

Structure of Sodium (7-Amino-2,3-dihydro-5-oxo-5H-thiazolo[3,2-a]pyrimidin-6-yl)sulfamate Trihydrate

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Abstract. $\text{Na}^+ \cdot \text{C}_6\text{H}_7\text{N}_4\text{O}_4\text{S}_2^- \cdot 3\text{H}_2\text{O}$, $M_r = 340.30$, triclinic, $P\bar{1}$, $a = 7.083$ (1), $b = 9.359$ (1), $c = 9.809$ (2) Å, $\alpha = 89.92$ (1), $\beta = 81.46$ (2), $\gamma = 80.66$ (1)°, $V = 634$ (1) Å³, $Z = 2$, $D_x = 1.78$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.472$ mm⁻¹, $F(000) = 352$, $T = 295$ K, $R = 0.025$ for 2259 unique reflections with $I \geq 3\sigma(I)$. Anions, cations and two crystallographically independent water molecules are arranged in a linear chain structure, determined by the coordination to the Na^+ ions. The thiazine ring shows an envelope conformation. The N atom of the — NHSO_3^- group displays fundamental sp^3 hybridization. There is a very extensive network of hydrogen-bond interactions, to which one lattice water molecule contributes.

Experimental. The title compound was obtained as a side product in the reduction reaction of 7-amino-2,3-dihydro-6-nitroso-5H-thiazolo[3,2-a]pyrimidin-5-one with sodium hydrosulfite in aqueous solution. Together with 6,7-diamino-2,3-dihydro-5H-thiazolo[3,2-a]pyrimidin-5-one as principal product (Pecorari, Rinaldi & Costi, 1989), another side product, 6,7-dihydro-5H-thiazolo[3,2-a][1,2,5]thiadiazolo[3,4-d]pyrimidin-9-one, was obtained. The three compounds were separated by fractionated concentration of the reaction solution, or by means of thin-layer chromatography. In fractionated crystallization the title compound was the last one to be collected, while in thin-layer chromatography it did not migrate when precoated silica gel F254 plates (Merck) and chloroform–methanol–water (5:5:3 v/v/v) as solvent system were used.

Colourless well formed prismatic crystals were obtained by slow evaporation from aqueous solution. Crystal dimensions were $0.33 \times 0.25 \times 0.15$ mm. Data were collected using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation at room temperature, using $\omega/2\theta$

scans of scan width $(0.65 + 0.35 \tan \theta)^\circ$, 25 ($18 \leq \theta \leq 25^\circ$) reflections were used for cell-parameter determination. Two standard reflections (124 and 244) measured at 1 h intervals showed no significant intensity decay. 3222 reflections were measured in the range $1.5 \leq \theta \leq 28^\circ$, $-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $0 \leq l \leq 12$; 2406 with $I \geq 3\sigma(I)$ were observed, and 2259 unique reflections ($R_{\text{int}} = 0.009$) were used for structure determination. Intensities were corrected for Lorentz–polarization effects and for absorption based on empirical ψ scans [$0.94 \leq T \text{ factor} \leq 0.99$]. The structure was solved by direct methods (SHELXS86; Sheldrick, 1986), and refined by full-matrix least squares with $\sum w\Delta F^2$ being minimized (SHELXL76; Sheldrick, 1976). All non-H atoms were refined anisotropically, and H atoms, located in ΔF maps, isotropically. The protons of one water molecule were found to occupy two alternative positions in the crystal; a value of 0.5 for their site-occupancy factors was assumed on the basis of peak heights in the ΔF map. 234 parameters were refined. $R = 0.025$, $wR = 0.026$, $S = 2.43$, $w = 1.0/(\sigma^2 F + 0.00013 F^2)$, maximum $\Delta/\sigma = 0.09$, $-0.31 \leq \Delta\rho \leq 0.30$ e Å⁻³. Complex neutral-atom scattering factors (except Na^+) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Major calculations were carried out on a VAX 6310 computer. Final fractional coordinates for non-H atoms are listed in Table 1.† ORTEP (Johnson, 1965) drawings of the anion and of the Na^+ coordination spheres, with atom-numbering scheme and bond distances, are shown in Figs. 1 and 2, respectively; a stereoview of the unit-cell contents is presented in Fig. 3.

† Lists of structure factors, anisotropic thermal parameters, positional and thermal parameters for H atoms, bond distances and bond angles, hydrogen-bond interactions, torsion angles, selected least-squares planes, and shortest non-bonded distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55259 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0303]

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (Å²) for non-H atoms
$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	B _{eq}
S(1)	0.16910 (6)	0.66948 (5)	0.37520 (4)	2.33 (2)
C(1)	0.1741 (3)	0.7995 (2)	0.5097 (2)	2.82 (7)
C(2)	0.1956 (3)	0.7199 (2)	0.6434 (2)	2.49 (6)
N(1)	0.2476 (2)	0.5641 (1)	0.6077 (1)	1.70 (5)
C(3)	0.2380 (2)	0.5248 (2)	0.4773 (2)	1.65 (5)
N(2)	0.2720 (2)	0.3914 (1)	0.4283 (1)	1.79 (5)
C(4)	0.3166 (2)	0.2855 (2)	0.5203 (2)	1.66 (5)
N(3)	0.3501 (2)	0.1484 (2)	0.4703 (2)	2.39 (6)
C(5)	0.3299 (2)	0.3166 (2)	0.6565 (2)	1.57 (5)
N(4)	0.3854 (2)	0.2009 (1)	0.7444 (1)	1.83 (5)
C(6)	0.2912 (2)	0.4614 (2)	0.7074 (2)	1.57 (5)
O(1)	0.2930 (2)	0.5036 (1)	0.8270 (1)	2.16 (4)
S(2)	0.21095 (6)	0.12683 (4)	0.83724 (4)	2.04 (1)
O(2)	0.3186 (2)	0.0252 (2)	0.9195 (2)	3.72 (6)
O(3)	0.0749 (2)	0.2393 (1)	0.9192 (1)	2.98 (5)
O(4)	0.1189 (2)	0.0607 (1)	0.7370 (1)	3.20 (5)
Na(1)	0.5	0.5	0.0	2.28 (3)
Na(2)	0.0	0.5	0.0	3.03 (4)
O(w1)	0.2370 (2)	0.3927 (2)	0.1367 (1)	2.72 (5)
O(w2)	0.3409 (2)	0.7479 (1)	0.0472 (2)	2.76 (5)
O(w3)	0.2272 (3)	0.0726 (2)	0.2172 (2)	4.01 (7)

Related literature. The octahedral six coordination of the Na⁺ cations, which have occupation factors $\frac{1}{2}$, determines a linear chain structure parallel to the *a* cell axis, because the coordination polyhedra share two opposite (symmetry related) edges. Bridging atoms are one water O atom and the carbonyl O(1) atom. The six coordination about the Na(1) ion is completed by two water O atoms, whereas two sulfonic O(3) atoms are bonded to the Na(2) atom, with formation of seven-membered chelate rings. The dimensions of the pyrimido-thiazine moiety of the anion comparé well with those previously observed for other pyrimido-thiazole (Pecorari, Rinaldi, Costi & Antolini, 1991), and pyrimido-thiazine derivatives (Antolini & Pecorari, 1991). The thiazine ring has an envelope conformation. The —NHSO₃⁻ moiety is bonded to the ring in an antiperiplanar conformation [the dihedral angle O(2)—S(2)—N(4)—H is 43°]. The short N(4)—S(2) distance of 1.667 (1) Å is close to that of 1.666 (6) Å found in KSO₃NH₂ (Cox, Sabine, Padmanabhan, Ban, Chung & Surjadi, 1967) and of 1.637 (4) Å observed in KSO₃NHCH₃ (Morris, Kennard & Hall, 1982). As found also for the above cited sulfamates, the N atom has *sp*³ hybridization.

In addition to the coordination to the Na⁺ ions, which appears to be the major contributor, the crystal packing is determined by a very extensive network of strong hydrogen-bond interactions.

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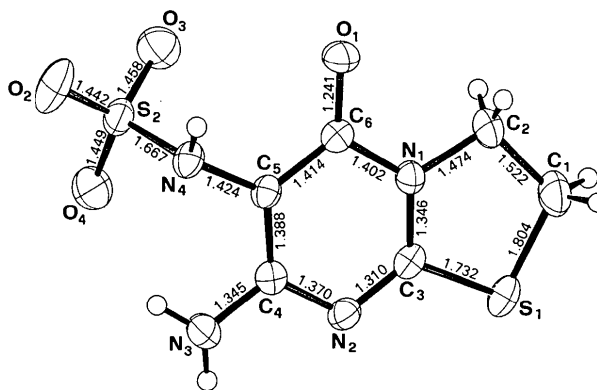


Fig. 1. ORTEP (Johnson, 1965) view of the anion with atom-numbering scheme and bond distances (Å, e.s.d.'s ± 0.001–0.003). Thermal ellipsoids enclose 60% probability.

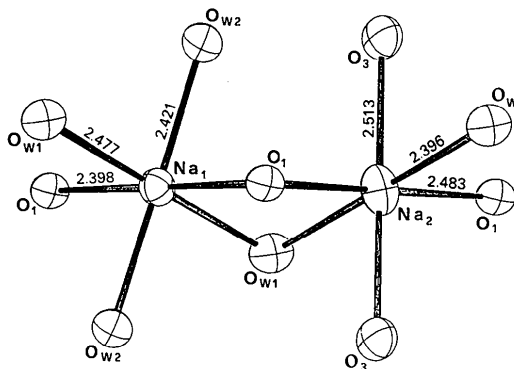


Fig. 2. The Na⁺ coordination spheres with bond distances (Å, e.s.d.'s ± 0.001).

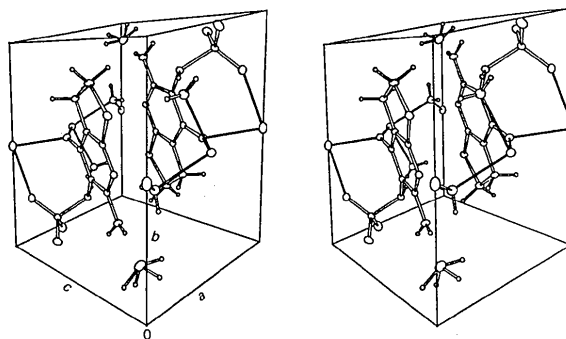


Fig. 3. Stereoview of the unit-cell contents.

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Penta[bis(5-oxoprolinato)platinate(II) d'Ammonium] Monohydrate

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Abstract. Pentaammonium penta[bis(5-oxoprolinato-*N,O*)platinate(II)] monohydrate, $5\{\text{NH}_4[\text{Pt}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_6)]\} \cdot \text{H}_2\text{O}$, $M_r = 2359.7$, monoclinic, $P2_1$, $a = 11.278$ (5), $b = 15.195$ (5), $c = 19.92$ (1) Å, $\beta = 91.60$ (4)°, $V = 3412$ (4) Å³, $Z = 2$, $D_m = 2.30$ (5), $D_x = 2.297$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 10.42$ mm⁻¹, $F(000) = 2240$, $T = 293$ (1) K, $R = 0.038$ for 5062 independent observed reflections. Each Pt atom displays a square-planar *cis* coordination. It is linked to two N and two O atoms which belong respectively to the amide and the carboxylic groups of two glutamic acid molecules. The ranges of bond lengths are 1.98 (1)–2.03 (1) Å for Pt—O and 1.94 (1)–2.03 (1) Å for Pt—N. All complex anions $[\text{Pt}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_6)]^-$ are almost planar and their geometry very similar to those previously described for the same anion. In each ligand, the amide function takes the tautomeric iminoalcohol form. The NH_4^+ cations are surrounded by four, five or six O atoms which constitute distorted polyhedra (tetrahedron, pyramid with a square base, bipyramid with a triangular base, octahedron). The water molecule is involved in three hydrogen bonds, one of them being bifurcated.

Partie expérimentale. Préparation: On chauffe pendant quatre jours, vers 320 K, une solution aqueuse de L-pyroglytamate d'ammonium (2 mmol) additionnée de tétrachloroplatinate d'ammonium (1 mmol) dont le pH est maintenu vers 7,5. Masse volumique par flottaison. Plaquette: 0,06 × 0,11 × 0,30 mm. Diffractomètre Enraf-Nonius CAD-4. Dimensions de la maille déterminées avec 25 réflexions telles que $7,24 \leq \theta \leq 13,50^\circ$, $0,049 \leq (\sin \theta) / \lambda \leq 0,595$ Å⁻¹. Balayage $\theta/2\theta$ d'amplitude $s = (1,20 + 0,35 \text{tg} \theta)^\circ$. $0 \leq h \leq 13$, $0 \leq k \leq 18$, $-23 \leq l \leq 23$. Réflexions de contrôle de l'intensité: 400, 400 et 342. Diminution de I au cours des mesures: 3,4%. Correc-

tions de décroissance. 6551 réflexions indépendantes mesurées, 1489 inobservées [$I \leq 2\sigma(I)$]. Programme *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H liés à C(3), C(4), C(5), C'(3), C'(4) et C'(5): positions calculées, autres H non localisés. Affinement basé sur les F , programme à matrice complète. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974, Tome IV, pp. 99, 149). Paramètres affinés: x, y, z et β_{ij} de Pt, O, N et C. $B(\text{H}) = B_{\text{eq}}$ de l'atome lié à H augmenté de 1 Å². Corrections d'absorption: programme *DIFABS* (Walker & Stuart, 1983). Valeurs maximale et minimale du coefficient de correction: 1,208 et 0,773. $R = 0,038$, $wR = 0,036$, $w = 1/\sigma^2(F)$, $S = 0,97$, $(\Delta/\sigma)_{\text{max}} = 0,02$, $\Delta\rho_{\text{max}} = 1,0$ (2), $\Delta\rho_{\text{min}} = -0,9$ (2) e Å⁻³. Programmes de calcul du système *SDP* (B. A. Frenz & Associates, Inc., 1982). Fig. 1 et 2: *ORTEPII* (Johnson, 1976). Ordinateur DEC VAX 3100.

Les coordonnées atomiques relatives et les facteurs de température isotropes équivalents sont rapportés dans le Tableau 1, les longueurs et les angles des liaisons dans le Tableau 2. La Fig. 1 représente l'un des anions $[\text{Pt}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_6)]^-$ et la Fig. 2 le contenu de la maille. Les numéros attribués aux atomes présents dans les cinq anions s'obtiennent en ajoutant les nombres 10, 20, 30, 40 ou 50 aux

* Les listes des facteurs de structure observés et calculés, des coefficients d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des angles de torsion, des distances C—H, des distances N—H et O—H susceptibles de correspondre à des liaisons hydrogène, des distances entre des atomes appartenant à des entités chimiques différentes et des distances des atomes aux plans moyens des anions ont été déposées aux archives de la British Library Document Supply Centre as Supplementary Publication No. SUP 55300 (47 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU0338]