSO_4^- \cdot H_2O$) and discuss the crystal qualities with respect to the stability of the anion aggregate $(HSO_4^- \cdot H_2O)_n$.

Experimental

2-Amino-3-nitropyridine (Aldrich, purity 99%, 0.01 mol) is dissolved in 20 cm^3 acidic aqueous solution containing 0.03 mol H_2SO_4 at 20 °C. The solution, evaporated at room temperature, yields pale yellow bulky crystals of dimensions $5 \times 5 \times 12$ mm^3 in size after a week. The chemical formula was established from the X-ray crystal structure investigation. The $P2_12_12_1$ space group of 2-amino-3-nitropyridinium hydrogensulfate hydrate (2A3NPS) was confirmed by the limiting conditions ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) and the

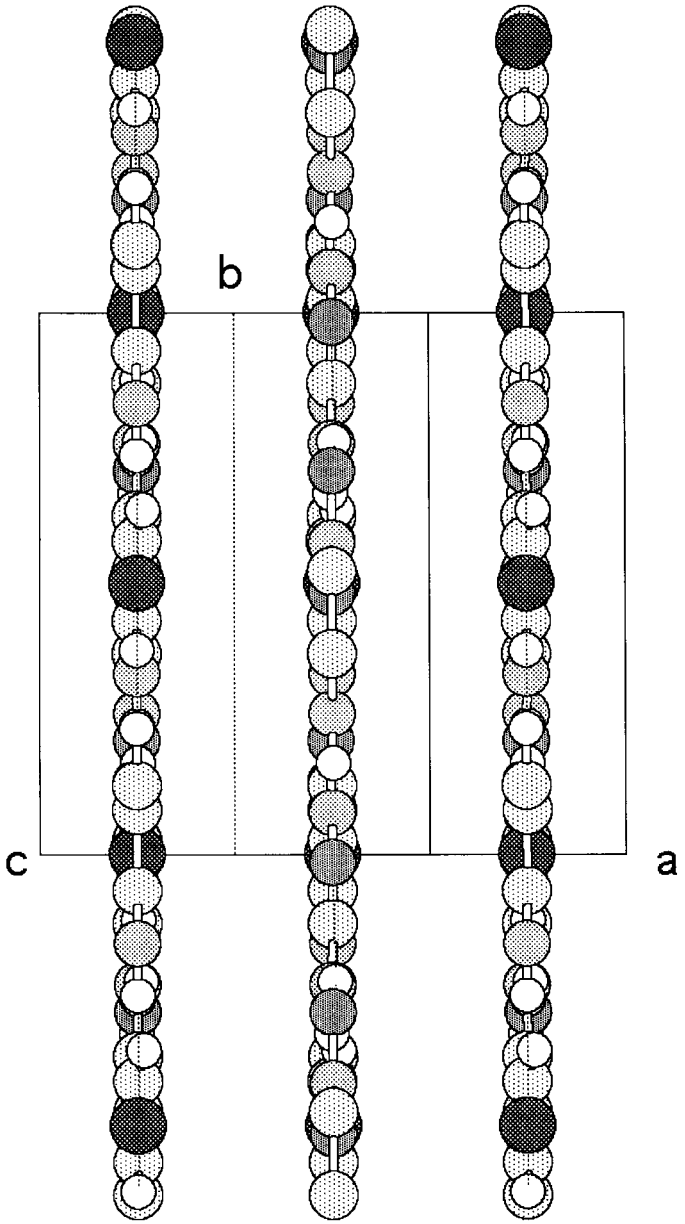

Fig. 1 View along the [102] direction of the perfect layered arrangement of ion-paired chromophores in the structure of 2A3NPCl

second harmonic signal based on the Kurtz and Perry powder test.[21]

The cell parameters, space group and crystal structure were determined from single crystal X-ray diffraction data obtained with a four-circle diffractometer.[22] Crystal data, experimental conditions and structural refinement parameters are given in Table 1. No absorption correction was applied; only Lorentz and polarization effects were taken into account. The structure was solved by direct methods using SIR89 program.[23] Full-matrix least-squares refinements were performed on F: the function minimized was $\Sigma\, w(F_o - F_c)$ with $w = 1/\sigma^2(F)$ as weighting scheme. Scattering factors for neutral atoms and f', $\Delta f'$, f'', $\Delta f''$ were taken from ref. 24. All the calculations were performed with the MolEN program[25] operating on a micro-Vax II computer. The structure was drawn using the MOLVIEW program.[26] Final atomic parameters are listed in Table 2. The main geometrical features of the 2-amino-3-nitropyridinium cation are described in Tables 3 and 4 and the hydrogen bonds in Table 5.

CCCD reference number 440/004.

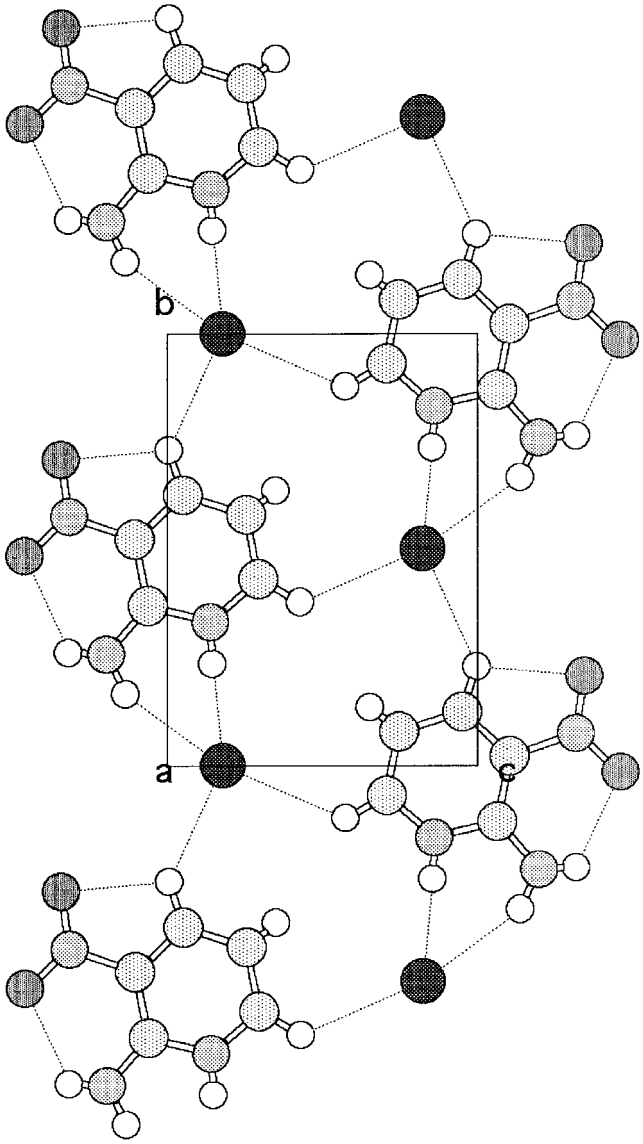

Fig. 2 Projection along the *a* direction of a cation–anion layer evidencing the herringbone motif formed in the 2A3NPCl crystal

Discussion

The crystal structure of 2A3NPS (Fig. 3) viewed in the (*b*,*c*) plane reveals the anionic aggregates $(HSO_4^- \cdot H_2O)_n$ organized in ribbons of 2_1 symmetry onto which the $2A3NP^+$ cations are anchored through a 3D network of hydrogen bonds. The cations and infinite anionic aggregates $(HSO_4^- \cdot H_2O)$ form herringbone motifs extending along the *a* direction. The main links are from the N—H···O bonds (Table 5). Long C—H···O contacts occurring between cations and cation–anion moieties maintain the cohesion between the herringbone motifs. Three-center H-bonds are evidenced: C4—HC4···O4, O6 and N2-H1N2···O3, O5. The intracation contact N2-H1N2···O5 is always present in nitroanilines in which nitro and amino groups are *ortho* to one another.[27] The limits of hydrogen interactions could be estimated on the basis of van der Waals radii of hydrogen and oxygen atoms:[28] H···O < 2.54Å. However recent work on C—H···O contacts[29–33] indicate that H···O distances in the range 2.5 up to 3Å may be taken into account. The twisting angle of the nitro group with respect to the planar heterocycle is 6°. This can unfavourably influence the efficiency of molecular charge transfer and consequently the values of β_{ijk} when these reach high values. This twisting angle is due to the combined effect of bonds C4—HC4···O6 (intercation) and N2-H1N2···O5 (intracation). On the other hand in the 2A3NPCl crystal the

Table 1 X-Ray experimental data for the crystal structure determination

Formula	$C_6H_6O_2N_3^+ \cdot HSO_4^- \cdot H_2O$
Molecular weight	255.21
Cell symmetry	Orthorhombic
Space group	$P2_12_12_1$
a/Å	6.523(1)
b/Å	11.302(1)
c/Å	13.517(2)
U/Å^3	996.5(4)
Z,D_x/g cm^{-3}	4, 1.700
Unit-cell refinement	25 reflections ($10.6 < \theta < 14.5°$)
F(000)	528
μ (mm^{-1})	0.359 (Mo Kα)
Crystal size/mm	0.20 × 0.32 × 0.30
Temperature/K	294
Apparatus	Nonius CAD4 diffractometer
Monochromator	Graphite (220)
Radiation/Å	0.71073 (Mo Kα)
Bragg angle limits/°	3–30
h,k,l Limits	−9 to 9, 0–15, 0–18
Scan technique	ω scan
Background/s	6–23
Scan speed/deg s^{-1}	0.024–0.094
Scan width/°	1.10
Control reflections	(2 4 3), (−2 4 3)
Intensity every	7200 s (no decay)
Orientation every	400 reflections (3 5 4), (−3 5 4)
Reflections collected	2533
Unique data	1395
Data used in refinement	1388 [$I > 3\sigma(I)$]
Refined parameters	181
R (R_w)	0.026(0.037)
Weighting scheme	$1/\sigma^2(F)$
Goodness of fit	0.774
Largest shift/error	0.262
Max.residual density/e Å^{-3}	0.24

nitro group is exactly in the plane of the heterocycle due to the internal bonds N—H···O and C—H···O (Fig. 2).

The structure of the $(HSO_4^- \cdot H_2O)_n$ aggregate, shown in Fig. 4, evidences clearly the role of each water molecule, which is to maintain the cohesion between three monomers of HSO_4^-, then build a ribbon with 2_1 symmetry. In the chemistry of sulfates the formation of cluster $(HSO_4^-)_2$ or chains $(HSO_4^-)_n$ as counter ions are frequently observed: these assemblies give the crystals in which they are present a better stability than the aggregate $(HSO_4^- \cdot H_2O)_n$. Actually in 2A3NPS the water molecule is lost between 56 and 75 °C and a new phase is formed, stable between 75 and 176 °C (TGA experiments). This transformation is associated with the destruction of the H-bond network in the aggregate (Fig. 4).

As observed in the structures of 2-amino-5-nitropyridinium salts, the anionic aggregates favour the arrangement of chromophores in herringbone motifs,[18] increasing the intercation distances: such herringbone motifs induce non-centrosymmetric structural packings. The $(HSO_4^- \cdot H_2O)_n$ aggregate plays the same role in the organisation of the 2A3NPS non-centrosymmetric structure.

The second harmonic signal $I_{2\omega}$ at 530 nm observed for a powder sample[21] of 2A3NPS can be qualitatively correlated with the signals of 3-methyl-4-nitropyridine *N*-oxide (POM, $P2_12_12_1$),[34] 2-amino-5-nitropyridinium dihydrogenphosphate[35] (2A5NPDP, $Pna2_1$), 2-amino-3-nitropyridinium chloride (2A3NPCl, $P2_1$) and urea ($P42_1m$) in the same experi-

Table 2 Fractional atomic coordinates

Atom	x	y	z
S	0.00240(6)	0.53707(4)	0.53665(3)
O1	−0.2076(2)	0.5118(2)	0.5596(1)
O2	0.0324(3)	0.6242(1)	0.4593(1)
O3	0.0908(3)	0.5903(2)	0.6329(1)
O4	0.1182(3)	0.4320(1)	0.5139(1)
OW	0.9571(2)	0.8507(1)	0.4047(1)
O5	0.2426(3)	0.1889(1)	0.2575(1)
O6	−0.0143(3)	0.0714(2)	0.2734(1)
N1	0.5492(2)	−0.0695(1)	0.1037(1)
N2	0.5633(3)	0.1249(1)	0.1487(1)
N3	0.1599(3)	0.0934(2)	0.2452(1)
C1	0.4633(3)	0.0237(1)	0.1505(1)
C2	0.2706(3)	0.0007(2)	0.1945(1)
C3	0.1835(3)	−0.1096(2)	0.1900(1)
C4	0.2824(4)	−0.2006(2)	0.1415(2)
C5	0.4655(3)	−0.1778(2)	0.0984(1)
HC3	0.051(4)	−0.121(2)	0.222(2)
HC4	0.220(4)	−0.280(2)	0.139(2)
HC5	0.536(4)	−0.239(2)	0.060(2)
HN1	0.662(4)	−0.052(2)	0.069(2)
H1N2	0.525(4)	0.184(2)	0.181(2)
H2N2	0.679(5)	0.131(2)	0.115(2)
HO3	0.211(4)	0.610(2)	0.620(2)
HW1	1.048(5)	0.893(3)	0.417(2)
HW2	0.993(5)	0.801(3)	0.436(2)

Table 3 Selected bond distances (in Å) and their e.s.d.s

S—O1	1.433(2)	C4—C5	1.354(3)
S—O2	2.430(2)	N3—C2	1.445(2)
S—O3	2.357(2)	N3—O5	1.218(2)
S—O4	2.390(2)	N3—O6	1.224(2)
O3—HO3	0.83(3)	N1—HN1	0.90(3)
N2—C1	1.316(2)	N2—H1N2	0.84(2)
N1—C1	1.350(2)	N2—H2N2	0.88(3)
N1—C5	1.342(2)	C3—HC3	0.98(3)
C1—C2	1.416(2)	C4—HC4	0.98(2)
C2—C3	1.371(3)	C5—HC5	0.98(2)
C3—C4	1.379(3)		

Table 4 Selected bond angles (°)

O1—S—O2	114.9(1)	N1—C1—N2	117.6(2)
O1—S—O3	104.57(9)	N1—C1—C2	115.0(2)
O1—S—O4	112.5(1)	N2—C1—C2	127.4(2)
O2—S—O3	106.98(9)	N3—C2—C1	120.7(2)
O2—S—O4	109.59(9)	N3—C2—C3	118.2(2)
O3—S—O4	107.8(1)	C1—C2—C3	121.1(2)
S—O3—HO3	106(1)	C2—C3—C4	120.4(2)
C1—N2—H1N2	122(1)	C2—C3—HC3	117(1)
C1—N2—H2N2	119(1)	C4—C3—HC3	121(1)
C1—N1—C5	124.6(2)	C3—C4—C5	118.4(2)
C1—N1—HN1	114(1)	C3—C4—HC4	120(1)
C5—N1—HN1	120(1)	C5—C4—HC4	121(1)
H1N2—N2—H2N2	117(2)	N1—C5—C4	120.7(2)
O5—N3—O6	123.3(2)	N1—C5—HC5	118(1)
O5—N3—C2	119.0(2)	C4—C5—HC5	120(1)
O6—N3—C2	117.7(2)		

Table 5 Hydrogen bonds

D—*H*···*A*	*D*—*H*	*H*···*A*	*D*···*A*	*D*—*H*···*A*
OW—HW1···O1	0.78(3)	1.95(3)	2.726(2)	173(3)
OW—HW2···O2	0.74(4)	2.04(4)	2.709(2)	150(3)
O3—HO3···OW	0.83(3)	1.70(3)	2.532(2)	178(2)
N1—HN1···O4	0.90(3)	1.83(3)	2.689(2)	160(1)
N2—H1N2···O3	0.84(2)	2.74(3)	3.378(2)	134(2)
N2—H1N2···O5	0.84(2)	2.11(2)	2.657(3)	122(2)
N2—H2N2···O2	0.88(3)	2.14(3)	3.015(3)	172(2)
C3—HC3···OW	0.98(3)	2.56(2)	3.287(2)	131(1)
C4—HC4···O4	0.98(2)	2.64(2)	3.199(2)	116(1)
C4—HC4···O6	0.98(2)	2.46(2)	3.319(3)	146(1)
C5—HC5···O4	0.98(2)	2.48(2)	3.140(2)	124(1)

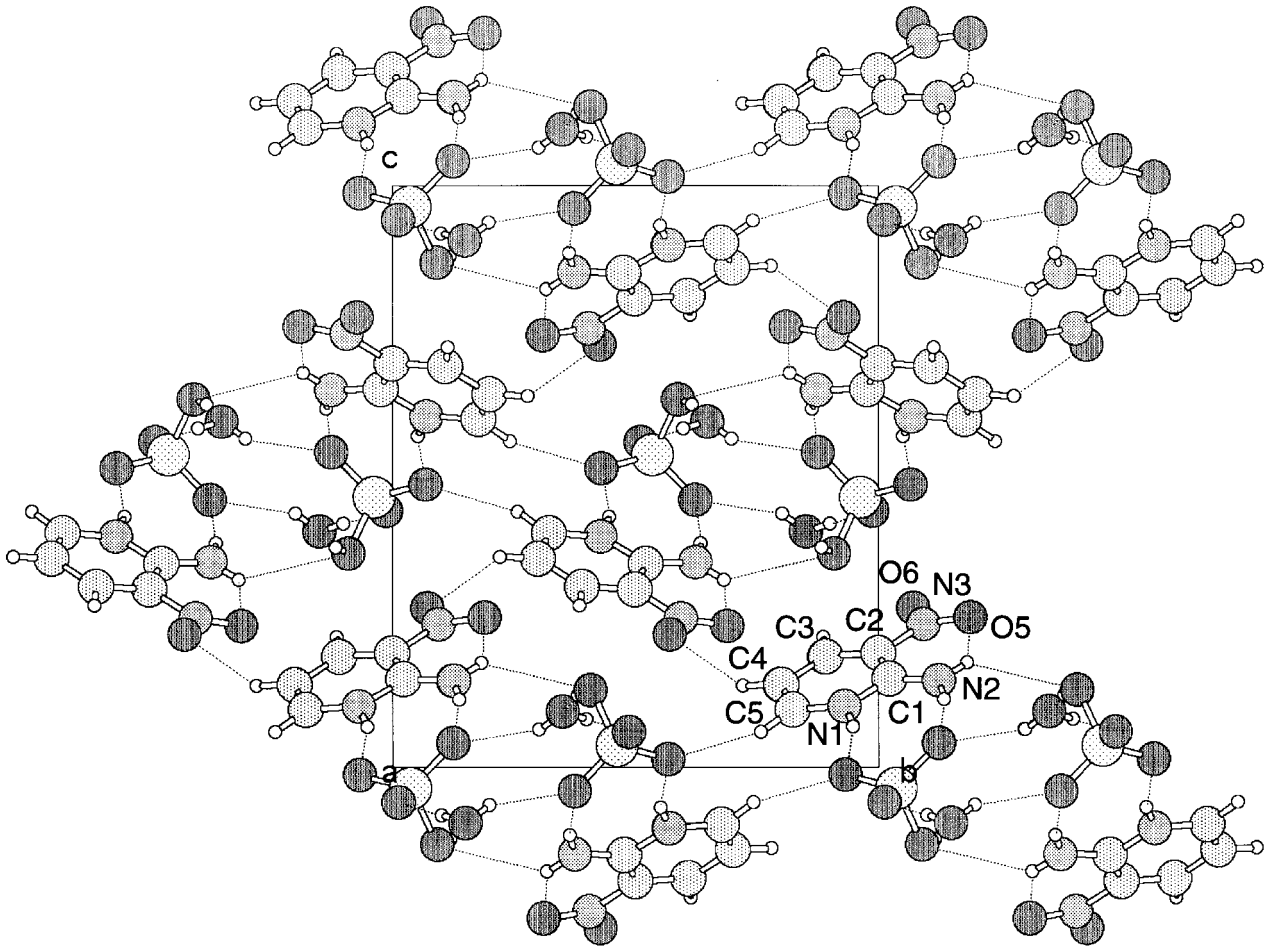

Fig. 3 Projection along the *a* direction of 2A3NPS showing the H-bond network

mental conditions (Nd^{+3}:YAG laser at 1.06 μm and powders with same particle sizes): $I_{2\omega}$ (urea) < $I_{2\omega}$ (2A3NPS) < $I_{2\omega}$ (2A5NPDP) < $I_{2\omega}$ (POM) < $I_{2\omega}$ (2A3NPCl).

Conclusion

The 2A3NPS crystal reveals some drawbacks compared to 2A5NPDP, 2A5NPCl[36] or 2A3NPCl crystals designed using the same strategy: a stability limited to 57 °C and a NLO efficiency lower than that of 2A5NPDP. This material cannot be a good candidate for applications of frequency conversion of laser sources although in contrast its crystal growth is simple and easy : samples from 1 to 1.5 cm^3 in size were easily obtained in H_2SO_4–H_2O solutions during the first syntheses. In this crystal, the solvent capture weakens the solidity of the aggregate and disperses the anion charge, lowering the packing stability. However this material proves the validity of our crystal engineering strategy: the formation of discrete herringbone motifs in which nitroaniline derivatives are grafted on an inorganic framework is always associated with a non-centrosymmetric crystal structure.[18] This result serves as a guideline for research into new inorganic host matrices which have the ability to induce non-centrosymmetric packing.

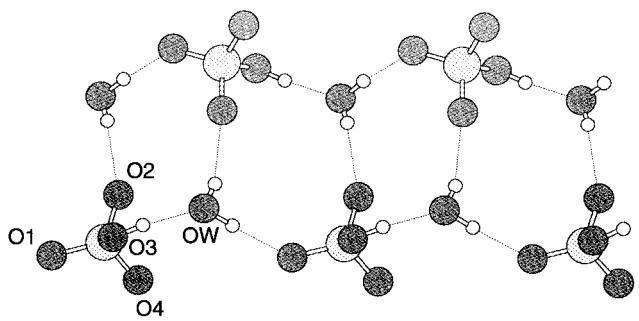

Fig. 4 Detailed drawing of the inorganic anion network of 2_1 symmetry $(HSO_4^- \cdot H_2O)_n$

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