Potassium 1,3,3a,8a-Tetrahydro-3a,8a-dihydroxy-2,8-dioxoindeno[1,2-*d*]imidazole-2-ethanesulfonate, K$^+$.C$_{12}$H$_{11}$N$_2$O$_7$S$^-$

By D. D. Bray and D. D. Clarke

Chemistry Department, Fordham University, Bronx, New York 10458, *USA*

and N. Chatterjie and B. Sinha

Institute for Basic Research in Developmental Disabilities, 1050 *Forest Hill Road, Staten Island, New York* 10314, *USA*

Abstract. $M_r = 366 \cdot 40$, monoclinic, $P2_1/c$, $Z = 4$, $a = 6 \cdot 795$ (1), $b = 17 \cdot 701$ (4), $c = 12 \cdot 864$ (3) Å, $\beta = 116 \cdot 25$ (2)°, $V = 1387 \cdot 8$ Å^3, $D_m = 1 \cdot 74$, $D_x = 1 \cdot 754$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1 \cdot 5418$ Å, $\mu = 5 \cdot 07$ mm^{-1}, $T = 298$ K, $F(000) = 752$, $R = 0 \cdot 074$ for 2091 observed independent intensity data. Crystals were prepared by reacting the K salt of ureidotaurine with ninhydrin in acid solution. The product shows that the unsubstituted N of the ureidotaurine reacts with the central C of ninhydrin.

Introduction. Taurine, β-aminoethanesulfonic acid, is believed to act as an inhibitory neurotransmitter and has been shown to decrease epileptic seizures, but its lipophobic nature allows only a small fraction of a peripherally administered dose to cross the blood–brain barrier to reach the epileptic foci (Mutani, Bergamini & Durelli, 1978). It has been suggested that derivatives involving lipophilic modification, but still containing the taurine core, would exhibit taurine-like inhibition (Oja, Kontro, Linden, Andersen & Gothoni, 1982; Lahdesmaki & Oja, 1973). These derivatives might more readily cross the blood–brain barrier and presumably be broken down metabolically to active taurine-like compounds within the brain.

One approach in synthesizing such compounds is to convert the taurine to its ureido derivative, which is then condensed with triketohydrindene hydrate (ninhydrin), to obtain a cyclic ureide belonging to the indeno[1,2-*d*]imidazole family (Crooks & Deeks, 1975). Previous studies have demonstrated that heterocyclic molecules of this type show anticonvulsive activity in the pentylenetetrazole threshold model in mice (Alexander & Chatterjie, 1980; Chatterjie, Sinha & Alexander, 1983). Although the title compound is a structural analog of those studied, it showed no significant anticonvulsive activity under the same conditions.

The title compound was prepared by reacting taurine with KCNO to produce the potassium salt of ureidotaurine (I), as described by Salkowski (1973);

this was then condensed with ninhydrin (II) to give one of two possible products (III*a,b*). In this synthesis, as in similar ones (Arens, Grunsbergs & Jurgevica, 1974), spectral data were not conclusive in determining the position of the *R* group relative to the rest of the molecule. While mechanistic arguments could be suggested to favor (III*b*), these are of questionable validity. An X-ray structure determination was undertaken to establish with certainty the position of the *R* group and thereby establish which N of the ureidotaurine reacts with the central C of ninhydrin.

(I) (II) (III)

(*a*) R$_1$=CH$_2$CH$_2$SO$_3$K
   R$_2$=H

(*b*) R$_1$=H
   R$_2$=CH$_2$CH$_2$SO$_3$K
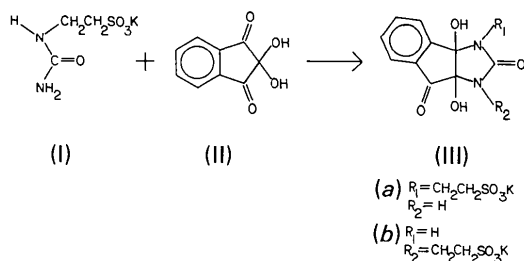
Experimental. Crystals suitable for X-ray work obtained by dissolving the title compound in ethanol and allowing the solvent to evaporate slowly. D_m determined by flotation in benzene/bromobenzene. Enraf–Nonius CAD-4 automated diffractometer. Monochromated Cu $K\alpha$ radiation. Crystal $0 \cdot 15 \times 0 \cdot 25 \times 0 \cdot 30$ mm. Unit cell: least-squares fit of the angular settings for 15 reflections. ω–2θ scanning mode; $\theta \le 73°$ for the range $0 \le h \le +8$, $0 \le k \le +21$, $-15 \le l \le +15$. Systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ uniquely defined the space group $P2_1/c$. Relative ranges of intensity variation for standard reflections $12\bar{2}$ and $10\bar{4}$: $4 \cdot 9$ and $6 \cdot 5\%$ respectively. Intensities corrected for Lorentz–polarization effects but not for absorption. 2773 possible independent reflections, 2091 accepted as observed [$I > 1 \cdot 5\sigma(I)$]. Structure solved by direct methods and refined by Fourier and least-squares

methods. A difference electron density map showed the positions of all the H atoms. In the final cycle $R = 0.074$ and $R_w = 0.040$ for the observed reflections only; mean and maximum Δ/σ values 0.129 and 0.595; $S = 1.23$; $\sum w(|F_o|-k|F_c|)^2$ minimized; $w = 1/\sigma^2(F)$ from counting statistics for the observed reflections; unobserved reflections weighted zero with $w = 1$ for observeds and zero for unobserveds; $R = 0.074$ and $R_w = 0.076$. Maximum and minimum peak heights in final difference Fourier synthesis 0.30 and -0.51 e Å^{-3}, the latter in the region of the K atom. Scattering factors for the non-H atoms from *International Tables for X-ray Crystallography* (1962), that for H from Stewart, Davidson & Simpson (1965). Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); all other structural calculations performed with the NRC System (Ahmed, Hall, Pippy & Huber, 1973).

Discussion. The atomic coordinates and equivalent isotropic B's for the non-H atoms (Willis & Pryor, 1975) are given in Table 1.*

The structure presented here shows that the unsubstituted N of ureidotaurine reacts with the central C of ninhydrin as shown in Fig. 1, corresponding to structure (IIIa) above. Bond distances and bond angles do not vary significantly from standard values. The K$^+$
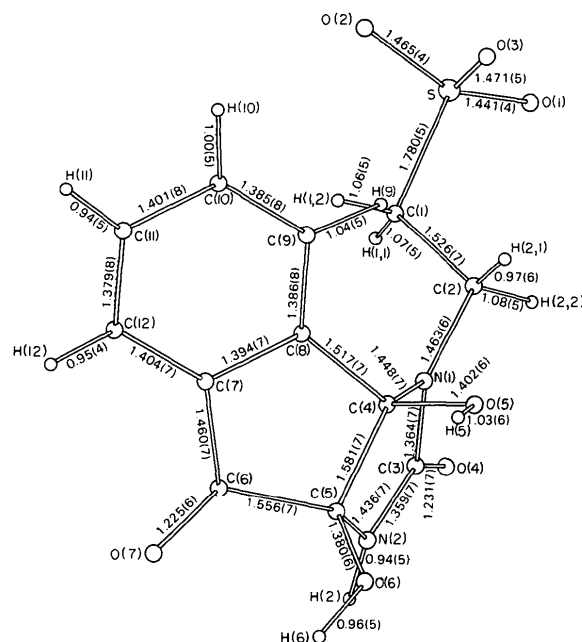
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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38922 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for nonhydrogen atoms*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
K	6485 (2)	7058 (1)	10532 (1)	2.75 (4)
S	9966 (2)	6995 (1)	8530 (1)	1.97 (4)
O(1)	12161 (6)	6909 (2)	9441 (3)	3.8 (2)
O(2)	9881 (6)	7457 (2)	7566 (3)	3.1 (2)
O(3)	8362 (6)	7250 (2)	8934 (3)	3.2 (2)
O(4)	10975 (5)	4219 (2)	8479 (3)	2.4 (1)
O(5)	5065 (5)	4682 (2)	8794 (3)	2.4 (1)
O(6)	4128 (5)	3375 (2)	7562 (3)	2.5 (1)
O(7)	3721 (6)	3578 (2)	5171 (3)	2.8 (2)
N(1)	7820 (6)	4840 (2)	8233 (3)	1.7 (2)
N(2)	7552 (6)	3666 (2)	7585 (3)	2.1 (2)
C(1)	9028 (8)	6088 (3)	7911 (4)	2.1 (2)
C(2)	8863 (8)	5548 (3)	8794 (4)	2.1 (2)
C(3)	8973 (7)	4234 (3)	8139 (4)	1.9 (2)
C(4)	5508 (7)	4680 (3)	7828 (4)	1.7 (2)
C(5)	5312 (7)	3880 (3)	7244 (4)	1.9 (2)
C(6)	4069 (8)	4053 (3)	5924 (4)	2.0 (2)
C(7)	3352 (7)	4840 (3)	5773 (4)	2.0 (2)
C(8)	4041 (7)	5193 (3)	6846 (4)	1.9 (2)
C(9)	3426 (8)	5930 (3)	6923 (5)	2.8 (2)
C(10)	2159 (8)	6313 (3)	5907 (5)	3.2 (2)
C(11)	1504 (8)	5965 (3)	4827 (5)	3.2 (2)
C(12)	2062 (8)	5227 (3)	4740 (4)	2.6 (2)

Fig. 1. Structure of $C_{12}H_{11}N_2O_7S^-$. (Distances in Å.)
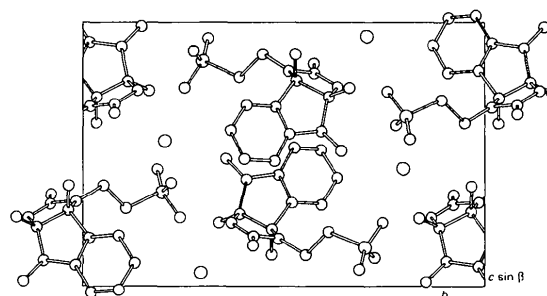
Fig. 2. Unit-cell contents. H atoms have been omitted for clarity.

ion (at x, y, z) is at the center of a slightly distorted octahedron formed by O(1) at $x-1, \tfrac{1}{2}-y, \tfrac{1}{2}+z$; O(2) at $2-x, -\tfrac{1}{2}+y, \tfrac{3}{2}-z$; O(3) at x, y, z; O(4) at $2-x, 1-y, 1-z$; O(6) at $1-x, 1-y, 1-z$; and O(7) at $1-x, -\tfrac{1}{2}+y, \tfrac{3}{2}-z$. The K—O distances range from 2.651 (4) to 2.878 (4) Å. Intermolecular hydrogen bonds exist between N(2) at x, y, z and O(2) at $2-x, \tfrac{1}{2}-y, \tfrac{3}{2}-z$; O(6) at x, y, z and O(3) at $1-x, -\tfrac{1}{2}+y, \tfrac{3}{2}-z$; and O(5) at x, y, z and O(4) at $x-1, y, z$. The corresponding distances are 2.821 (6), 2.766 (5) and 2.750 (6) Å while the H$\cdots$O distances are 1.91 (6), 1.82 (5) and 1.74 (6) Å respectively. The six-membered ring shows less deviation from planarity than either of the five-membered rings. The ureido ring has an r.m.s. deviation of 0.044 (5) Å from its least-squares plane with C(4) showing the largest deviation, 0.065 (5) Å. The other five-membered ring has an r.m.s. deviation of

0·047 (5) Å with a maximum deviation of 0·059 (5) Å, again for C(4). The benzene ring shows no significant deviation from planarity, the r.m.s. deviation being 0·007 (6) Å. The dihedral angle between the two five-membered rings is 116·6 (4)° and that between the five- and six-membered rings is 175·6 (5)°. The packing is shown in Fig. 2.

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Nitratopentakis(thiourea)bismuth(III) Nitrate Monohydrate, [Bi(NO₃){SC(NH₂)₂}₅](NO₃)₂.H₂O, and Trinitratotris(thiourea)bismuth(III), [Bi(NO₃)₃{SC(NH₂)₂}₃]

BY GEOFFREY B. JAMESON

Department of Chemistry, Georgetown University, Washington, DC 20057, USA

AND EVA BLASZÓ AND HANS R. OSWALD

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

Abstract. [Bi(NO₃){SC(NH₂)₂}₅](NO₃)₂.H₂O: $M_r = 793.61$, red, triclinic, $P\bar{1}$, $a = 9.292$ (1), $b = 9.788$ (1), $c = 15.729$ (1) Å, $\alpha = 118.55$ (1), $\beta = 92.99$ (1), $\gamma = 93.72$ (1)°, $V = 1248.3$ Å³, $Z = 2$, $D_m = 2.12$ (1), $D_x = 2.11$ Mg m⁻³, Mo Kα radiation, $\lambda = 0.7107$ Å, $\mu = 7.056$ mm⁻¹, $T = 295$ K, $F(000) = 772$, $R(F) = 0.039$, $R_w(F) = 0.039$ [5300 data in the range $0.0467 < (\sin\theta)/\lambda < 0.7049$ Å⁻¹ with $F_o^2 > 3\sigma(F_o^2)$]; Bi–S 2.637 (2)–2.937 (2) Å; Bi–O 2.814 (5) and 2.916 (5) Å. [Bi(NO₃)₃{SC(NH₂)₂}₃]: $M_r = 623.36$, yellow, monoclinic, $P2_1/c$, $a = 6.9556$ (9), $b = 15.801$ (3), $c = 15.561$ (2) Å, $\beta = 91.87$ (1)°, $V = 1709.3$ Å³, $Z = 4$, $D_m = 2.422$ (5), $D_x = 2.421$ Mg m⁻³, Mo Kα radiation, $\lambda = 0.7107$ Å, $\mu = 10.692$ mm⁻¹, $T = 295$ K, $F(000) = 1184$, $R(F) = 0.042$, $R_w(F) = 0.047$ [3263 data in the range $0.0443 < (\sin\theta)/\lambda < 0.5958$ Å⁻¹ with $F_o^2 > 3\sigma(F_o^2)$]; Bi–S 2.668 (3)–2.681 (3) Å; Bi–O 2.579 (9)–2.94 (1) Å (two bridging NO₃ groups). Extensive hydrogen bonding and probable C···N π-donor–π-acceptor interaction occur for both structures.

Introduction. In the course of a systematic investigation into the interaction of thiourea with Bi^III salts, the title compounds were isolated. In order to understand the solid-state thermal decomposition of these species it became necessary to determine their crystal and molecular structures. The compounds were prepared by slow evaporation of solutions containing Bi(NO₃)₃ and thiourea. The product composition was controlled by thiourea concentration.