

Synthesis, Recrystallization and Structural Characterization of a Novel Sodium Structure $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$

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Summary: A novel sodium Alizarin Yellow R structure $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$ has been observed by accident when 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid mono sodium salt (mono sodium salt of Alizarin Yellow R) was used as a ligand. The tetramer was characterized by single-crystal X-ray diffraction, FT-IR spectroscopy and UV/Vis spectroscopy. The tetramer crystallizes in triclinic space group $P\bar{1}$ with $a = 7.2202(9)$ Å, $b = 13.0624(15)$ Å, $c = 17.0605(19)$ Å, $\alpha = 77.137(2)^\circ$, $\beta = 80.922(2)^\circ$, $\gamma = 83.354(2)^\circ$. $V = 1543.56(3)$ Å³, $Z = 2$. There are two crystallographically independent sodium centers in the crystal structure. The local coordination geometry of the two sodium centers $[\text{NaO}_6]$ can be best described as slightly distorted octahedrons. The aromatic π - π stacking plays an important role in the formation of 3D network.

Keywords: Metal-organic complex; Alizarin Yellow R; Crystal structure; Recrystallization; tetramer.

Introduction

In recent years, the syntheses of metal-organic complexes have received great attentions from researchers. In the sodium complexes, the coordination number of sodium atoms ranges from four to eight [1-5], giving rise to different dimensional architectures. Owing to the ligands, the sodium complexes have been studied for catalysis in ring-opening polymerization [6], antibacterial and antifungal activities [7] and other fields [8]. Because of the widespread applications in many areas, aromatic azo complexes constitute a very important series of organic complexes, which are well known for their use as analytical reagents [9], in dye industry [10] or as drugs [11].

Alizarin Yellow R is a kind of azo dyes with the structure combining nitrobenzene and salicylic acid through a diazo group. It is occasionally used as a pH indicator. Through the same functional groups as those of salicylic acid to form a metal complex, this reagent can be expected to react with a metal ion, regarded as a metal scavenger [12].

Herein, a new sodium Alizarin Yellow R structure $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$ has been observed in solution by accident when 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid mono sodium salt was used as ligands. While the major application of Alizarin Yellow R is in the chemical industry and its performance is exploring, this paper focuses on the new crystal structure to remedy the shortage of its structure research. Strong hydrogen bonds exist between aqua and oxygen atoms of carboxyl and nitril in the structure. The aromatic π - π stacking plays an important role in the formation of 3D network.

Results and Discussion

Fig. 1 shows the tetramer structure of the crystal $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$. Each tetramer structure consists of four sodium atoms, four 2-hydroxy-5-((4-nitrophenyl)azo) benzoic anions and twelve water molecules. There are two crystallographically independent sodium centers (Na1 and Na2) in the crystal structure. The local coordination geometry of the two sodium centers $[\text{NaO}_6]$ can be best described as slightly distorted octahedrons (the selected bond lengths and angles in Table-1). The coordination polyhedrons of the tetramer are connected by sharing common edges in each molecule (Fig. 1). The Na1 coordinate environment involves one oxygen atom from 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid and five oxygen atoms from water molecules (three of them are terminal coordinated water, and others are μ_2 -bridged water molecules). Na2 is also coordinated by six oxygen atoms, four from μ_2 -bridged water molecules while the rest two from 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid (one of them belongs to carboxyl, the other one belongs to nitro). Both two Na cations are linked by two μ_2 -bridged water molecules. The distance between Na1 and Na2 is 3.4987(15) Å, which is slightly longer than a sodium ditetrazole coordination polymer [3.4413(18) Å] synthesized by Huang [13], while the distance of Na2-Na2 [3.355(2) Å] is shorter than it (4.174 Å). The distance [2.304(2) Å-2.497(2) Å] of Na-O_w bonds are shorter than that [2.4014(12) Å-2.5072(14) Å] in $[\text{Na}(\text{C}_6\text{H}_4\text{N}_5)(\text{H}_2\text{O})_2]_n$ [14].

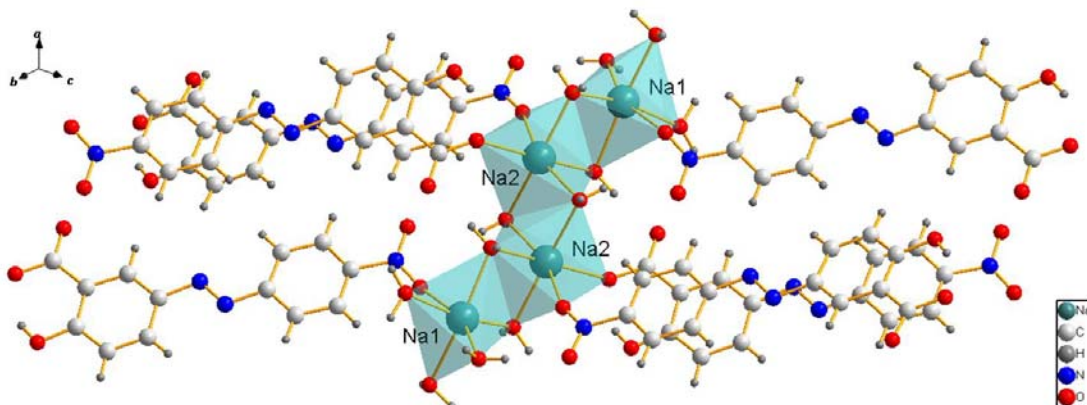


Fig. 1: The tetramer structure of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$. The slightly distorted octahedrons $[\text{NaO}_6]$ share common edges in each molecule.

Table-1: Select bond distances (\AA) and angles ($^\circ$) for $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$.

Na1—O16	2.304(2)	Na2—O3	2.3588(19)
Na1—O15	2.373(2)	Na2—O13	2.368(2)
Na1—O12	2.419(2)	Na2—O12	2.371(2)
Na1—O13	2.4219(19)	Na2—O11 ⁱⁱ	2.4187(19)
Na1—O14	2.484(2)	Na2—O11	2.464(2)
Na1—O2 ^j	2.497(2)	Na2—O6	2.677(2)
Na1—Na2	3.4987(15)	Na2—Na2 ⁱⁱ	3.355(2)
O16—Na1—O15	87.37(9)	O13—Na2—O11 ⁱⁱⁱ	97.65(7)
O16—Na1—O12	86.84(9)	O12—Na2—O11 ⁱⁱⁱ	84.40(7)
O15—Na1—O12	111.81(8)	O3—Na2—O11	91.14(7)
O16—Na1—O13	159.92(10)	O13—Na2—O11	165.29(7)
O15—Na1—O13	112.67(8)	O12—Na2—O11	84.48(7)
O12—Na1—O13	84.45(7)	O11 ⁱⁱⁱ —Na2—O11	93.18(7)
O16—Na1—O14	96.61(9)	O3—Na2—O6	95.40(7)
O12—Na1—O14	165.40(8)	O13—Na2—O6	76.17(7)
O13—Na1—O14	87.68(7)	O12—Na2—O6	74.12(7)
O16—Na1—O2 ^j	79.04(9)	O11 ⁱⁱⁱ —Na2—O6	157.86(7)
O15—Na1—O2 ^j	159.10(8)	O11—Na2—O6	90.09(7)
O12—Na1—O2 ^j	83.45(7)	O3—Na2—Na2 ⁱⁱ	102.60(6)
O13—Na1—O2 ^j	82.00(7)	O13—Na2—Na2 ⁱⁱ	143.73(7)
O14—Na1—O2 ^j	83.29(7)	O12—Na2—Na2 ⁱⁱ	81.90(6)
O16—Na1—Na2	128.61(8)	O11 ⁱⁱⁱ —Na2—Na2 ⁱⁱ	47.15(5)
O15—Na1—Na2	115.29(6)	O11—Na2—Na2 ⁱⁱ	46.03(5)
O12—Na1—Na2	42.54(5)	O6—Na2—Na2 ⁱⁱ	131.98(7)
O13—Na1—Na2	42.48(5)	O3—Na2—Na1	135.64(6)
O14—Na1—Na2	130.02(6)	O13—Na2—Na1	43.68(5)
O2 ^j —Na1—Na2	85.61(6)	O12—Na2—Na1	43.61(6)
O3—Na2—O13	95.28(7)	O11 ⁱⁱⁱ —Na2—Na1	96.98(6)
O3—Na2—O12	168.59(8)	O11—Na2—Na1	125.13(6)
O13—Na2—O12	86.71(7)	O6—Na2—Na1	63.69(5)
O3—Na2—O11 ⁱⁱⁱ	106.41(7)	Na2 ⁱⁱ —Na2—Na1	120.68(5)

Symmetry codes: ⁱ x, -1+y, 1+z; ⁱⁱ -x, 1-y, 1-z; ⁱⁱⁱ x, 1+y, -1+z.

In addition, π - π stacking effects are formed by the two adjacent benzene rings from different 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acids. One ring connects carboxyl, and the other one connects nitro. They are almost parallel to each other, because the dihedral angle is 9.79° . The angle is larger than pair of phen skeletons (dihedral angle is 7.8°) in $[\text{Cu}(\text{phen})_2(\mu\text{-IDA}) \text{Cu}(\text{phen})\cdot(\text{NO}_3)] (\text{NO}_3)\cdot 4(\text{H}_2\text{O})$ [15]. The vertical distance of the adjacent benzene rings is 3.731 \AA (Fig. 2), and the normal range of this interaction is usually between 3.3 \AA and 3.8 \AA [16]. The hydrogen bonds exist between water molecule

and 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid (hydrogen bonding geometry data in Table-2), which also increases the stability of the molecule.

Table-2: Selected hydrogen bonds lengths and angles.

D—H...A	D—H (Å)	H...A (Å)	D...A (Å)	D—H...A ($^\circ$)
O(5)—H(5A)...O(3)	0.82	1.82	2.542(3)	147
O(10)—H(10)...O(8)	0.82	1.79	2.519(3)	148
O(11)—H(11A)...O(1) ^{iv}	0.85	2.39	3.513(3)	150
O(11)—H(11B)...O(9) ^{vi}	0.8	2.08	2.835(3)	157
O(12)—H(12A)...O(8) ^{vi}	0.83(3)	2.01(3)	2.837(3)	175(3)
O(12)—H(12B)...O(4) ⁱⁱ	0.93(3)	1.90(3)	2.820(3)	169(3)
O(13)—H(13A)...O(9) ^v	0.94	1.83	2.754(3)	171
O(13)—H(13B)...O(3) ⁱⁱⁱ	0.84	2.05	2.887(2)	170
O(14)—H(14A)...O(8) ^v	0.98	1.95	2.929(3)	170
O(14)—H(14B)...O(4) ⁱⁱⁱ	0.95	1.91	2.850(3)	168
O(15)—H(15A)...O(7)	0.88	2.06	2.923(3)	165
O(15)—H(15B)...O(14) ^{vii}	0.89	2.04	2.864(3)	154
O(16)—H(16A)...O(10) ⁱ	0.92	2.14	3.003(4)	157
O(16)—H(16B)...O(15) ^{viii}	1	1.99	2.903(3)	151
C(3)—H(3)...O(7) ^v	0.93	2.59	3.397(3)	145
C(16)—H(16)...O(1) ^{iv}	0.93	2.34	3.127(3)	142

Symmetry codes: ⁱ x, -1+y, 1+z; ⁱⁱ -x, 1-y, 1-z; ⁱⁱⁱ 1-x, 1-y, 1-z; ^{iv} -x, 2-y, -z; ^v 1-x, 1-y, 1-z; ^{vi} -x, 1-y, -z; ^{vii} 1-x, -y, 1-z

Fig. 3 shows the IR spectrum of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$. It is noteworthy that one intense band was observed at 3448.05 cm^{-1} , attributed to $\nu(\text{OH})$ of the crystal water molecules. The infrared spectrum exhibited the band at 1348.76 cm^{-1} , arising from the $\nu(\text{N}=\text{N})$ vibration. The two absorption peaks at 1654.13 and 1261.76 cm^{-1} were assignable to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ vibrations, respectively.

The UV/Vis spectrum of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$ was measured in the solid state at room temperature (Fig. 4). It shows that the tetramer exhibits absorption bands at the range of $250\text{--}400 \text{ nm}$. The main absorption band at about 380 nm may be ascribed to an intramolecular charge transfer interaction [17]. The band appearing at 281 nm may arise from $\pi \rightarrow \pi^*$ transition of the heterocyclic moiety and aromatic rings [17, 18].

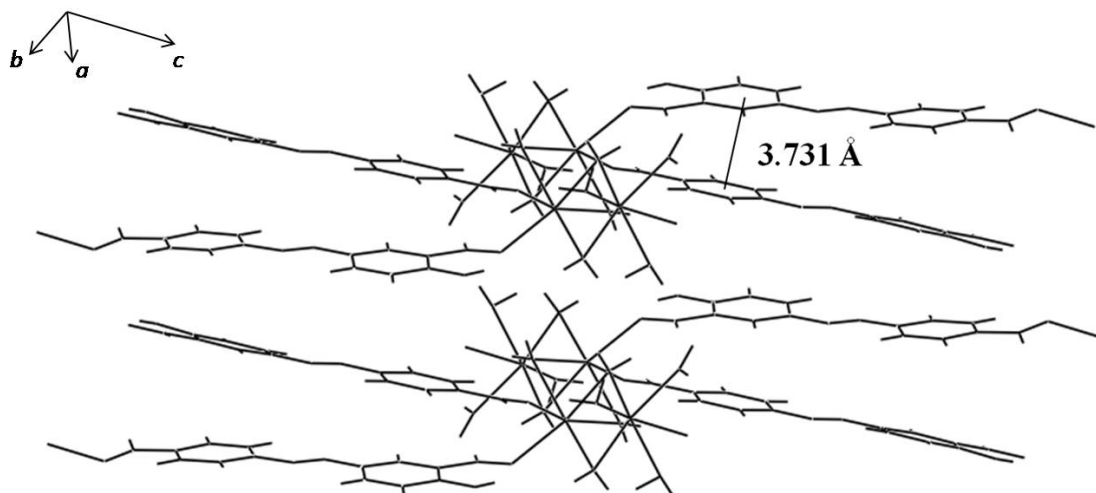


Fig. 2: The packing of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$ and the distance of the adjacent organic molecules.

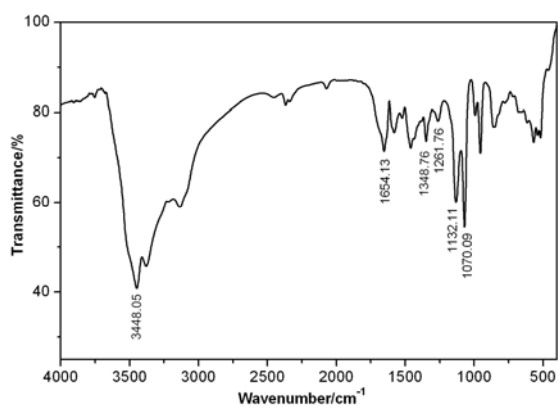


Fig. 3: The infrared spectrum of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$.

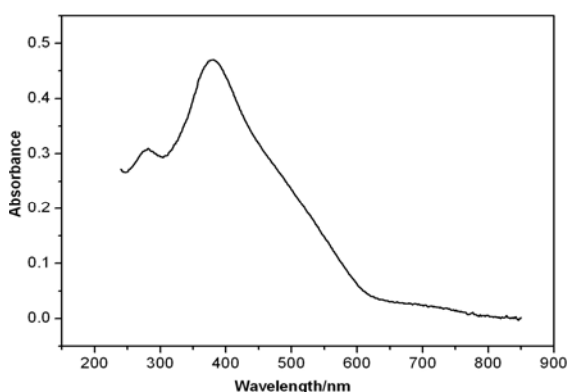


Fig. 4: The UV/Vis spectrum of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$.

As the novel yellow tetramer crystal has been obtained, the differences in properties and performances between the new Alizarin Yellow R crystal and Alizarin Yellow R powder will be discussed in our following research.

Experimental

Materials and Methods

All chemicals we used were of analytical grade, and employed without further purification. IR spectrum was collected with KBr pellets in the range 4000–400 cm^{-1} . The compound was characterized by powder X-ray diffraction (PXRD) using a X'Pert PRO diffractometer with monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The UV/Vis spectrum was measured on UV-2550.

Synthesis of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$

A mixture of zinc nitrate (0.25 mmol, 0.072 g), 2-hydroxy-5-((4-nitrophenyl)azo) benzoic acid mono sodium salt (mono sodium salt of Alizarin Yellow R, 0.5 mmol, 0.154 g) and imidazo[4,5-f][1,10]phenanthroline (0.5 mmol, 0.111 g) were dissolved in methanol (10 ml) and distilled water (5 ml) with stirring at room temperature for 30 minutes. Then the solution pH value was adjusted to 5 with a dilute NaOH aqueous solution (6 mol/L). After stirring for 1.5 hours at room temperature, the dark red solution obtained was filtered. Two days later yellow block crystals of the complex were generated.

After filtration and collection, the crystals were washed with distilled water and dried in the air.

However, after characterized by single X-ray crystal determination, the structure was found under recrystallization. Another synthesis was tried out without zinc nitrate and imidazo[4,5-f][1,10]phenanthroline. The sole reactant mono sodium salt of Alizarin Yellow R was dissolved in methanol and distilled water again. Same method above was used and after one week, new yellow crystals were generated. XRD patterns of the new crystals and the old ones were compared in Fig. 5. The two patterns are matched with each other, which indicates that zinc nitrate and imidazo[4,5-f][1,10]phenanthroline may make no contributions to the structure. As Alizarin Yellow R is easily dissolved in organic solvent, methanol may encourage the forming of this novel structure.

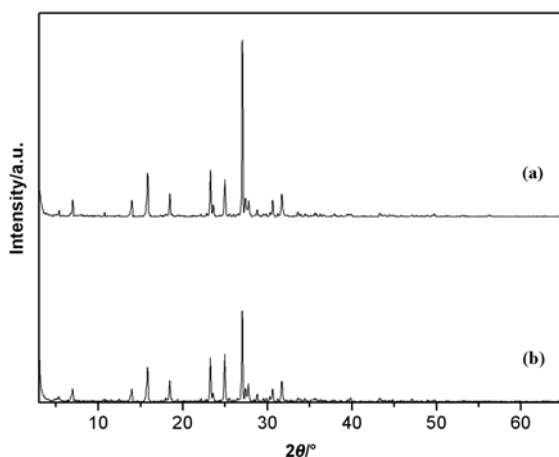


Fig. 5: The XRD patterns of $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$ (a) and the new generated crystals (b).

Single X-ray crystal determination

The crystallographic data for the structure are listed in Table-3. Diffraction data were collected at 298 (2) K on a Bruker Smart Apex CCD diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in φ and ω scan modes. The structure was solved by direct methods [19] and refined on F^2 using all data by full matrix least squares procedures with SHELXS 97 [20] and SHELXL 97 [21], respectively. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The selected bond lengths and angles are listed in Table-1. Hydrogen bonding geometry data

are listed in Table-2. Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC No. 833513 for $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$. Copies of this data may be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail for inquiry: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Table-3: Crystal data and structure refinement for $\text{Na}_2(\text{C}_{13}\text{H}_8\text{N}_3\text{O}_5)_2(\text{H}_2\text{O})_6$.

Parameter	Value
Chemical formula	$\text{C}_{26}\text{H}_{28}\text{N}_6\text{Na}_2\text{O}_{16}$
Formula weight	726.52
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
$a, \text{ \AA}$	7.2202(9)
$b, \text{ \AA}$	13.0624(15)
$c, \text{ \AA}$	17.0605(19)
$\alpha, \text{ deg}$	77.137(2)
$\beta, \text{ deg}$	80.922(2)
$\gamma, \text{ deg}$	83.354(2)
$V, \text{ \AA}^3$	1543.56(3)
Z	2
$F(000)$	752
$\rho_{\text{calc}}, \text{ g/cm}^3$	1.563
$\mu_{\text{Mo}}, \text{ mm}^{-1}$	0.154
Crystal size, mm	0.20×0.10×0.10
θ Range for data collection, deg	1.81–26.00
Index ranges	$-8 \leq h \leq 8, -16 \leq k \leq 16, -17 \leq l \leq 21$
Reflections collected/unique	10511 / 5988 ($R_{\text{int}} = 0.0466$)
Number of reflections with $I > 2\sigma(I)$	3857
Max and min transmission	0.9848 and 0.9699
Data/restraints/parameters	5988/0/457
Goodness-of-fit on F^2	0.956
R factor, $I > 2\sigma(I)$	$R_1 = 0.0562, wR_2 = 0.0964$
R factor (all data)	$R_1 = 0.0913, wR_2 = 0.1291$
Largest diff. peak and hole, $e\text{ \AA}^{-3}$	0.250 and -0.246

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