

Sodium 4-nitrophenolate 4-nitrophenol dihydrate crystal: a new herringbone structure for quadratic nonlinear optics

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Sodium 4-nitrophenolate 4-nitrophenol dihydrate is a new nonlinear optical crystal of C_2 monoclinic symmetry composed of two distinct organic chromophores of respective calculated molecular hyperpolarisabilities $\beta_{xxx} = 18.2 \times 10^{-30}$ and 5.2×10^{-30} esu. The chromophores are organised in herringbone motifs along inorganic chains of NaO_6 edge shared octahedra. A short H-bond network assembles the herringbone motifs. A remarkable feature is the unique proton shared between the two chromophores respecting the twofold symmetry. The structure is isotypic with that of the magnesium bis(4-nitrophenolate) dihydrate. Structural analogies with other known metal nitrophenolates are pointed out and the nonlinear optical efficiency is discussed.

Introduction

Crystal engineering of non-centrosymmetric structures built from 4-nitrophenolate anions as hyperpolarisable chromophores has recently been proposed and justified.¹ Proton loss from acidic 4-nitrophenol strongly increases the hyperpolarisability of the anionic conjugate base. For the 4-nitrophenol (4NP) entity the value of β_{xxx} increases from 5.2×10^{-30} to 18.2×10^{-30} esu. Two types of engineering routes have been explored: (a) the formation of organic salts in which proton transfer increases the hyperpolarisability of the host base simultaneously to that of the anion,^{1a} and (b) the formation of metal phenolates in which the hyperpolarisability of the 4-nitrophenolate anion can be favourably influenced by the metal cation.^{1c} Another advantage of the latter route would be the formation of an inorganic network between the chromophores increasing the stability of the crystal packing and, hopefully, its mechanical hardness. Among the numerous crystal structures of metal nitro- and dinitrophenolates already known, few exhibit non-centrosymmetric packing, examples of those which do include sodium 4-nitrophenolate dihydrate (Na4NP) of $Ima2$ symmetry, which has been fully characterised through its nonlinear optical properties² and crystal growth conditions;³ magnesium bis(4-nitrophenolate) dihydrate (Mg4NP) of C_2 symmetry;⁴ and sodium 3-methyl-4-nitrophenolate dihydrate (Na3M4NP) of Cc symmetry.^{1c} The common feature of their crystal packing is the organisation of 4-nitrophenolate anions in herringbone motifs. In Na4NP the sodium atom is octahedrally surrounded by four water molecules and two anions and the final herringbone motif is formed by stacking of the octahedral units (Fig. 1) along the c axis of the orthorhombic cell. In Na3M4NP a chain of NaO_6 edge shared octahedra builds up the herringbone motif of anions stretching along the a axis of the monoclinic cell (Fig. 2). In Mg4NP a chain of NaO_6 edge shared octahedra is also formed but distinct from that observed in Na3M4NP. Here we wish to report the discovery of a new organometallic salt obtained from 4-nitrophenol, sodium 4-nitrophenolate 4-nitrophenol dihydrate (further abbreviated as Na4NP·4NP). The yellow-orange crystalline powder of this new material is moderately efficient in second harmonic generation (SHG) at

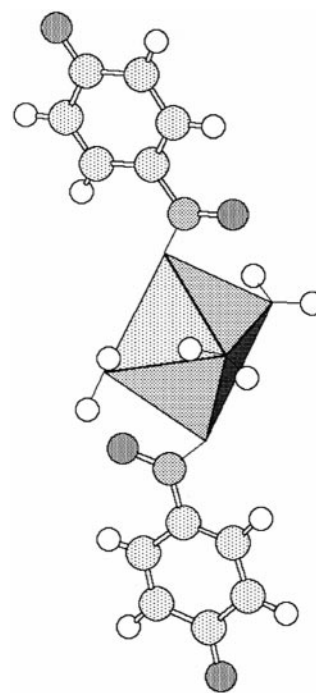


Fig. 1 Octahedral unit involved in the sodium 4-nitrophenolate dihydrate structure of $Ima2$ symmetry.

1.06 μm . The crystal structure of Na4NP·4NP has been investigated to study the non-centrosymmetric arrangement of the chromophores. It is shown to be isotypic with that of Mg4NP.

Experimental

Preparation and characterisation

Aqueous solutions of sodium 4-nitrophenolate hydrate (2×10^{-3} M) (Aldrich) and zinc sulfate heptahydrate (10^{-3} M) (Prolabo) were prepared. On mixing the two reagents, a white crystalline precipitate appeared immediately.

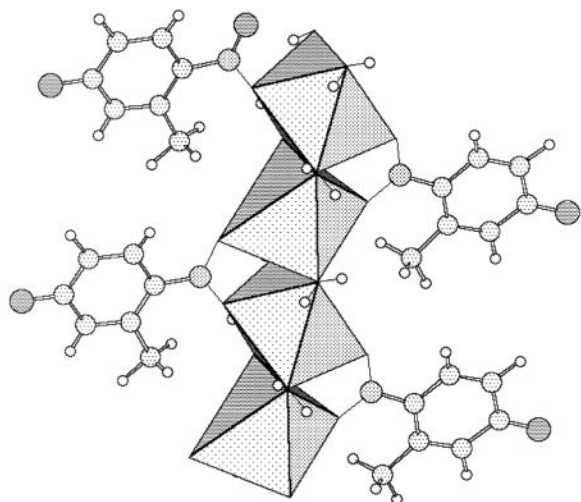


Fig. 2 Herringbone motifs of chromophores built through NaO_6 edge shared octahedra in the crystal structure of sodium 3-methyl-4-nitrophenolate dihydrate of C_c symmetry.

This precipitate was identified by X-ray powder diffraction as the mixed salt $\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (ASTM Powder file 11–287). The filtered solution was slowly evaporated at room temperature yielding crystalline orange platelets. The crystal was characterised by elemental analysis, thermal analysis (SETARAM, TG92), X-ray diffraction (Nonius CAD4) and SHG powder testing (YAG- Nd^{3+} laser light at $1.06 \mu\text{m}$). Elemental analysis (obs: C, 42.84; H, 3.90; N, 8.24, calc: C, 42.86; H, 3.87; N, 8.33%) and X-ray structural investigation confirmed the chemical formula of the crystal: $\text{Na}^+(\text{C}_6\text{H}_4\text{NO}_3^-)(\text{C}_6\text{H}_5\text{NO}_3) \cdot 2\text{H}_2\text{O}$.

Crystal structure determination

The orange crystal used for the diffraction studies was $0.64 \times 0.48 \times 0.16 \text{ mm}$ in size. The space group of $\text{Na}_4\text{NP}^- 4\text{NP}$ ($C2$) was established by the diffraction limiting conditions (hkl with $h+k=2n$) associated with the second harmonic signal based on the Kurtz and Perry powder test.⁵ The cell parameters and crystal structure were determined from single crystal X-ray diffraction data obtained with a four circle diffractometer. Crystal data, experimental conditions and structural refinement parameters are presented in Table 1. No absorption correction was applied; only Lorentz and polarisation effects were taken into account. The structure was solved by direct methods using the SIR 92 program.⁶ Full-matrix least-squares refinements were performed on F using the teXsan software.⁷ Scattering factors for neutral atoms and f' , $\Delta f'$, f'' and $\Delta f''$

Table 1 X-Ray experimental details for the crystal structure determination of sodium 4-nitrophenolate 4-nitrophenol dihydrate

Formula	$\text{C}_{12}\text{H}_{13}\text{N}_2\text{NaO}_8$
Molecular weight	336.23
Space group	$C2$
$a/\text{\AA}$	21.173(5)
$b/\text{\AA}$	3.669(1)
$c/\text{\AA}$	10.352(1)
$\beta/^\circ$	117.21(2)
$V/\text{\AA}^3$	715.2(3)
Z	2
$D_x/\text{g cm}^{-3}$	1.561
μ/cm^{-1}	1.570 (λ Mo-K α)
Crystal size/mm	$0.64 \times 0.48 \times 0.16$
Temperature/K	296
Radiation/ \AA	0.7107 (Mo-K α)
Number of data collected	2020
Unique data	1115 [$R(\text{int})=0.042$]
Data used in refinement	1079 [$I > 3\sigma(I)$]
Refined parameters	120

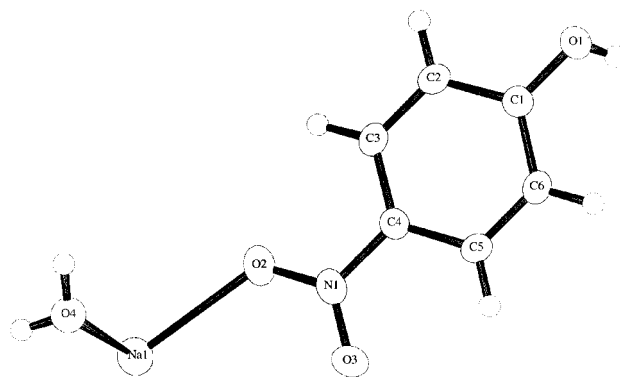


Fig. 3 Asymmetric unit in the crystal structure of sodium 4-nitrophenolate 4-nitrophenol dihydrate. The thermal ellipsoids of non-H atoms are plotted at 50% probability level.

were taken from *International Tables for X-ray Crystallography*.⁸ The crystal structure was drawn using the MOLVIEW⁹ and ORTEP¹⁰ programs (Fig. 3) included in the teXsan software. The main interatomic distances and bond angles are listed in Table 2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/159.

See <http://www.rsc.org/suppdata/jm/1999/1471/for> crystallographic files in .cif format.

Results and discussion

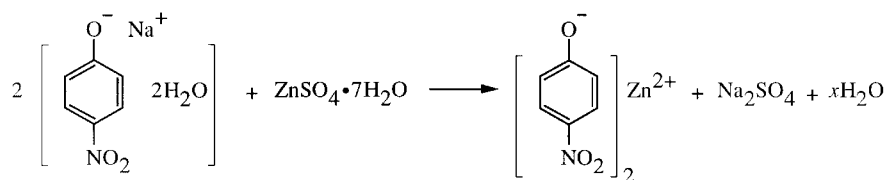
Preparation

$\text{Na}_4\text{NP}^- 4\text{NP}$ crystals were prepared adventitiously during the attempted synthesis of zinc 4-nitrophenolate in aqueous solution by an exchange reaction between purified sodium 4-nitrophenolate dihydrate and zinc sulfate heptahydrate, according to the expected reaction:

At room temperature, the above reaction was not observed.

Table 2 Main interatomic distances (\AA) and bond angles ($^\circ$) in the asymmetric unit. Estimated standard deviations are given in parentheses

Na–O2	2.490(1)	C1–C2	1.414(2)	O1–C1	1.311(1)
Na–O4	2.410(2)	C1–C6	1.415(2)	C4–C5	1.399(2)
Na–O4	2.457(2)	C2–C3	1.373(2)	C5–C6	1.370(2)
O2–N1	1.238(2)	C3–C4	1.393(2)		
O3–N1	1.237(2)	N1–C4	1.426(1)		
O4–Na–O4	83.3(1)	O1–C1–C2	119.5(1)		
O4–Na–O4	97.85(4)	C5–C4–N1	119.0(1)		
O4–Na–O4	178.81(9)	C6–C5–C4	118.8(1)		
O4–Na–O2	90.69(7)	C5–C6–C1	121.0(1)		
O4–Na–O2	94.00(6)	O3–N1–O2	121.8(1)		
O2–Na–O2	173.7(2)	O3–N1–C4	119.0(1)		
O4–Na–O4	80.95(9)	O2–N1–C4	119.2(1)		
O4–Na–O2	89.23(7)	O1–C1–C6	121.7(1)		
O4–Na–O2	85.99(6)	C2–C1–C6	118.7(1)		
C3–C2–C1	120.5(1)	C2–C3–C4	119.3(1)		
C3–C4–C5	121.6(1)	C3–C4–N1	119.4(1)		
H7–O1–C1	110(3)	H2–O4–H1	107(2)		
Hydrogen bonds					
D...H...A	D...A	D–H	H...A	D–H...A	
O1...H7...O1	2.477(2)	0.68(2)	1.83(2)	161(3)	
O4...H1...O1	2.785(1)	0.84(2)	1.96(2)	169(2)	
O4...H2...O3	2.855(2)	0.80(2)	2.07(2)	165(2)	



Instead a precipitate of zinc carbonate hydroxide monohydrate was formed, as described in the experimental section. More than 90% of the original Zn^{2+} was recovered in the precipitate. The carbonate is formed from atmospheric carbon dioxide absorbed by solutions with pH *ca.* 10. The same procedure was carried out with zinc nitrate hexahydrate and aluminium trichloride hexahydrate instead of zinc sulfate. With zinc nitrate hexahydrate we still obtained orange crystals of $\text{Na}_4\text{NP}^-4\text{NP}$, but with aluminium trichloride hexahydrate only sodium 4-nitrophenolate dihydrate (Na_4NP) crystallised. In the first two experiments the solution was maintained at pH 7, while in the third the pH value during the crystallisation was 9.3. The zinc sulfate and nitrate salts induce a buffer effect fixing the pH of the solution at 7. We have verified that Na_4NP always crystallises in solution at pH 9. This new sodium salt $\text{Na}_4\text{NP}^-4\text{NP}$ was formed in solution at pH 7 in which the 4-nitrophenol was not completely dissociated, so explaining the co-crystallisation of a 4-nitrophenol molecule as revealed by the crystal structure.

Thermal characterisation

The melting point measurement of $\text{Na}_4\text{NP}^-4\text{NP}$ by the visual method shows a colour change to orange red at 120 °C and partial melting at 155 °C. The compound slowly changes colour and becomes black above 300 °C. The thermogravimetry (TG)–differential thermal analyses (DTA) reveal the loss of two water molecules between 75–145 °C with a broad endotherm at 100 °C and a sharp endotherm at 131 °C. The compound loses one molecule of 4-nitrophenol between 160–250 °C, coinciding with a sharp endotherm at 153.2 °C and a broad endotherm at 217.5 °C. The sharp exotherm at 312.7 °C with corresponding severe weight loss in TG indicates the complete decomposition of the compound. In contrast to Na_4NP , which decomposes at 325 °C after dehydration at 100 °C,³ $\text{Na}_4\text{NP}^-4\text{NP}$ decomposes in two stages, at 217.5 and 312.7 °C. This further confirms the co-crystallisation of 4-nitrophenol molecule.

Crystal structure analysis

The structure of $\text{Na}_4\text{NP}^-4\text{NP}$ is composed of 4-nitrophenol molecules, 4-nitrophenolate anions and water molecules surrounding the sodium cations (Fig. 4) resulting in NaO_6 octahedral coordination. These octahedra share edges, composed of water molecules, between them, so building a polymeric chain stretching along the twofold axis. The infinite chains $[\text{Na}^+(\text{C}_6\text{H}_4\text{NO}_3^-)(\text{C}_6\text{H}_5\text{NO}_3) \cdot 2\text{H}_2\text{O}]$ are connected through H-bonds originating from the water molecules and short H-bonds between the phenolate anions and phenol molecules (2.477 Å). The unique H atom involved in this contact has been found in the last difference Fourier synthesis split in two symmetrical positions around the twofold axis and perfectly refined. The structure is isotypic with that of magnesium 4-nitrophenolate dihydrate Mg_4NP $[\text{Mg}^{2+}(\text{C}_6\text{H}_4\text{NO}_3^-)(\text{C}_6\text{H}_5\text{NO}_3) \cdot 2\text{H}_2\text{O}]$ except for the unique H atom of the phenol molecule. Through the infinite chain of octahedra (Fig. 5) a herringbone motif of 4-nitrophenol-4-nitrophenolate chromophores is formed. The structural differences and similarities appear on comparing Fig. 1, 2 and 5. The chains of octahedra in $\text{Na}_4\text{NP}^-4\text{NP}$ are a condensation of the independent octahedral units of Na_4NP .

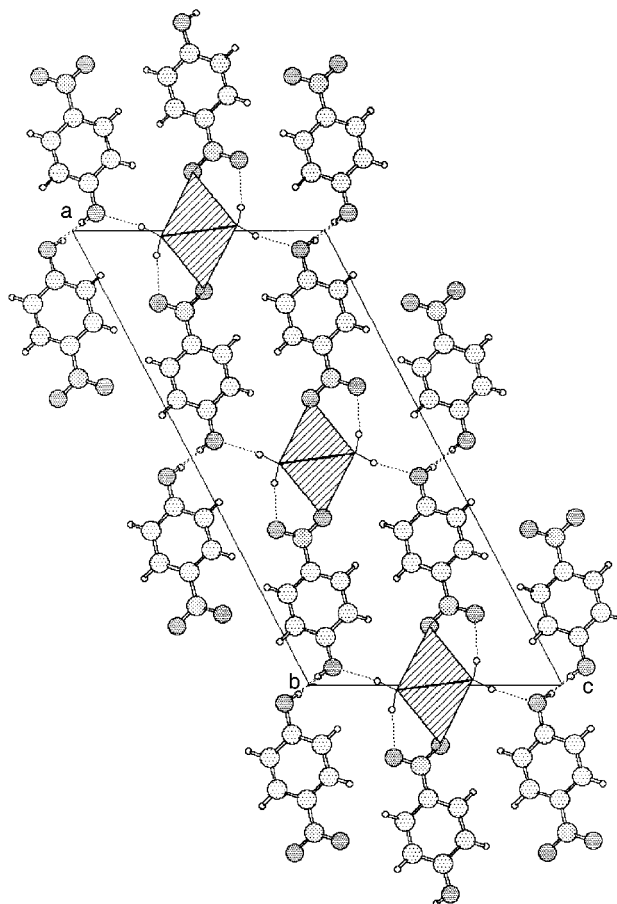


Fig. 4 Projection of the sodium 4-nitrophenolate 4-nitrophenol dihydrate structure along the *b* axis.

Nonlinear optical efficiency

Neutral 4-nitrophenol and the 4-nitrophenolate anion are both hyperpolarisable species and are arranged in a non-centrosymmetric fashion in the crystal, an arrangement which is responsible for second harmonic generation. The angle θ between

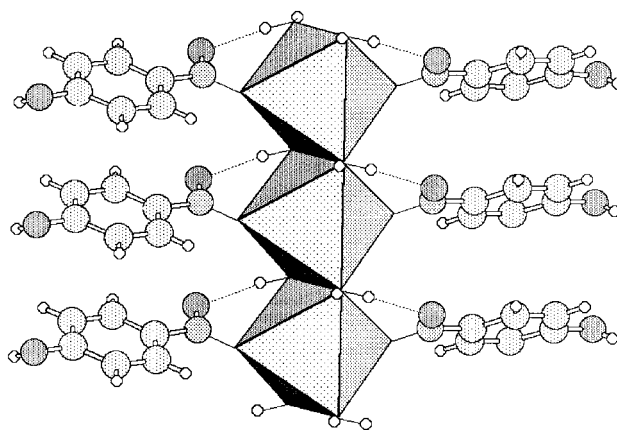


Fig. 5 Chains of NaO_6 edge shared octahedra in the crystal structure of sodium 4-nitrophenolate 4-nitrophenol dihydrate.

the molecular or anionic charge transfer axis and the main symmetry operator of the point group is an important parameter for the quantitative appreciation of macroscopic susceptibilities $\chi(2)$ following the model of Zyss and Oudar applied to one-dimensional charge transfer chromophores.¹¹ In the Na4NP crystal of *Ima2* symmetry $\theta = 78.7^\circ$ and in the Na4NP-4NP crystal with *C2* symmetry $\theta = 86.4^\circ$. The ideal angle for the maximum nonlinear efficiency should be 54.74° in the *mm2* and *2* point groups. In these two cases we observe that only one oxygen atom of the nitro group participates in sodium atom coordination. The H-bond which links the second oxygen atom of the nitro group (Fig. 3) adjusts the orientation of the molecular charge transfer axis with respect to the twofold axis acting unfavourably in the Na4NP-4NP structure. The chromophore orientation is better in the Na4NP structure. The chromophores in the Na3M4NP structure of *Cc* symmetry (Fig. 2) are not ideally oriented $\theta = 10.7^\circ$ compared with the ideal value 35.26° in the point group *m* (here θ is the angle between the molecular charge transfer axis and the *b* axis perpendicular to the mirror *m*). We have established in a previous report^{1c} that the nonlinear optical efficiencies of Na4NP and Na3M4NP crystals are comparable, reaching 49% of that of an ideal chromophore orientation. For the present crystal the efficiency is calculated as $\cos\theta\sin^2\theta = 0.0625$, i.e. 16% of the maximum efficiency (0.3849) that could be obtained by an ideal orientation of chromophores in the same point group *2*. The signal of second harmonic generation $I_{2\omega}$ observed for powder samples of Na3M4NP, Na4NP and Na4NP-4NP can be correlated qualitatively with the signals of urea and 3-methyl-4-nitropyridine-1-oxide (POM)¹² under the same experimental conditions: powders with similar particle sizes illuminated by a Nd³⁺-YAG laser at 1.064 μm gave the following results: $I_{2\omega}(\text{urea}) < I_{2\omega}(\text{Na4NP-4NP}) < I_{2\omega}(\text{Na4NP}) = I_{2\omega}(\text{Na3M4NP}) = I_{2\omega}(\text{POM})$.

Conclusion

With this new sodium salt we confirm the design of herringbone structures based on highly polarisable anionic chromophores as an attractive route for the syntheses of nonlinear optical materials. The crystal growth of this class of materials is relatively easy. However, there are some drawbacks: (a) the systematic presence of water molecules which contribute to the octahedral coordination of the metal cation limits the crystal stability to that of many hydrates and (b) the framework of these herringbone structures based on weakly distorted

octahedral coordination of the cation does not allow a sufficient tilting of chromophores with respect to the main symmetry element, *m* or *2*, to reach the ideal values $\theta = 35.26^\circ$ or 54.74° , respectively, with which the structure would be optimised for its NLO efficiency. The weak MO₆ octahedral distortion is the main limiting condition of this engineering route. Selection of transition metals which allow relatively large distortion of their MO₆ coordinations or research into tetrahedral coordinations in which the chromophores could be involved might be good solutions to these problems.

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