

Alkali Salts of Nitranilic and Cyanochloranilic Acids

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Abstract: Series of novel alkali salts of nitranilic acid (3,6-dinitro-2,5-dihydroxyquinone) and cyanochloranilic acid (3-cyano-6-chloro-2,5-dihydroxyquinone), and also of neutral cyanochloranilic acid dihydrate, were prepared and their structures were studied. The nitranilate dianion revealed a considerable conformational flexibility of nitro groups. Steric and inductive effects exerted by different substituents (nitro, cyano and chloro) and their influence on molecular geometry and crystal packing are discussed.

Keywords: nitranilic acid, cyanochloranilic acid, quinone, crystal structure.

INTRODUCTION

2,5-DIHYDROXYQUINONES are a class of versatile multifunctional ligands^[1] capable of forming various interactions, such as coordination, hydrogen bonding, ionic interactions, π -interactions etc.^[2] They can bind to transition metal ions as terminal or bridging ligands,^[2] and are able to form a wide variety of topologies, ranging from discrete complexes,^[3–8] 1D and 2D coordination polymers^[9–14] to porous 3D metal-organic frameworks.^[15,16]

A unique property of 2,5-dihydroxyquinones is their capability for face-to-face π -stacking. While aromatic compounds form either parallel, offset stacks or "T-shaped" species, face-to-face stacking is for them energetically unfavourable.^[17,18] π -stacking of quinoid compounds has been little studied; however due to their different electronic structure,^[19,20] different types of π -interactions can be expected. For 2,5-dihydroxyquinones face-to-face stacking is energetically favourable, and they form very close contacts, with centroid separation of only *ca.* 3.3 Å,^[19–22] which is significantly shorter than the sum of van der Waals radii for C atoms (3.40 Å). According to spectroscopic data and quantum chemical calculations, energy of such interactions exceeds 10 kcal mol^{−1},^[23] which is comparable to medium strong O–H...O hydrogen bonds and is for at least an order of a magnitude stronger than aromatic π -interactions (typically less than 1 kcal mol^{−1}).

Electronegative substituents reduce electron density in the quinoid ring, enhancing its redox potential and proton donor capability. Quinones are known to form relatively stable semiquinone radicals;^[24–26] in some complexes of chloranilic acid (3,6-dichloro-2,5-dihydroxyquinone) charge transfer from the metal ion to the quinoid ring was observed.^[5,27]

Electron-withdrawing substituents also enhance acidity of hydroxyl groups. Therefore, unsubstituted 2,5-dihydroxyquinone is a weak acid (its pK_a values are 2.76 and 5.18^[28]), while chloranilic acid (3,6-dichloro-2,5-dihydroxyquinone) is a medium strong one with pK_a 's of 0.76 and 3.08.^[2,29] Nitranilic acid (2,5-dihydroxy-3,6-dinitroquinone, Scheme 1a), which comprises two nitro groups, is a stronger acid than the hydronium ion: it crystallises as a hydronium salt, rather than a hydrate;^[30,31] its pK_a values are −3.0 and −0.5, respectively.^[28]

Although nitranilic acid has been known since 19th century,^[32] it has been surprisingly little studied. Only several crystal structures comprising a nitranilate anion have been deposited in the Cambridge Structural Database (CSD). Those include the hydronium,^[30] ammonium^[33] and hydrazinium^[34] nitranilate, its calcium and strontium salts^[35] and a few salts with organic cations.^[34,36] Of alkali salts, there are potassium nitranilate and monoclinic sodium nitranilate dihydrate.^[37] Despite its obvious potential as a ligand, only a few complexes with iron^[38] and manganese^[39] have been studied.

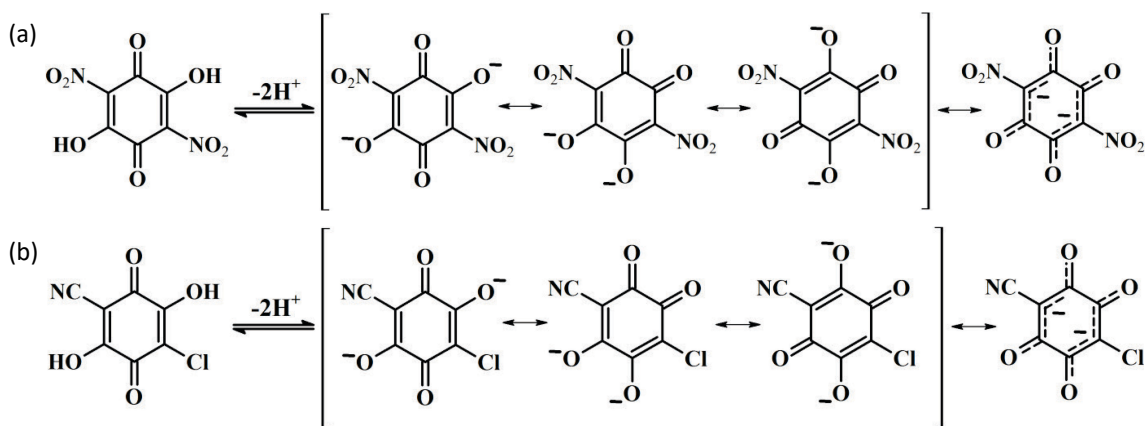
There is even less data on cyanochloranilic acid (3-cyano-6-chloro-2,5-dihydroxyquinone, Scheme 1b). Its ability to coordinate transition metals is well known,^[40] however, only a single recent publication describes a few metal complexes.^[41]

As a part of our study of crystal chemistry of quinones and semiquinone radicals, we present two novel alkali salts of nitranilic acid, neutral cyanochloranilic acid and its two alkali salts. Compared to hydrogen^[20] and halogen substituents,^[19,21,22] the nitro and cyano groups are bulky and very strongly electron-withdrawing substituents, so it is interesting to assess their steric and electronic influence on the molecular conformation and crystal packing, especially on the quinoid π -stacking.

recrystallization from boiling water.

Nitranilic acid hexahydrate was prepared by dropwise addition of *conc.* nitric acid to a wet solid sodium nitranilate. The acid is added until all solid is dissolved; after *ca.* 1 hour, orange needle-like crystals of nitranilic acid hexahydrate are formed, and are then scooped up and dried. It is necessary to remove the crystals from the solution, because nitranilic acid is unstable in highly acidic media and slowly decomposes into oxalic acid.

Sodium nitranilate dihydrate was prepared by addition of equivalent amount of sodium carbonate into a fresh aqueous solution of nitranilic acid, while for preparation of lithium caesium nitranilate monohydrate a half-equivalent of lithium carbonate and a half-equivalent



Scheme 1. The dissociation of nitranilic acid (a) and cyanochloranilic acid (b). The dianion has two delocalised π -systems separated by single C–C bonds.

EXPERIMENTAL

Preparation

All reagents used were purchased from commercial sources (Merck, Sigma-Aldrich, Kemika), were of p.a. grade and were used without further purification.

Sodium nitranilate hexahydrate was prepared according to a modified procedure by Nef:^[32] saturated acetone solution of tetrachloroquinone (chloranil, 4.00 g) was heated to 80 – 90 °C with constant stirring; saturated aqueous solution of sodium nitrite (10.00 g) was slowly added. The yellow solution quickly turned dark red and orange-yellow crystalline powder (sodium nitranilate) began to precipitate. After *ca.* 1 hour, the solution became colourless. The orange-yellow precipitate was filtered off, and a little solid NaOH was added to the solution to precipitate sodium nitranilate which was still dissolved, and then it was again filtered off. 2.51 g of raw sodium nitranilate dihydrate was obtained (η = 98.8 %). Pure crystalline sodium nitranilate dihydrate was obtained by

of caesium carbonate were used. The crystals were formed upon slow evaporation at room temperature.

Sodium cyanochloranilate trihydrate was prepared according to a modified method of Gräbe:^[42] 1.00 g of 5,6-dichloro-2,3-dicyanoquinone was added to a solution of sodium hydroxide (0.9 g in 30 mL of water) and heated to 80 – 90 °C for 2 h. The colour of the solution turned dark purple. Purple sodium cyanochloranilate trihydrate was precipitated upon addition of 2 g NaCl; the precipitate was washed with 10 % aqueous NaOH until the filtrate turned colourless.

The neutral cyanochloranilic acid dihydrate was prepared by addition of *conc.* hydrochloric acid to a solid sodium cyanochloranilate until all solid is dissolved. The orange prismatic crystals of cyanochloranilic acid dihydrate were formed upon slow evaporation at room temperature. Potassium salt of cyanochloranilic acid was prepared by addition of excess of potassium carbonate into a fresh methanol solution of sodium cyanochloranilate. The crystals were formed upon slow evaporation at room temperature.

Table 1. Crystallographic, data collection and structure refinement details

Compound	Na ₂ NA · 2H ₂ O, orthorhombic	LiCsNA · H ₂ O	H ₂ CNCA · 2H ₂ O	K ₂ CNCA · H ₂ O	Na ₂ CNCA · 3H ₂ O
Empirical formula	C ₆ H ₄ N ₂ Na ₂ O ₁₀	C ₆ H ₂ CSLiN ₂ O ₉	C ₇ H ₆ ClNO ₆	C ₇ H ₆ ClK ₂ NO ₅	C ₇ H ₆ ClNNa ₂ O ₇
Formula wt. / g mol ⁻¹	310.09	385.95	235.58	293.75	297.56
Colour	yellow	yellow	orange	red	red
Crystal dimensions / mm	0.20 × 0.18 × 0.03	0.20 × 0.09 × 0.04	0.28 × 0.18 × 0.08	0.15 × 0.10 × 0.05	0.30 × 0.05 × 0.05
Space group	<i>Pbc</i> 2 ₁	<i>Pnam</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 2/a
<i>a</i> / Å	6.6431(3)	7.6218(2)	4.9975(7)	6.962(5)	18.5638(11)
<i>b</i> / Å	9.8940(4)	17.7831(5)	8.7247(5)	9.078(5)	3.6243(2)
<i>c</i> / Å	15.6387(5)	7.7173(2)	11.1609(10)	9.180(5)	16.4606(9)
α / °	90	90	75.866(6)	63.769(5)	90
β / °	90	90	79.427(10)	74.808(5)	107.983(7)
γ / °	90	90	88.273(8)	74.916(5)	90
<i>Z</i>	4	4	2	2	4
<i>V</i> / Å ³	1027.88(7)	1046.00(5)	463.84(8)	495.2(5)	1053.38(10)
<i>D</i> _{calc} / g cm ⁻³	2.004	2.451	1.687	1.97	1.876
λ / Å	1.54179 (CuK α)	1.54179 (CuK α)	1.54179 (CuK α)	1.54179 (CuK α)	1.54179 (CuK α)
μ / mm ⁻¹	2.416	28.156	3.825	1.229	4.350
θ range / °	5.66–75.56	4.97–75.59	4.15–77.61	5.5–76.265	5.01–76.17
<i>T</i> / K	293(2)	293(2)	293(2)	293(2)	293(2)
Diffractometer type	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Range of <i>h</i> , <i>k</i> , <i>l</i>	–8 < <i>h</i> < 7; –12 < <i>k</i> < 8; –15 < <i>l</i> < 19	–9 < <i>h</i> < 9; –21 < <i>k</i> < 22; –4 < <i>l</i> < 9	–6 < <i>h</i> < 6; –10 < <i>k</i> < 8; –13 < <i>l</i> < 14	–8 < <i>h</i> < 8; –8 < <i>k</i> < 11; –11 < <i>l</i> < 11	–20 < <i>h</i> < 23; –2 < <i>k</i> < 4; –20 < <i>l</i> < 19
Reflections collected	2759	2851	3460	3245	2058
Independent reflections	1550	1167	1875	1857	1079
Observed reflections (<i>I</i> ≥ 2 σ)	1424	1070	1667	1720	1045
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>T</i> _{min} , <i>T</i> _{max}	0.2071; 1.0000	0.0754; 1.0000	0.5569; 1.0000	0.6992; 1.0000	0.75058; 1.0000
<i>R</i> _{int}	0.0356	0.094	0.0511	0.0344	0.0275
<i>R</i> (<i>F</i>)	0.0817	0.0542	0.0505	0.0387	0.0569
<i>R</i> _w (<i>F</i> ²)	0.2127	0.1593	0.1615	0.1102	0.1381
Goodness of fit	1.043	1.124	1.119	1.031	1.156
H atom treatment	Restrained	Restrained	Restrained	Restrained	Restrained
No. of parameters, restraints	197, 7	101, 13	154, 8	151, 3	103, 7
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (eÅ ⁻³)	1.080; –0.502	1.415; –1.257	0.374; –0.415	0.334; –0.33	0.323; –0.405

X-ray Structural Analysis

Single-crystal X-ray measurements were performed on an Oxford Diffraction Xcalibur Nova R diffractometer with a microfocus Cu-tube using mirror-monochromated CuK α radiation (λ = 1.54179 Å). Program package CrysAlis PRO^[43] was used for data reduction and multi-scan absorption correction.

The structures were solved using SHELXS97^[44] and refined with SHELXL-2017.^[44] The structures were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined using the

following restraints: for water molecules $d(\text{O} \cdots \text{H}) = 0.95$ Å; $d(\text{H} \cdots \text{H}) = 1.50$ Å; hydrogen atoms bound to the neutral cyanochloranilic acid were refined without restraints.

Molecular geometry calculations were performed by PLATON,^[45] and molecular graphics were prepared using ORTEP-3,^[46] and CCDC-Mercury.^[47] Crystallographic and refinement data for the structures reported in this paper are shown in Table 1.

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic

Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC 1832846-1832850 contain the supplementary crystallographic data for this paper.

RESULTS AND DISCUSSION

We have prepared and structurally characterised two alkali salts of nitranilic acid, orthorhombic polymorph of sodium nitranilate dihydrate ($\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$), lithium caesium nitranilate monohydrate ($\text{LiCsNA} \cdot \text{H}_2\text{O}$); neutral cyanochloranilic acid dihydrate ($\text{H}_2\text{CNCA} \cdot 2\text{H}_2\text{O}$) and its two salts, sodium cyanochloranilate trihydrate ($\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$) and potassium cyanochloranilate monohydrate ($\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$).

Molecular Geometries

The molecular geometries of the nitranilate anions (Table 2) are in a good agreement with the previously determined ones^[30,31,33,34] and also dianions of other substituted 2,5-dihydroxyquinones.^[2,19–21] Therefore, the resonance depicted in Scheme 1a is well-justified. In $\text{LiCsNA} \cdot \text{H}_2\text{O}$ the molecular symmetry is C_s , and the mirror plane is normal to the ring plane; C–N bonds are located on the mirror plane (Figure 1a). In orthorhombic $\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$ the anion is located in a general position, with C_1 symmetry (Figure 1b).

In $\text{LiCsNA} \cdot \text{H}_2\text{O}$ the anion is planar within the experimental error - the nitro groups are located in the ring plane (Figure 1a, Table 3), while in the orthorhombic $\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$ both nitro groups are twisted outside of the ring plane (Figure 1b, Table 3) and the ring is slightly puckered [its Cremer-Pople^[48] puckering amplitude Q is 0.057(5) Å]. Dihedral angles between the quinoid ring plane and a nitro group for the previously known structures range between 3.9 °^[34] and 56.6 °;^[36] in the nitranilic acid hexahydrate it is 23 °.^[31,31] Apparently, rotation about the C–N bond is easy and the orientation of the nitro group depends on the molecular environment.

Molecular geometry of the cyanochloranilate anion in $\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$ (Table 2) is also in a good agreement with the literature data,^[40,41] and the π electrons are delocalised as in Scheme 1b; the anion is located in a general position (Figure 2a). However, the centroid of the cyanochloranilate in $\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$ is located at an inversion centre (Figure 2b), so the anion is disordered over two positions (due to symmetry, p.p. is 0.5 for both components). In both cases the anion is planar within experimental error.

Geometry of the cyanochloranilate dianion in $\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$ revealed a slight asymmetry due to a stronger electron-withdrawing capability of the cyano group compared to the chlorine: the double C=C bond next to the

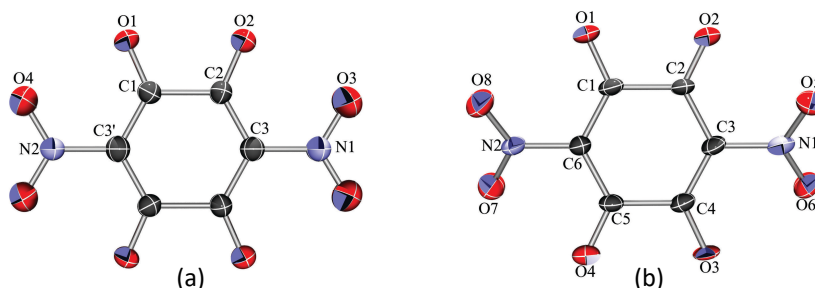


Figure 1. ORTEP-3^[46] drawings of nitranilate anions from a) $\text{LiCsNA} \cdot \text{H}_2\text{O}$, and b) orthorhombic $\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$ with atom numbering schemes. Displacement ellipsoids are drawn for the probability of 50 %.

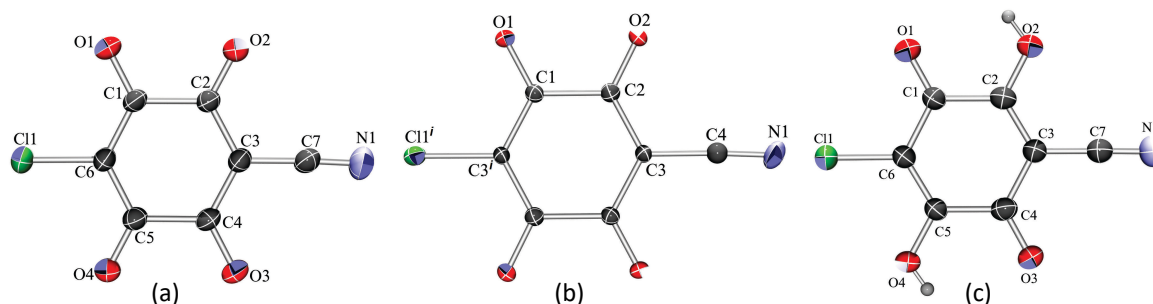


Figure 2. ORTEP-3^[46] drawings of cyanochloranilate anions from $\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$ (a) and $\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$ (b), and neutral cyanochloranilic acid from $\text{H}_2\text{CNCA} \cdot 2\text{H}_2\text{O}$ (c) with atom numbering schemes. Displacement ellipsoids are drawn for the probability of 50 %.

Table 2. Bond lengths (Å) in studied quinoid rings. Symmetry operators: *i*) $1-x, y, 2-z$; *ii*) $1-x, -y, 2-z$

LiCsNA · H ₂ O			
C1 – C2	1.562(8)	C1 – O1	1.240(8)
C2 – C3	1.411(7)	C2 – O2	1.237(7)
C1 – C3 ^{<i>i</i>}	1.413(8)	C3 – N1	1.448(11)
N1 – O3	1.193(8)	C3 ^{<i>i</i>} – N2	1.434(12)
N2 – O4	1.212(8)		
Na ₂ NA · 2H ₂ O, orthorhombic			
C1 – C2	1.551(6)	C1 – O1	1.247(7)
C2 – C3	1.434(7)	C2 – O2	1.216(6)
C3 – C4	1.410(7)	C4 – O3	1.225(7)
C4 – C5	1.555(6)	C5 – O4	1.241(7)
C5 – C6	1.414(8)	N1 – O5	1.234(6)
C6 – C1	1.427(6)	N1 – O6	1.213(7)
C3 – N1	1.455(6)	N2 – O7	1.223(7)
C6 – N2	1.448(6)	N2 – O8	1.229(7)
H ₂ CNCA · 2H ₂ O			
C1 – C2	1.515(4)	C1 – O1	1.212(3)
C2 – C3	1.363(4)	C2 – O2	1.299(3)
C3 – C4	1.452(4)	C4 – O3	1.221(3)
C4 – C5	1.497(4)	C5 – O4	1.315(3)
C5 – C6	1.356(4)	C3 – C7	1.432(4)
C6 – C1	1.452(4)	C7 – N1	1.136(4)
K ₂ CNCA · H ₂ O			
C1 – C2	1.547(3)	C1 – O1	1.246(3)
C2 – C3	1.420(3)	C2 – O2	1.228(3)
C3 – C4	1.413(4)	C4 – O3	1.241(3)
C4 – C5	1.542(3)	C5 – O4	1.242(3)
C5 – C6	1.405(3)	C3 – C7	1.421(4)
C6 – C1	1.397(4)	C7 – N1	1.140(4)
Na ₂ CNCA · 3H ₂ O			
C1 – C2	1.529(4)	C1 – O1	1.247(4)
C2 – C3	1.400(5)	C2 – O2	1.257(4)
C3 – C1 ^{<i>ii</i>}	1.418(4)	C4 – O3	

Table 3. Dihedral angles (°) between nitro groups and least-squares quinoid ring planes. The nitro groups are labelled according to their nitrogen atom

	N1	N2
LiCsNA · H ₂ O	0.6(11)	3.3(9)
Na ₂ NA · 2H ₂ O, orthorhombic	32.5(6)	30.5(6)

cyano group (C2-C3, Table 2) is by 0.015 Å shorter than the one next to chlorine atom (C5-C6, Table 2). This effect could not be observed in Na₂CNCA·3H₂O due to the disorder, while in the neutral cyanochloranilic acid (Table 2, Figure 2c) it is within 3 e.s.d.'s. Otherwise, the neutral cyanochloranilic acid is similar to other neutral 2,5-dihydroxyquinones.^[2,22,49–51] Similar asymmetry was observed in 5,6-dichloro-2,3-dicyanoquinone (DDQ) and its radical anion.^[52–54]

Crystal Packings

In orthorhombic $\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$ two symmetry-independent sodium ions are present, both having a distorted octahedral coordination typical for sodium. Na1 bonds to three carbonyl and one nitro oxygen, from two anions; in addition there are two water molecules in a *trans*-arrangement. Coordination of Na2 is similar, however, the water molecules are in a *cis*-arrangement. The packing is layered, with alternating layers of cations and anions parallel to (001) (Figure 3). Water molecules further stabilise the packing by hydrogen bonding to nitro- and carbonyl oxygens (Table 4).

In $\text{LiCsNA} \cdot \text{H}_2\text{O}$ Cs ions are coordinated by five carbonyls, five nitro oxygens (from five different anions) and a single water molecule. The shape of the coordination polyhedron may be described as a severely distorted tricapped square antiprism. Li cations have a usual square pyramidal coordination, being surrounded by four carbonyl oxygens (from two anions) and a single water molecule occupying the apical position. 3D packing is achieved through cation-anion interactions and water-carbonyl oxygen hydrogen bonds (Table 4, Figure 4).

In $\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$ the sodium cation has distorted trigonal bipyramidal coordination (CN 6); it forms three contacts with O atoms from the dianion and two with the water molecule. The crystal packing is layered with cation-anion layers parallel to (001), which are connected by hydrogen bonds (Figure 5). Asymmetric unit comprises one and a half water molecules (three proton donors) which form four symmetry-independent hydrogen bonds with

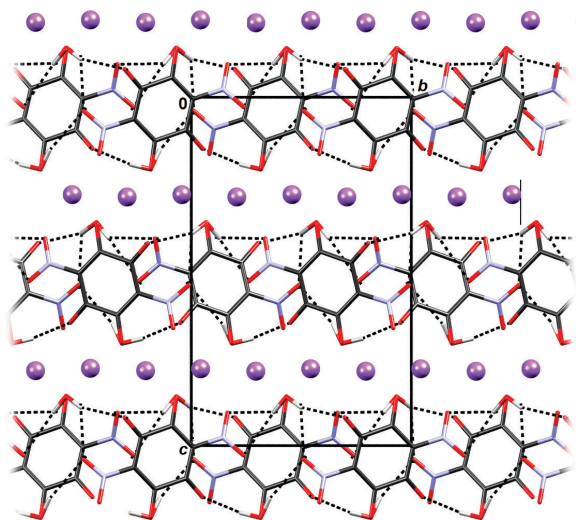


Figure 3. Crystal packing of orthorhombic $\text{Na}_2\text{NA} \cdot 2\text{H}_2\text{O}$ viewed in the direction [100]. Sodium cations are shown as spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.

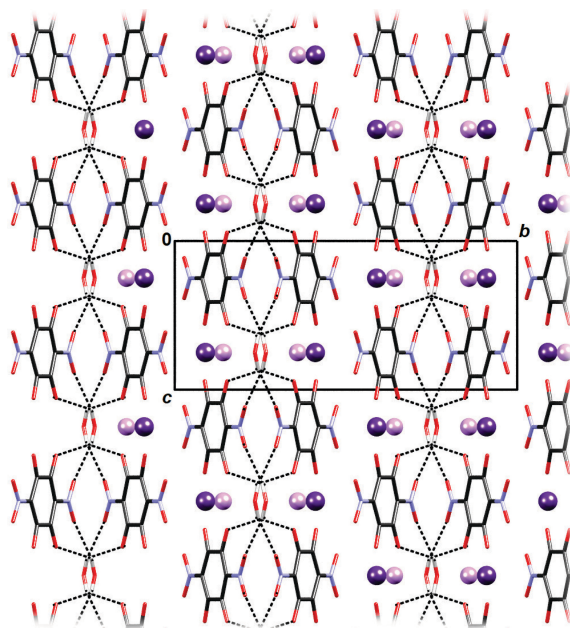


Figure 4. Crystal packing of $\text{LiCsNA} \cdot \text{H}_2\text{O}$ viewed in the approximate direction [100]. Lithium and caesium cations are shown as violet and magenta spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.

water molecules, anion O atoms and cyano groups as acceptors (Table 4). In addition, π -stacking of cyanochloranilate dianions can be observed (Table 5) with geometry similar to stacking of other 2,5-dihydroxyquinonate dianions.^[2,19–21]

Asymmetric unit of $\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$ contains two potassium cations with different coordinations. K1 is heptacoordinated, in a shape of a capped distorted octahedron and forms contacts with 3 oxygens from the dianions, N and Cl atoms and a water molecule; K2 has a severely distorted hexacoordinated environment which could be best described as a badly distorted capped square pyramid. A single water molecule links two neighbouring cyanochloranilate anions through three symmetry-independent hydrogen bonds (Table 4, Figure 6), forming chains parallel to [001]. There are infinite π -stacks (Table 5) extending in the direction [100], with geometry similar to other 2,5-dihydroxyquinonate dianions.^[2,19–22] Thus, 3D packing is achieved (Figure 6).

Asymmetric unit of $\text{H}_2\text{CNCA} \cdot 2\text{H}_2\text{O}$ comprises six strong proton donors (two hydroxyl groups and two water molecules) forming seven symmetry-independent hydrogen bonds (Table 4). The main motive are 2D hydrogen-bonded double layers lying in the plane (001) (Figure 7), and only dispersion interaction exist between those double layers.

Table 4. Geometric parameters of hydrogen bonds (Å, °)

	$d(D-H) / \text{\AA}$	$d(H\cdots A) / \text{\AA}$	$d(D\cdots A) / \text{\AA}$	$d(D-H\cdots A) / ^\circ$	Sym. op. on A
LiCsNA · H₂O					
O5–H5 \cdots O3	0.94(6)	2.33(7)	3.116(8)	141(9)	$-1 + x, y, z$
Na₂NA · 2H₂O, orthorhombic					
O9–H9A \cdots O2	0.95(4)	2.04(6)	2.973(5)	169(8)	$1 - x, 1 - y, -1/2 + z$
O9–H9A \cdots O5	0.95(4)	2.60(8)	2.941(7)	102(5)	$1 - x, 1 - y, -1/2 + z$
O9–H9B \cdots O5	0.95(6)	2.38(6)	2.941(7)	117(6)	$1 - x, 1 - y, -1/2 + z$
O9–H9B \cdots O7	0.95(6)	2.37(6)	3.293(7)	163(7)	$1 - x, 1 - y, -1/2 + z$
O9–H9B \cdots O8	0.95(6)	2.41(8)	2.939(6)	115(5)	$1 - x, 1 - y, -1/2 + z$
O10–H10A \cdots O5	0.95(8)	2.39(7)	3.299(6)	162(8)	$1 - x, 1/2 + y, z$
O10–H10A \cdots O6	0.95(8)	2.24(9)	2.978(6)	134(6)	$1 - x, 1/2 + y, z$
O10–H10B \cdots O4	0.95(6)	2.08(6)	2.952(6)	151(6)	$1 - x, -1/2 + y, z$
O10–H10B \cdots O4	0.95(6)	2.34(6)	2.952(8)	122(5)	$1 - x, -1/2 + y, z$
K₂CNCA · H₂O					
O5–H5A \cdots O4	0.93(4)	1.94(4)	2.849(3)	164(3)	$-x, -1/2 + y, 3/2 - z$
O5–H5B \cdots O4	0.92(4)	2.02(4)	2.908(3)	161(2)	$-x, 2 - y, 2 - z$
O5–H5B \cdots Cl1	0.92(4)	2.85(4)	3.467(2)	125(4)	$-x, 2 - y, 2 - z$
Na₂CNCA · 3H₂O					
O3–H3A \cdots N1	0.93(4)	2.43(5)	3.099(4)	129(5)	$1/2 - x, -1/2 - y, 3/2 - z$
O3–H3A \cdots N1	0.93(4)	2.56(5)	3.150(8)	122(4)	$1/2 - x, 1/2 - y, 3/2 - z$
O3–H3B \cdots O4	0.96(3)	1.82(3)	2.773(2)	170(6)	$1 - x, -y, 1 - z$
O4–H4 \cdots O1	0.94(4)	1.90(5)	2.781(3)	155(5)	$x, -1/2 - y, -1/2 + z$
H₂CNCA · 2H₂O					
O2–H2 \cdots O5	0.84(4)	1.71(4)	2.536(3)	168(4)	x, y, z
O4–H4 \cdots O6	0.75(4)	1.89(4)	2.586(3)	95(2)	x, y, z
O5–H5A \cdots O3	0.93(3)	2.03(4)	2.935(3)	166(4)	$x, -1 + y, z$
O5–H5B \cdots N1	0.93(3)	2.07(3)	2.874(4)	143(4)	$3 - x, 1 - y, -z$
O6–H6A \cdots O1	0.93(3)	2.37(4)	3.086(4)	134(4)	$x, 1 + y, z$
O6–H6A \cdots O5	0.93(3)	2.32(4)	3.056(4)	136(4)	$-1 + x, 1 + y, z$
O6–H6B \cdots O6	0.90(4)	2.57(2)	2.907(5)	103(2)	$1 - x, 2 - y, 1 - z$

CONCLUSIONS

We have prepared and structurally characterised four novel compounds, lithium caesium nitrilic acid monohydrate (LiCsNA · H₂O), neutral cyanochloranilic acid dihydrate (H₂CNCA · 2H₂O) and its two salts, sodium cyanochloranilic trihydrate (Na₂CNCA · 3H₂O) and potassium cyanochloranilic monohydrate (K₂CNCA · H₂O); also we have determined structure of novel, orthorhombic, polymorph of Na₂NA · 2H₂O.

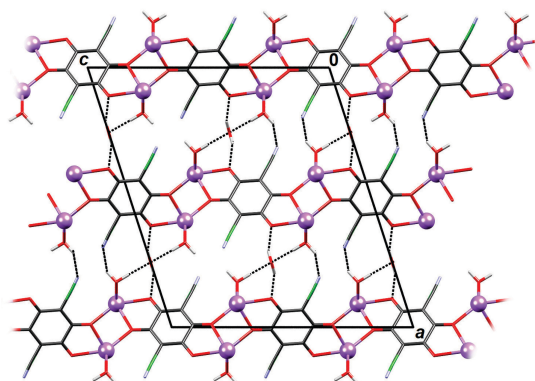
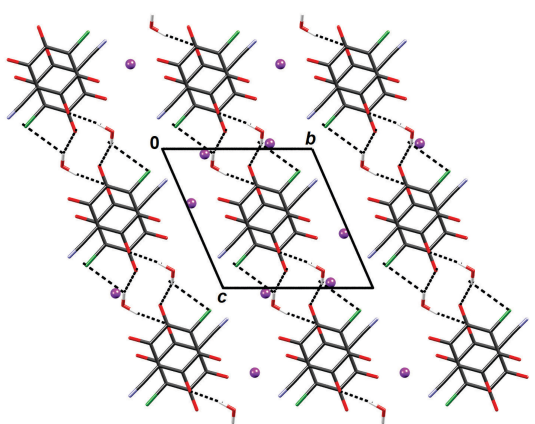
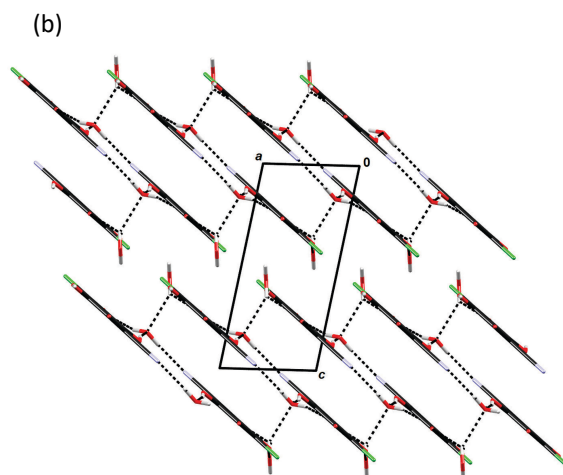
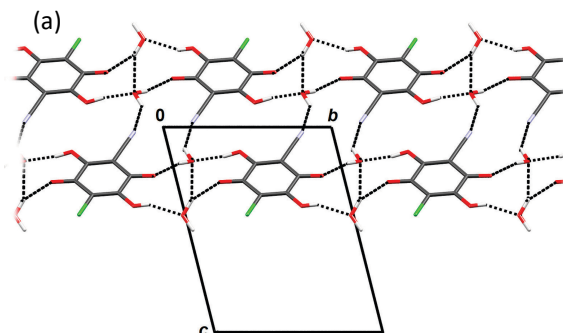
Bulky, out-of-plane nitro groups effectively prevent π -stacking, so no stacking was observed in the structures of nitrilates. On the other hand, in salts of planar cyanochloranilates the dianions stack in an offset fashion, similar

to other planar 2,5-dihydroxyquinones.^[2,19,21,22] According to geometric parameters, these interactions are much weaker than in face-to-face stacks of hydrogen chloranilates,^[23] and can be compared to aromatic stacks.

Inductive effect of the substituents affects not only acidity of hydroxyl groups, but also molecular geometry: double C=C bond and also the delocalised C–C bond next to the cyano group (C2–C3, Table 2) are shorter than the corresponding bond next to the chlorine substituent (C5–C6, Table 2). This effect may be used to fine-tune proton-donor and complexation capabilities of the 2,5-dihydroxyquinones, and could be therefore used in design and construction of coordination polymers and metal-organic frameworks.^[1]

Table 5. Geometric parameters of π interactions (\AA , $^\circ$)

$\pi \cdots \pi$	$\text{Cg}^{(a)} \cdots \text{Cg} / \text{\AA}$	$\alpha^{(b)}$	$\beta^{(c)}$	$\text{Cg} \cdots \text{plane}(\text{Cg2}) / \text{\AA}$	Offset/ \AA	Symm. op. on Cg2
$\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$						
$\text{C1} \rightarrow \text{C6} \cdots \text{C1} \rightarrow \text{C6}$	3.6243(19)	0	26.9	3.2313(13)	1.641	$x, -1 + y, z$
$\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$						
$\text{C1} \rightarrow \text{C6} \cdots \text{C1} \rightarrow \text{C6}$	3.536(3)	0	17.5	3.3713(9)	1.066	$-x, 1 - y, 3 - z$
$\text{C1} \rightarrow \text{C6} \cdots \text{C1} \rightarrow \text{C6}$	3.782(3)	0	31.5	3.2309(9)	1.966	$1 - x, 1 - y, 3 - z$

^(a) Cg = centre of gravity of the aromatic ring;^(b) α = angle between planes of two interacting rings;^(c) β = angle between $\text{Cg} \cdots \text{Cg}$ line and normal to the plane of the first interacting ring.**Figure 5.** Crystal packing of $\text{Na}_2\text{CNCA} \cdot 3\text{H}_2\text{O}$ viewed in the direction $[010]$. Sodium cations are shown as spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.**Figure 6.** Crystal packing of $\text{K}_2\text{CNCA} \cdot \text{H}_2\text{O}$ viewed in the direction $[100]$. Potassium cations are shown as spheres of arbitrary radii and hydrogen bonds are shown as dashed lines.**Figure 7.** Crystal packing of $\text{H}_2\text{CNCA} \cdot 2\text{H}_2\text{O}$ viewed in the directions $[100]$ (a) and $[010]$ (b). Hydrogen bonds are shown as dashed lines.

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