

Mustafa Tombul,^{a*} Kutalmış
Güven^b and Nazım Alkış^a^aDepartment of Chemistry, University of Kırıkkale, Campus, Yahşihan 71450, Kırıkkale, Turkey, and ^bDepartment of Physics, University of Kırıkkale, Campus, Yahşihan 71450, Kırıkkale, TurkeyCorrespondence e-mail:
mustafatombul@hotmail.com

Key indicators

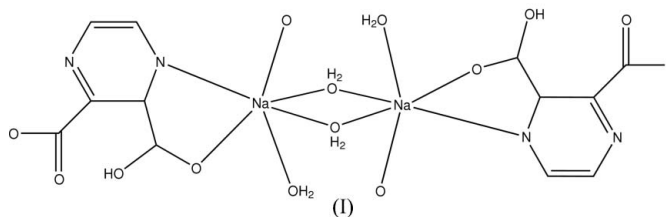
Single-crystal X-ray study
T = 295 K
Mean $\sigma(C-C)$ = 0.002 Å
R factor = 0.029
wR factor = 0.089
Data-to-parameter ratio = 15.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Poly[μ -aqua-aqua- μ -3-carboxypyrazine-2-carboxylato-sodium(I)]

The crystal structure of the title compound, $[\text{Na}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, consists of molecular ribbons containing octahedral NaO_5N units. Two adjacent Na atoms are bridged by two water molecules to give a centrosymmetric dimeric unit. Each Na centre is coordinated by two carboxylate groups. The ligand also uses one N atom to coordinate to Na. In addition, each Na atom is coordinated by one water O atom, raising the coordination number to six. One of the carboxyl groups retains its H atom, which takes part in an $\text{O}-\text{H}\cdots\text{O}$ [$\text{O}\cdots\text{O} = 2.563(1) \text{ \AA}$] intramolecular hydrogen bond.

Received 28 February 2006
Accepted 6 March 2006

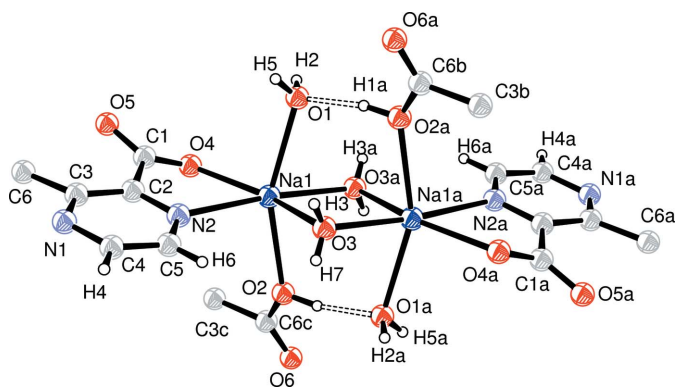
Comment

The title compound (I), was obtained as a colourless powder during an attempt to synthesize a borate ester product from the reaction of Na_2CO_3 with $\text{B}(\text{OH})_3$ and pyrazine-2,3-dicarboxylic acid. Recrystallization yielded crystals suitable for a diffraction study, the results of which are reported here.



The structure of (I) is shown in Fig. 1 and selected bond lengths and angles are presented in Table 1. Since the single-crystal X-ray analysis of pyrazine-2,3 dicarboxylic acid was first determined (Takusagawa & Shimada, 1973), a variety of metal-organic compounds of pyrazine-2,3-dicarboxylic acid have been characterized crystallographically due to the growing interest in supramolecular chemistry. These include the calcium (Ptasiewicz-Bak & Leciejewicz, 1997*a*; Starosta & Leciejewicz, 2005) and magnesium (Ptasiewicz-Bak & Leciejewicz, 1997*b*) complexes.

The asymmetric unit of the solvated title compound, (I), contains a ribbon-like Na–O core, which is bridged above and below by two water molecules. The ribbon consists of Na^{I} cations surrounded by five O atoms and one N atom in a distorted octahedral arrangement. The hydrogen pyrazine-2,3-dicarboxylate anion chelates to the Na^{I} cation *via* one heterocyclic N atom and the deprotonated carboxylate O atom, and the protonated carboxyl group coordinates to another Na^{I} cation of a neighbouring unit. In addition, each Na atom is coordinated by three water O atoms, two of which are bridging water molecules. The bond lengths and angles within the ligand are in fair agreement with those reported for


Figure 1

A segment of the polymeric structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

the parent acid (Takusagawa & Shimada, 1973). The Na—O(carboxylate) interaction modes, the Na coordination scheme and the range of Na—O bond lengths agree well with those most frequently observed in a large number of Na complexes with carboxylate ligands (Evans *et al.*, 2001). The bridged Na \cdots Na distance of 3.464 (2) Å is similar to those reported for other bridged systems (Evans *et al.*, 2001; Albertsson *et al.*, 1973). The planes of the carboxylate groups (C6/O2/O6) and (C1/O4/O5) form dihedral angles with the ring plane of 71.99 (5) and 17.43 (1)°, respectively.

An interesting feature to note in compound (I) is that an asymmetrical intramolecular hydrogen bond of 2.563 (1) Å occurs, linking the coordinated water O atoms with the hydroxyl O atoms of adjacent ribbons (Table 2). Atom H1 involved in this bond maintains the charge balance within the structure.

The two crystallographically independent water molecules are involved in normal, slightly bent, hydrogen bonds with hydrogen pyrazine-2,3-dicarboxylate (Table 2); the acceptors are carboxylate O atoms, with the exception of the water acceptor O1 noted above.

We note the following details for the configuration of the water molecules, in which marked differences occur in their environment. Atom O3 is coordinated to two Na^I cations and, from the valence bond argument, this interaction involves sp^3 -type water lone pairs. In contrast, atom O1 is coordinated to only one Na^I cation, with the Na—O interaction approximately along the bisector of the H—O—H angle, and the interaction therefore involves sp^2 -type water lone pairs. This coordination situation with respect to the lone-pair side of water molecules is typical for a monovalent metal salt hydrate (Chiari & Ferraris, 1982).

In compound (I), there are appreciable differences between the two carboxyl groups. The C—O distances at C6 are 1.208 and 1.304 Å, and these are fairly typical for a carboxylic acid group (Speakman, 1972). On the other hand, those at C1 are 1.245 and 1.253 Å, giving a strong indication of a carboxylate ion. As is typically the case, the mean value of the two C—O distances in the different carboxyl/carboxylate groups is almost the same, at 1.256 and 1.249 Å, respectively.

Experimental

To an aqueous solution (50 ml) containing Na₂CO₃ (2 mmol, 0.212 g) and B(OH)₃ (4 mmol, 0.248 g), pyrazine-2,3-dicarboxylic acid (8 mmol, 1.34 g) was added gradually with the immediate evolution of H₂ gas. The reaction mixture produced a colourless solution which was stirred at 333 K for 7 h, until all became was formed. Single crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a saturated aqueous solution at 298 K.

Crystal data

[Na(C₆H₃N₂O₄)(H₂O)₂]
M_r = 226.13
 Triclinic, *P* $\bar{1}$
a = 7.8581 (14) Å
b = 8.4416 (19) Å
c = 7.602 (2) Å
 α = 108.05 (3)°
 β = 93.71 (2)°
 γ = 70.139 (14)°
V = 450.45 (19) Å³

Z = 2
D_x = 1.667 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.3–18.3°
 μ = 0.19 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.4 × 0.4 × 0.2 mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (MSC/AFC Diffractometer
 Control Software; Molecular
 Structure Corporation, 1991)
T_{min} = 0.928, *T_{max}* = 0.963
 2737 measured reflections
 2561 independent reflections

2171 reflections with *I* > 2σ(*I*)
R_{int} = 0.007
 θ_{\max} = 30.0°
h = 0 → 10
k = -11 → 11
l = -10 → 10
 3 standard reflections
 every 150 reflections
 intensity decay: 0.1%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.029
wR(*F*²) = 0.089
S = 1.03
 2561 reflections
 164 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1279P)^2 + 0.6038P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Na1—O4	2.3333 (12)	O5—C1	1.2402 (14)
Na1—O3	2.3407 (12)	C2—N2	1.3388 (14)
Na1—O3 ⁱ	2.3976 (12)	N1—C3	1.3387 (13)
Na1—O2	2.4523 (10)	N1—C4	1.3381 (15)
Na1—O1	2.4734 (10)	N2—C5	1.3333 (15)
Na1—N2	2.5093 (13)	C6—O6	1.2081 (14)
O4—C1	1.2570 (14)		
O4—Na1—O3	118.02 (4)	O1—Na1—N2	104.74 (4)
O4—Na1—O2	105.90 (4)	O4—Na1—O3 ⁱ	155.20 (4)
O3—Na1—O2	80.13 (4)	O3—Na1—O3 ⁱ	86.07 (4)
O4—Na1—O1	92.02 (4)	O2—Na1—O3 ⁱ	82.79 (4)
O3—Na1—O1	78.04 (4)	O1—Na1—O3 ⁱ	87.15 (4)
O2—Na1—O1	156.50 (3)	N2—Na1—O3 ⁱ	87.42 (4)
O4—Na1—N2	68.81 (4)	C6—O2—Na1	135.32 (7)
O3—Na1—N2	172.79 (4)	Na1—O3—Na1 ⁱ	93.93 (4)
O2—Na1—N2	96.00 (4)		

Symmetry code: (i) $-x + 2, -y + 1, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H1 ⁱ ···O1 ⁱ	0.91 (2)	1.66 (2)	2.563 (1)	168.18 (3)
O1—H5 ⁱ ···O4 ⁱⁱ	0.89 (1)	1.79 (1)	2.671 (1)	176.61 (3)
O1—H2 ⁱ ···N1 ⁱⁱⁱ	0.83 (2)	2.11 (2)	2.902 (2)	164.67 (3)
O3—H3 ⁱ ···O5 ⁱⁱ	0.81 (2)	1.88 (2)	2.688 (2)	177.33 (3)
O3—H7 ⁱ ···O6 ^{iv}	0.84 (2)	1.95 (2)	2.788 (2)	174.45 (3)

Symmetry codes: (i) $-x+2, -y+1, -z$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+3, -y+1, -z$.

All H atoms were found in a difference Fourier map and refined freely.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge financial support from the Kırıkkale University Research Fund.

References

- Albertsson, J., Grenthe, I. & Herbertsson, H. (1973). *Acta Cryst.* **B29**, 1855–1860.
- Chiari, G. & Ferraris, G. (1982). *Acta Cryst.* **B38**, 2331–2341.
- Evans, M. B. J., Kapitan, A., Rosair, G. M., Roberts, K. J. & White, G. (2001). *Acta Cryst.* **C57**, 1277–1278.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Ptasiewicz-Bak, H. & Leciejewicz, J. (1997a). *Pol. J. Chem.* **71**, 493–500.
- Ptasiewicz-Bak, H. & Leciejewicz, J. (1997b). *Pol. J. Chem.* **71**, 1603–1610.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Speakman, J. C. (1972). *Struct. Bonding (Berlin)*, **12**, 141–199.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Starosta, W. & Leciejewicz, J. (2005). *J. Coord. Chem.* **58**, 963–968.
- Takusagawa, T. & Shimada, A. (1973). *Chem. Lett.* pp. 1121–1126.