METAL-ORGANIC COMPOUNDS

Acta Cryst. (1996). **C52**, 2970-2972

The Sodium Salt of N1-Deprotonated Inosine, $Na^+.C_{10}H_{11}N_4O_5^-.2.5H_2O$†

Peter Klüfers and Peter Mayer

Institut für Anorganische Chemie der Universität, Engesserstraße, Gebäude 30.45, D-76128 Karlsruhe, Germany. E-mail: kluefers@achibm2.chemie.uni-karlsruhe.de

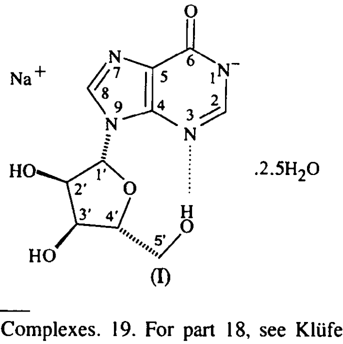
(Received 11 June 1996; accepted 3 July 1996)

Abstract

The title compound, sodium inosinate(1−)–water (1/2.5), Na(inosineH_{-1}).2.5H_2O, crystallizes from aqueous alkaline solution. Each N1-deprotonated monoanion has a *syn* conformation which is stabilized by intramolecular O5′—H···N3 hydrogen bonds. Face-shared pentaaqua–disodium dications bind to ribose O2′ and O5′ atoms, but are not ligated by the hypoxanthine moiety.

Comment

Inosine is a well characterized ligand which coordinates in its neutral form preferentially *via* the N7 atom to various metal ions. When deprotonation of the weakly acidic inosine (pK_a ~ 8.8; Sigel, Massoud & Corfù, 1994) occurs, the metal binding site changes to N1, which is the formally deprotonated site (Lönnberg, 1990). The crossover pH values depend on the metal ion present, typically varying around the point of neutrality with divalent 3*d* metal ions (Kim & Martin, 1984). At still higher pH, deprotonation of the ribose moiety may occur. As a result of attempts to synthesize an inosineH_{-3} complex of beryllium from alkaline aqueous solution according to a method successfully applied to simple polyols (Klüfers, Mayer & Schuhmacher, 1995), the title compound, (I), crystallized as a by-product.



(I)

The quality of the crystals allowed satisfactory H-atom localization, even with X-rays. The crystal structure determination (Table 1; water O atoms are coded O9*n* for *n* = 1, 2, 3) established an ionic structure made up of N1-deprotonated inosine monoanions and six-coordinate Na cations, which bind to all of the water molecules present according to the formula $[Na_2(\mu\text{-}H_2O)_3(H_2O)_2](\text{inosine}H_{-1})_2$. In the anion, the deprotonation of N1 results in an increase of electron delocalization, which is seen in the increased lengths of the formal double bonds and the decreased formal single-bond lengths of the pyrimidine ring (Table 2), when compared with the structures of the polymorphs of inosine itself (Thewalt, Bugg & Marsh, 1970; Munns & Tollin, 1970; Subramanian, 1979). The ribofuranose ring is C2′-*endo* puckered. The puckering amplitude [Q = 0.404 (2) Å] is normal; the conformation is more precisely described as being between a C2′-envelope and a twist conformation, with the twist axis running through the O4′ atom [^2E and $^2T_3$, respectively, according to a puckering phase angle of φ = 224.2 (2)° for the sequence C1′—C2′—C3′—C4′—O4′ (Cremer & Pople, 1975)]. The glycosyl torsion angle C8—N9—C1′—O4′ of −121.2 (2)° indicates a *syn* conformation of the nucleoside, which is stabilized by an intramolecular O5′—H···N3 hydrogen bond [*cf.* the exocyclic torsion angle O4′—C4′—C5′—O5′ of −68.2 (2)°].

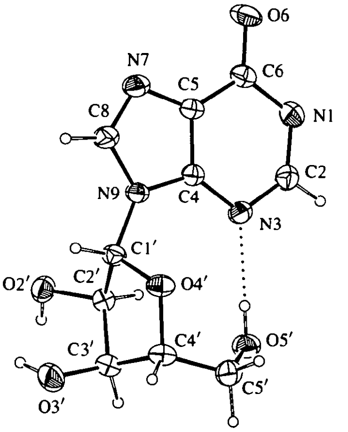


Fig. 1. The structure of the inosine monoanion (50% probability displacement ellipsoids).

Instead of binding to the N atoms of the hypoxanthine moiety, *i.e.* those usually assumed as cation binding sites (Lönnberg, 1990; Bariyanga & Theophanides, 1985), the Na cation binds to the O2′ and O5′ atoms of the ribose residue. The dinuclear dications exhibit crystallographic twofold symmetry (Fig. 2). Two distorted octahedra around the Na atoms are connected in a face-sharing

---

† Polyol Metal Complexes. 19. For part 18, see Klüfers, Piotrowski & Schuhmacher (1996).

mode, with water molecules acting exclusively as bridging ligands. All of the ribose and water hydroxy groups act as donors in hydrogen bonds (Table 3). In particular, each of the electron-rich sites of the hypoxanthine residue is involved in hydrogen bonds, with N1, N3 and N7 acting as single acceptors, and O6 accepting one longer and two shorter hydrogen bonds. In addition, the ribose ring O atom is an acceptor of a hydrogen bond. Two more weak contacts are included in Table 3, *i.e.* an intramolecular contact in the ribose diol group giving rise to a bifurcated bond and an intermolecular C—H···O link between two ribose moieties. The fact that the intramolecular O5′—H···N3 hydrogen bond is associated with the delocalized anionic acceptor group in the title compound is not a unique situation, but is, in fact, a rather usual feature in nucleoside crystal structures. It also occurs in the orthorhombic polymorph of neutral inosine itself (Subramanian, 1979).

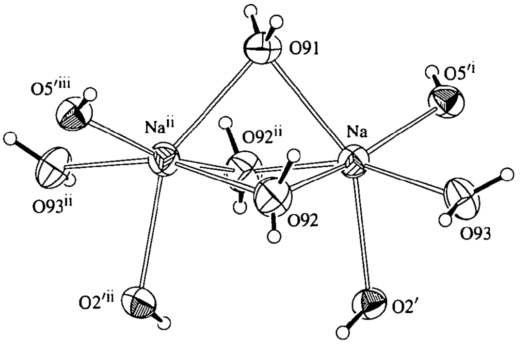


Fig. 2. The structure of the C_2-symmetric pentaaqua–disodium moiety with coordinating 2′ and 5′ ribose O atoms (50% probability displacement ellipsoids). [Symmetry codes: (i) $x, y, 1+z$; (ii) $1-x, 1-y, z$; (iii) $1-x, 1-y, 1+z$.]

Molecules link *via* hydrogen bonds into a three-dimensional network. No infinite cooperative hydrogen-bond system is present. The individual bonds are linked only by short cooperative sequences, the most extended of which is of the type C5′—H···O3′—H···O93—H···O4/N7 (including the weak C—H···O contact).

Experimental

Beryllium hydroxide (2.54 mmol, freshly prepared from the reaction of 2.54 mmol of beryllium sulfate tetrahydrate and 5.08 mmol of sodium hydroxide), sodium hydroxide (10.16 mmol) and inosine (5.08 mmol) were dissolved in water (17 ml). After filtration, ethanol (37 ml) was added. Large colourless crystals of the title compound grew onto small crystals of a precipitate, which formed within one day, over a period of four months.

Crystal data

$Na^+.C_{10}H_{11}N_4O_5^-.2.5H_2O$
$M_r = 335.26$
Orthorhombic
$P2_12_12$
$a = 20.568\ (4)$ Å
$b = 9.057\ (2)$ Å
$c = 7.295\ (2)$ Å
$V = 1358.9\ (5)$ Å^3
$Z = 4$
$D_x = 1.639$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 276 reflections
$\theta = 5$–20°
$\mu = 0.166$ mm^{-1}
$T = 300\ (2)$ K
Brick-shaped
0.24 × 0.20 × 0.15 mm
Colourless

Data collection

Stoe IPDS diffractometer
φ scans; imaging-plate-type area detector
Absorption correction: none
3551 measured reflections
2001 independent reflections

1911 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0185$
$\theta_{\rm max} = 26°$
$h = -23 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R(F) = 0.0233$
$wR(F^2) = 0.0614$
$S = 1.058$
2001 reflections
268 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.1773P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.143$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.125$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter indeterminate

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Na	0.57736 (4)	0.51071 (7)	0.70714 (8)	0.0310 (2)
O2′	0.59471 (7)	0.52613 (12)	0.38446 (14)	0.0306 (3)
H82′	0.5695 (18)	0.448 (3)	0.329 (4)	0.066 (8)
O3′	0.71703 (8)	0.41137 (14)	0.3192 (2)	0.0399 (3)
H83′	0.6906 (19)	0.397 (3)	0.401 (4)	0.058 (8)
O4′	0.72647 (6)	0.72323 (11)	0.1793 (2)	0.0283 (3)
O5′	0.65925 (7)	0.65526 (13)	−0.1721 (2)	0.0331 (3)
H85′	0.6510 (18)	0.733 (3)	−0.116 (4)	0.058 (8)
O6	0.53441 (8)	1.29002 (13)	0.2267 (2)	0.0370 (3)
N1	0.55473 (8)	1.14083 (14)	−0.0209 (2)	0.0301 (3)
N3	0.60981 (8)	0.90590 (13)	0.0047 (2)	0.0273 (3)
N7	0.60735 (10)	1.06140 (15)	0.4553 (2)	0.0369 (4)
N9	0.64346 (8)	0.85519 (13)	0.3202 (2)	0.0260 (3)
C1′	0.67479 (8)	0.7124 (2)	0.3085 (2)	0.0240 (3)
C2′	0.63209 (9)	0.5856 (2)	0.2408 (2)	0.0240 (3)
C3′	0.68441 (9)	0.4806 (2)	0.1696 (2)	0.0275 (3)
C4′	0.73269 (9)	0.5839 (2)	0.0784 (2)	0.0276 (3)
C5′	0.72343 (10)	0.6128 (2)	−0.1236 (2)	0.0312 (4)
H52′	0.7560 (16)	0.686 (3)	−0.161 (3)	0.047 (6)
C6	0.55901 (9)	1.1719 (2)	0.1623 (2)	0.0272 (3)
C2	0.57886 (10)	1.0142 (2)	−0.0842 (2)	0.0302 (4)
C8	0.63787 (11)	0.9364 (2)	0.4776 (2)	0.0340 (4)
C5	0.59178 (10)	1.0648 (2)	0.2688 (2)	0.0271 (3)
C4	0.61453 (9)	0.9378 (2)	0.1845 (2)	0.0240 (3)
O91	1/2	1/2	0.9639 (2)	0.0345 (4)
H911	0.4935 (16)	0.578 (3)	1.035 (3)	0.054 (7)
O92	0.50148 (8)	0.30181 (15)	0.6524 (2)	0.0431 (3)
H921	0.514 (3)	0.243 (4)	0.756 (4)	0.094 (12)
H922	0.502 (2)	0.267 (3)	0.567 (4)	0.069 (10)
O93	0.65562 (8)	0.31289 (13)	0.6549 (2)	0.0384 (3)
H931	0.6901 (17)	0.283 (3)	0.716 (3)	0.046 (6)
H932	0.639 (2)	0.235 (3)	0.617 (4)	0.061 (8)

Table 2. *Selected geometric parameters (Å, °)*

Na—O5′^{i}	2.3077 (15)	N1—C6	1.369 (2)
Na—O92^{ii}	2.382 (2)	N3—C2	1.337 (2)
Na—O2′	2.3849 (13)	N3—C4	1.346 (2)
Na—O93	2.4384 (15)	N7—C8	1.305 (2)
Na—O91	2.4599 (14)	N7—C5	1.398 (2)
Na—O92	2.485 (2)	N9—C8	1.369 (2)
Na···Na^{ii}	3.188 (2)	N9—C4	1.376 (2)
O2′—C2′	1.407 (2)	N9—C1′	1.448 (2)
O3′—C3′	1.426 (2)	C1′—C2′	1.527 (2)
O4′—C1′	1.424 (2)	C2′—C3′	1.527 (2)
O4′—C4′	1.466 (2)	C3′—C4′	1.518 (2)
O5′—C5′	1.420 (2)	C4′—C5′	1.509 (2)
O6—C6	1.273 (2)	C6—C5	1.414 (2)
N1—C2	1.332 (2)	C5—C4	1.386 (2)
C2—N1—C6	119.44 (14)	C8—N9—C4	105.98 (12)
C2—N3—C4	110.46 (12)	N1—C6—C5	115.22 (13)
C8—N7—C5	104.55 (13)	N1—C2—N3	129.85 (14)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2′—H82′···O6^{i}	0.97 (3)	1.77 (3)	2.727 (2)	171 (3)
O3′—H83′···O2′	0.82 (3)	2.30 (4)	2.763 (2)	117 (3)
O3′—H83′···O93	0.82 (3)	2.13 (3)	2.896 (2)	156 (3)
O5′—H85′···N3	0.83 (3)	1.99 (3)	2.802 (2)	166 (4)
O91—H911···O6^{ii}	0.89 (3)	1.93 (3)	2.792 (2)	165 (3)
O92—H921···N1^{iii}	0.96 (3)	2.05 (4)	3.001 (2)	170 (5)
O92—H922···O6	0.70 (3)	2.58 (3)	3.180 (2)	146 (3)
O93—H931···O4′^{iv}	0.88 (3)	1.95 (3)	2.829 (2)	172 (3)
O93—H932···N7	0.83 (3)	2.07 (3)	2.880 (2)	164 (3)
C5′—H52′···O3′^{v}	0.98 (3)	2.41 (3)	3.293 (2)	150 (2)

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

H atoms were located from a difference map and their positions and $U_{\rm iso}$ values refined.

Data collection: *IPDS Diffractometer Software* (Stoe & Cie, 1993). Cell refinement: *IPDS Diffractometer Software*. Data reduction: *IPDS Diffractometer Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1990).

This work was supported by the Deutsche Forschungsgemeinschaft (grant Kl 624/4-1). PM gratefully acknowledges a scholarship from the Stiftung zur Förderung körperbehinderter Hochbegabter.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SK1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bariyanga, J. & Theophanides, T. (1985). *Inorg. Chim. Acta*, **108**, 133–140.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kim, S. H. & Martin, R. B. (1984). *Inorg. Chim. Acta*, **91**, 19–24.
Klüfers, P., Mayer, P. & Schuhmacher, J. (1995). *Z. Anorg. Allg. Chem.* **621**, 1373–1379.
Klüfers, P., Piotrowski, H. & Schuhmacher, J. (1996). *Z. Anorg. Allg. Chem.* In the press.
Lönnberg, H. (1990). *Biocoordination Chemistry*, edited by K. Burger, pp. 284–346. New York: Ellis Horwood.
Munns, A. R. I. & Tollin, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sigel, H., Massoud, S. S. & Corfù, N. A. (1994). *J. Am. Chem. Soc.* **116**, 2958–2971.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Stoe & Cie (1993). *Scanner Stoe IPDS Diffractometer Software*. Version 1.08. Stoe & Cie, Darmstadt, Germany.
Subramanian, E. (1979). *Cryst. Struct. Commun.* **8**, 777–785.
Thewalt, U., Bugg, C. E. & Marsh, R. E. (1970). *Acta Cryst.* B**26**, 1089–1101.

Acta Cryst. (1996). C**52**, 2972–2975

A Homoleptic Cuprate(II) Complex with Deprotonated 1,6-Anhydro-β-D-glucose (Levoglucosan) Ligands†

CLAUDIA GACK AND PETER KLÜFERS

Institut für Anorganische Chemie der Universität, Engesserstraße, Gebäude 30.45, D-76128 Karlsruhe, Germany. E-mail: kluefers@achibm2.chemie.uni-karlsruhe.de

(*Received 11 June 1996; accepted 12 July 1996*)

Abstract

The cuprate anion in the title complex, dilithium bis[1,6-anhydro-β-D-glucosidato(2−)-O^2,O^4]cuprate(II) octahydrate, $Li_2[Cu(C_6H_8O_5)_2].8H_2O$, is a homoleptic mononuclear 1,3-polyolato(2−) complex. The ligator atoms of the levoglucosan ligand are closer together by *ca* 0.4 Å with respect to the uncomplexed 1,3-diol moiety of the anhydro sugar, thus exhibiting an enhanced flexibility compared with 1,2-diols.

Comment

The 'bite' of a chelate ligand is of limited variability, particularly when the ligator atoms are attached to a further cyclic fragment, above all, to a six-membered ring in its energetically favoured chair conformation. In the coordination chemistry of carbohydrates, this general statement may be quantified for 1,2-

---

† Polyol Metal Complexes. 20. For part 19, see Klüfers & Mayer (1996).