

Sodium 5-nitro-2-pyridonate
trihydrateMeiyappan Muthuraman,^a Jean-François Nicoud^b and
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The title compound, alternatively sodium pyridin-2-olate trihydrate, $\text{Na}^+\cdot\text{C}_5\text{H}_3\text{N}_2\text{O}_3^-\cdot 3\text{H}_2\text{O}$, crystallizes in the $P\bar{1}$ space group. It is made up of edge-shared chains of NaO_6 octahedra with five water molecules and one 5-nitro-2-pyridonate anion. Four of these water molecules are bicoordinating, involved in connecting the adjacent octahedra, and the fifth is coordinated to only one octahedron. The crystal structure is stabilized by a network of strong $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ interactions. The organic moieties occupy the space between the chains with an antiparallel alignment.

Comment

Metal-organic salts containing non-linear optically (NLO) active organic chromophores have attracted much attention in recent decades. Sodium 4-nitrophenolate dihydrate (Na4NP), which crystallizes in the non-centrosymmetric space group $Ima2$ (Minemoto *et al.*, 1992), is one of the extensively studied forerunners in this class of materials (Minemoto *et al.*, 1993, 1994; Brahadeeswaran *et al.*, 1998). Other sodium salts of 4-nitrophenolates have also been studied within the context of designing efficient organic-inorganic hybrid crystals for NLO applications (Masse *et al.*, 1999; Muthuraman *et al.*, 1999). In these non-centrosymmetric salts, the nitrophenolate chromophores are attached to the distorted octahedral chain with a herring-bone motif and thus their molecular polarizabilities contribute efficiently to the macroscopic NLO activity (Muthuraman *et al.*, 2000). Another analogous NLO chromophore is 5-nitro-2-pyridone (5N2py), in which one C-H (*ortho* to OH) is replaced by N. The sodium salt of 5N2py (Na5N2py) crystallizes as pale yellow needles. This crystal does not show any second harmonic generation activity when irradiated with a 1064 nm Nd^{3+} :YAG laser, indicating a centrosymmetric crystal structure. We undertook the crystal structure investigation of this sodium salt in order to compare its crystal structure with that of non-centrosymmetric Na4NP

and to understand the effects caused by the replacement of the phenyl ring by a pyridyl ring.

A view of the asymmetric unit is shown in Fig. 1. The present crystal structure contains three water molecules, unlike Na4NP which is a dihydrate. Na5N2py consists of a chain of edge-shared NaO_6 octahedra with five water molecules and one 5-nitro-2-pyridonate anion. The packing

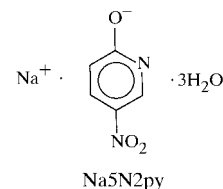


diagram is shown in Fig. 2. The adjacent octahedral units do not share the opposite edges but form a *cis*-chain (Fig. 2), as in the case of MoOCl_3 (Drew & Tomkins, 1970). The distortion arises due to strong $\text{O}-\text{H}\cdots\text{N}$ [$\text{O4}\cdots\text{N1}$ 3.011 (2) and $\text{O5}\cdots\text{N1}$ 2.992 (2) Å] interactions of the pyridine N atom with the adjacent chain. The adjacent octahedral chains are held together by strong $\text{O}-\text{H}\cdots\text{O}^-$ interactions [$\text{O1}\cdots\text{O4}$ 2.755 (2), $\text{O1}\cdots\text{O6}$ 2.797 (2) and 2.875 (2) Å], in addition to the $\text{O}-\text{H}\cdots\text{N}$ interactions. Moreover, in the present crystal structure, only one nitro oxygen (O3) is involving in metal coordination [$\text{Na1}-\text{O3}$ 2.556 (2) Å] and the other (O2) forms $\text{C}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ interactions [$\text{C5}\cdots\text{O2}$ 3.320 (3) and $\text{O2}\cdots\text{O5}$ 2.891 (2) Å], whereas in Na4NP , both the nitro-O atoms are involved in metal coordination [$\text{Na}-\text{O}$ 2.320 (9) and 2.664 (8) Å]. The $\text{N2}-\text{O3}$ distance [1.213 (2) Å] is significantly less than those in Na4NP [1.238 (12) and 1.253 (12) Å], which could be attributed to the lone pair of electrons on the pyridyl N atom. The organic moieties adopt an antiparallel alignment between the octahedral chains and are connected to each other by $\text{C}-\text{H}\cdots\text{O}$ interactions [$\text{C5}\cdots\text{O2}$ 3.320 (3) Å]. Thus, the crystal structure is stabilized by an extensive strong hydrogen-bond network.

Comparison of the crystal structure of Na5N2py with the non-centrosymmetric metal 4-nitrophenolates suggests that the nitro-group bicoordination and the opposite edge-shared octahedral chain play major roles in the non-centrosymmetric crystal packing. In magnesium 4-nitrophenolate dihydrate (Sharma *et al.*, 1997) and the isotopic sodium 4-nitro-

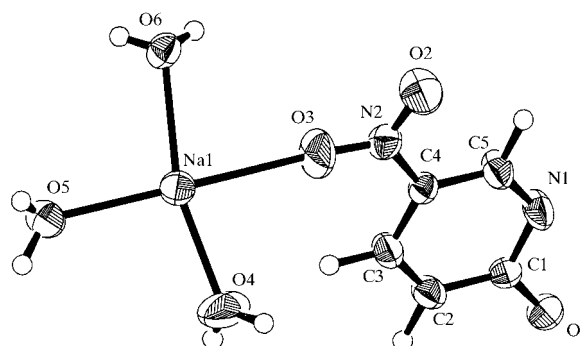


Figure 1

A labelled drawing of the asymmetric unit of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

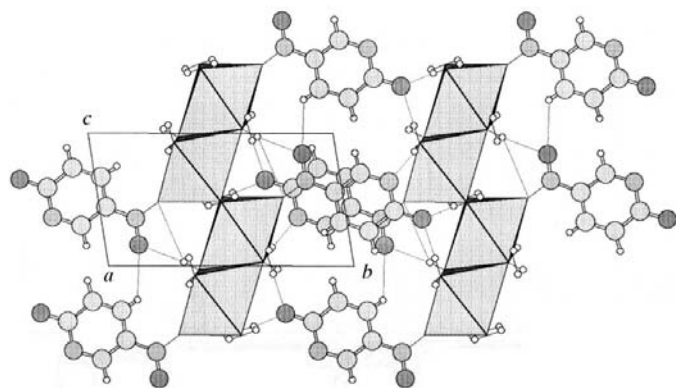


Figure 2
The molecular packing viewed in the *bc* plane. The NaO_6 octahedra are shown in an octahedral representation. All constituents of the organic molecules are represented. The small empty circles are H atoms.

phenolate-4-nitrophenol dihydrate (Muthuraman *et al.*, 1999), the octahedral chain is formed by opposite-edge sharing. However, in these crystals, only one nitro-O atom is involved in metal coordination, which is revealed in the nearly centrosymmetric octahedra, even though they belong to the C_2 space group.

Experimental

The title compound was prepared by dissolving 5-nitro-2-pyridone (0.01 mol) in NaOH solution (0.01 *N*, 10 ml) at 313 K. Pale yellow needle crystals suitable for diffraction studies appeared after a few days and were separated from the mother liquor and air dried.

Crystal data

$\text{Na}^+\cdot\text{C}_5\text{H}_3\text{N}_2\text{O}_3\cdot 3\text{H}_2\text{O}$	$Z = 2$
$M_r = 216.13$	$D_x = 1.562 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Ag $K\alpha$ radiation
$a = 7.0044 (5) \text{ \AA}$	Cell parameters from 2258 reflections
$b = 11.182 (1) \text{ \AA}$	$\theta = 2.81\text{--}22.61^\circ$
$c = 6.3971 (8) \text{ \AA}$	$\mu = 0.102 \text{ mm}^{-1}$
$\alpha = 102.978 (8)^\circ$	$T = 296.2 \text{ K}$
$\beta = 104.697 (4)^\circ$	Needle, yellow
$\gamma = 74.017 (8)^\circ$	$0.34 \times 0.14 \times 0.11 \text{ mm}$
$V = 459.40 (9) \text{ \AA}^3$	

Data collection

KappaCCD diffractometer	$\theta_{\text{max}} = 22.61^\circ$
φ scans	$h = -9 \rightarrow 8$
2258 measured reflections	$k = -15 \rightarrow 14$
2258 independent reflections	$l = 0 \rightarrow 8$
1573 reflections with $I > 3\sigma(I)$	

Refinement

Refinement on F	H-atom parameters not refined
$R = 0.051$	$w = 1/[\sigma^2(F_o)]$
$wR = 0.057$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.910$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
1573 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
127 parameters	

Water H atoms were found by difference Fourier syntheses and not refined. H atoms on carbon were fixed at distances of 1.08 Å. The

Table 1
Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{O4--H5}\cdots\text{O1}^{\text{i}}$	0.71	2.05	2.755 (2)	173
$\text{O6--H8}\cdots\text{O1}^{\text{ii}}$	0.84	2.06	2.875 (2)	166
$\text{O6--H9}\cdots\text{O1}^{\text{iii}}$	0.84	1.96	2.797 (2)	171
$\text{O5--H7}\cdots\text{O2}^{\text{iv}}$	0.66	2.24	2.891 (2)	170
$\text{C5--H3}\cdots\text{O2}^{\text{v}}$	1.08	2.46	3.320 (3)	136
$\text{O4--H4}\cdots\text{N1}^{\text{vi}}$	0.96	2.10	3.011 (2)	160
$\text{O5--H6}\cdots\text{N1}^{\text{vii}}$	0.97	2.08	2.992 (2)	157

Symmetry codes: (i) $2-x, -y, 2-z$; (ii) $x-1, 1+y, z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, -y, -z$; (vi) $2-x, -y, 1-z$; (vii) $x, 1+y, 1+z$.

isotropic displacement parameters of all the H atoms were fixed at $U(\text{H})_{\text{iso}} = 1.5U_{\text{eq}}$ of the parent atom and not refined.

Data collection: *KappaCCD Operation Manual* (Enraf–Nonius, 1998); cell refinement: *KappaCCD Operation Manual*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997–1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976) and *MOLVIEW* (Cense, 1990); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1079). Services for accessing these data are described at the back of the journal.

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