

INORGANIC COMPOUNDS

Acta Cryst. (1998). **C54**, 1729–1731

Pentasodium Bis[dihydroxytetraoxotellurium(VI)]gold(III) Hexadecahydrate†

WILLIAM LEVASON AND MICHAEL WEBSTER

Department of Chemistry, University of Southampton,
Southampton SO17 1BJ, England. E-mail:
m.webster@soton.ac.uk

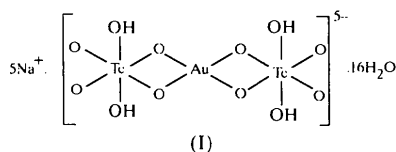
(Received 16 January 1998; accepted 29 May 1998)

Abstract

The title compound, $\text{Na}_5[\text{Au}\{\text{TeO}_4(\text{OH})_2\}_2] \cdot 16\text{H}_2\text{O}$, contains discrete centrosymmetric $[\text{Au}\{\text{TeO}_4(\text{OH})_2\}_2]^{5-}$ anions in which the hydroxy H atoms have been located. The Te—O distances are 1.971 (4) and 1.966 (4) Å for the bridging oxo ligands, 1.850 (4) and 1.861 (4) Å for the terminal oxo ligands, and 1.992 (4) and 1.978 (4) Å for the hydroxy ligands.

Comment

A recent review of tellurate ligands (Levason, 1997) drew attention to the rather small number of complexes that have been characterized, and to the difficulties that remain even when a crystal structure has been reported but for which H-atom positions have not been determined. The copper(III) tellurate structure $\text{Na}_5[\text{Cu}\{\text{TeO}_4(\text{OH})_2\}_2] \cdot 16\text{H}_2\text{O}$ has been reported (Levason *et al.*, 1988) but, as in many cases, the OH groups bonded to Te were inferred from the Te—O distances. We have recently synthesized the corresponding gold(III) compound, (I), according to the method of Balikungeri & Pelletier (1978) and we report its crystal structure here. Suitable crystals were obtained by recrystallizing the sodium salt from aqueous KOH by slow evaporation. Although the more obvious NaOH was also tried, the KOH solution was used as it had been noted that crystals with mixed cations are often obtained; furthermore, in this case, KOH yielded better quality crystals, although they turned out to contain no K^+ ions.



† Alternative name: pentasodium tetrahydroxo- $2\kappa^2\text{O}, 3\kappa^2\text{O}$ -tetra- μ -oxo- $1:2\kappa^4\text{O}:\text{O}; 1:3\kappa^4\text{O}:\text{O}$ -tetraoxo- $2\kappa^2\text{O}, 3\kappa^2\text{O}$ -gold(III)ditellurium(VI) hexadecahydrate.

The structure consists of discrete centrosymmetric $[\text{Au}\{\text{TeO}_4(\text{OH})_2\}_2]^{5-}$ anions, in which the H atoms were convincingly located. As expected, the terminal Te—O bond lengths [1.861 (4) and 1.850 (4) Å] are about 0.1 Å shorter than the terminal Te—O(H) bond lengths [1.992 (4) and 1.978 (4) Å] and agree well with the values for the analogous Cu compound. The Au—O distances [1.985 (4) and 2.001 (4) Å] are *ca* 0.16 Å longer than those of the Cu compound, and as a consequence the O—Au—O angle is smaller [78.9 (2)°]. The Au—O distance is comparable to that found in the periodate complex $\text{Na}_4\text{K}[\text{Au}\{\text{IO}_5(\text{OH})_2\}_2] \cdot \text{KOH} \cdot 15\text{H}_2\text{O}$ (Dengel *et al.*, 1992). The absence of potassium is demonstrated by the Na···O distances [minimum values 2.380 (5) (Na1), 2.361 (4) (Na2) and 2.302 (5) Å (Na3)], and each Na^+ ion is approximately octahedrally coordinated. These NaO_6 groups form chains by face (Na1), edge (Na2) and face and edge (Na3) sharing, and only O4 and O5 of the anion are involved [Na2···O4 2.361 (4), Na2···O5 2.566 (5) Å], with the remaining O atoms belonging to water molecules. Lying between these parallel chains are the discrete anions and O9. The O···O distances and the O—H···O angles indicate extensive hydrogen bonding; the shortest O···O distance is 2.616 (6) Å. There are 13 distances less than 2.9 Å and all but two are $\text{O}_{\text{water}} \cdots \text{O}_{\text{anion}}$ contacts; the four shortest distances are shown in Table 3. Atom O9, which is neither part of the anion nor part of the Na-containing chain, is hydrogen bonded to O2, O8 and O12.

This Au compound is isomorphous with the corresponding Cu compound (Levason *et al.*, 1988).

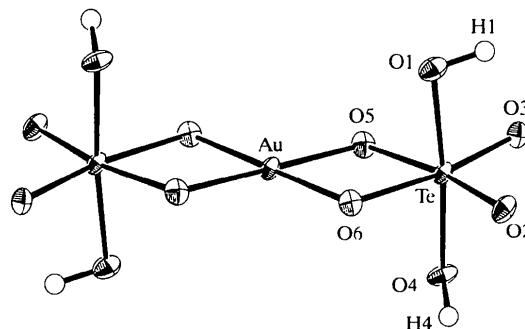


Fig. 1. The molecular structure of the $[\text{Au}\{\text{TeO}_4(\text{OH})_2\}_2]^{5-}$ anion, showing the atom-labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

Experimental

The crystal was mounted in a sealed glass capillary containing a small amount of mother liquor.

Crystal data

Na₅[Au(H₂O₆Te)₂].16H₂O
M_r = 1051.40
 Triclinic
P $\bar{1}$
a = 9.003 (2) Å
b = 12.643 (3) Å
c = 5.937 (1) Å
 α = 98.41 (2)°
 β = 93.13 (2)°
 γ = 97.95 (2)°
V = 660.2 (2) Å³
Z = 1
D_x = 2.645 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 20 reflections
 θ = 7.2–8.0°
 μ = 7.927 mm⁻¹
T = 295 (2) K
 Column
 0.8 × 0.2 × 0.2 mm
 Colourless

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.136, *T_{max}* = 0.205
 2474 measured reflections
 2313 independent reflections

2227 reflections with *I* > 2σ(*I*)
R_{int} = 0.093
 θ_{\max} = 25°
h = 0 → 10
k = -15 → 14
l = -7 → 7
 3 standard reflections every 150 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.031
wR(*F*²) = 0.084
S = 1.058
 2313 reflections
 167 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.8488P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.062
 $\Delta\rho_{\max} = 2.352 \text{ e \AA}^{-3}$
 (1.01 Å from Au)
 $\Delta\rho_{\min} = -3.351 \text{ e \AA}^{-3}$
 (0.98 Å from Au)
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Au	0	0	0	0.01300 (13)
Te	0.24067 (4)	0.19225 (3)	0.18010 (5)	0.01245 (13)
Na1	1	1/2	0	0.0478 (11)
Na2	0.3271 (3)	-0.04631 (19)	0.3457 (4)	0.0247 (5)
Na3	0.2255 (3)	-0.31956 (19)	0.3237 (4)	0.0253 (5)
O1	0.1935 (4)	0.2397 (3)	-0.1179 (6)	0.0211 (8)
O2	0.2253 (5)	0.3272 (3)	0.3431 (7)	0.0196 (9)
O3	0.4449 (4)	0.2115 (3)	0.1429 (7)	0.0177 (9)
O4	0.2766 (4)	0.1309 (3)	0.4627 (6)	0.0188 (8)
O5	0.2216 (5)	0.0421 (3)	0.0215 (8)	0.0176 (9)
O6	0.0220 (5)	0.1496 (3)	0.1761 (8)	0.0173 (9)
O7	0.5600 (5)	0.2083 (4)	-0.2640 (7)	0.0260 (9)
O8	0.2632 (6)	0.5016 (3)	0.1357 (8)	0.0319 (10)
O9	0.3917 (5)	0.4219 (4)	-0.2812 (7)	0.0287 (10)
O10	-0.1157 (5)	0.3262 (4)	0.0583 (8)	0.0307 (10)
O11	-0.1006 (5)	0.1580 (4)	-0.3999 (8)	0.0308 (10)
O12	-0.3436 (5)	0.3631 (4)	0.3490 (8)	0.0300 (10)
O13	-0.4237 (5)	0.0452 (4)	-0.7250 (7)	0.0275 (10)
O14	1.0223 (7)	0.4077 (6)	-0.3868 (11)	0.067 (2)

Table 2. Selected geometric parameters (Å, °)

Au—O5	1.985 (4)	Te—O5	1.971 (4)
Au—O6	2.001 (4)	Te—O4	1.978 (4)
Au...Te	3.0456 (9)	Te—O1	1.992 (4)
Te—O3	1.850 (4)	O1—H1	0.95
Te—O2	1.861 (4)	O4—H4	0.91
Te—O6	1.966 (4)		
O5—Au—O6	78.86 (18)	O2—Te—O4	92.31 (17)
O3—Te—O2	99.33 (19)	O6—Te—O4	91.97 (18)
O3—Te—O6	169.77 (18)	O5—Te—O4	85.67 (17)
O2—Te—O6	90.50 (19)	O3—Te—O1	91.98 (18)
O3—Te—O5	90.28 (18)	O2—Te—O1	92.35 (17)
O2—Te—O5	170.20 (18)	O6—Te—O1	84.76 (17)
O6—Te—O5	80.01 (19)	O5—Te—O1	89.19 (17)
O3—Te—O4	90.45 (18)	O4—Te—O1	174.33 (16)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O7—H7A...O3	0.96	1.73	2.678 (6)	168
O8—H8B...O2	0.96	1.72	2.669 (6)	172
O9—H9A...O2 ⁱ	0.86	1.82	2.648 (6)	162
O12—H12B...O3 ⁱⁱ	0.87	1.75	2.616 (6)	174

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

The heavy atoms (Au/Te) were located by Patterson methods and lighter atoms were found by repeated structure-factor and Fourier calculations. All the H atoms were convincingly located in a later electron-density map and included in the model in fixed positions and with fixed displacement parameters.

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFD Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

We would like to thank the EPSRC for funds to purchase the X-ray diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1229). Services for accessing these data are described at the back of the journal.

References

- Balikungeri, A. & Pelletier, M. (1978). *Inorg. Chim. Acta*, **29**, 137–140.
- Dengel, A. C., El-Hendawy, A. M., Griffith, W. P., Mostafa, S. I. & Williams, D. J. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3489–3495.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Levason, W. (1997). *Coord. Chem. Rev.* **161**, 33–79.
- Levason, W., Spicer, M. D. & Webster, M. (1988). *J. Chem. Soc. Dalton Trans.* pp. 1377–1381.
- Molecular Structure Corporation (1988). *MSCI/AFD Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN, Crystal Structure Analysis Package*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). **C54**, 1731–1733

$\text{Na}_5\text{Bi}_2(\text{AsO}_4)(\text{As}_2\text{O}_7)_2$

HABIB BOUGHZALA ET TAHAR JOUINI

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisie. E-mail: tahar.jouini@cck.rnu.tn

(Reçu le 30 octobre 1997, accepté le 8 mai 1998)

Abstract

Pentasodium dibismuth arsenate bis(diarsenate) has been synthesized by solid-state reaction and characterized by single-crystal X-ray diffraction. The structure is a three-dimensional framework comprising distorted BiO_6 octahedra, As_2O_7 groups and AsO_4 tetrahedra sharing corners. Along the c axis, the structure exhibits large tunnels where Na^+ cations are located.

Commentaire

Les systèmes renfermant Bi^{3+} présentent un intérêt particulier du fait de l'existence d'une paire d'électrons libre. Ceci peut engendrer des coordinences oxygénées, assymétriques autour du bismuth et entraîne dans certains cas des structures non-centrosymétriques. Seuls quelques composés ternaires ont été identifiés dans les systèmes $(\text{Na}_2\text{O}-\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5/\text{As}_2\text{O}_5)$: $\text{NaBi}_7\text{P}_2\text{O}_{16}$, $\text{NaBi}_7\text{As}_2\text{O}_{16}$ (Eysel & Jie, 1992), $\text{Na}_3\text{Bi}(\text{PO}_4)_2$ ($P2_1/c$ et $Pnam$; Mairesse *et al.*, 1990).

La charpente de ce composé est tridimensionnelle mixte, formée par des octaèdres BiO_6 distordus et des tétraèdres AsO_4 partageant des sommets. L'édifice anionique laisse libre des canaux parallèles à l'axe c où logent les cations Na^+ . L'unité assymétrique (Fig. 1) est formée de deux octaèdres reliés par deux unités As_2O_7 et un tétraèdre AsO_4 . Ces unités sont empilées en colonnes parallèlement à l'axe c , deux unités successives étant reliées par les ponts $\text{As}_2-\text{O}_5-\text{Bi}_2$ et $\text{As}_5-\text{O}_{16}-\text{Bi}_1$. Chaque colonne est connectée à trois voisines par les trois ponts $\text{As}_5-\text{O}_{17}-\text{Bi}_1$, $\text{As}_4-\text{O}_{13}-\text{Bi}_2$, $\text{As}_1-\text{O}_2-\text{Bi}_2$ et leur centrosymétriques (Fig. 1). Cet arrangement laisse libre des canaux parallèles à c où logent les cations Na^+ , vers lesquels pointent les sommets libres des unités As_2O_7 . Les dimensions maximales et minimales de ces canaux sont de 3,91 (1) Å entre O_{12} et O_{15} et 3,11 (1) Å entre O_{12} et O_1 . Les deux groupements diarsénates présents

dans l'unité assymétrique sont en conformation quasi-éclipsée, en effet leurs angles de torsion sont de 8,4 (6)° pour $\text{O}_1-\text{As}_1-\text{As}_2-\text{O}_5$ et 2,0 (5)° pour $\text{O}_9-\text{As}_3-\text{As}_4-\text{O}_{13}$.

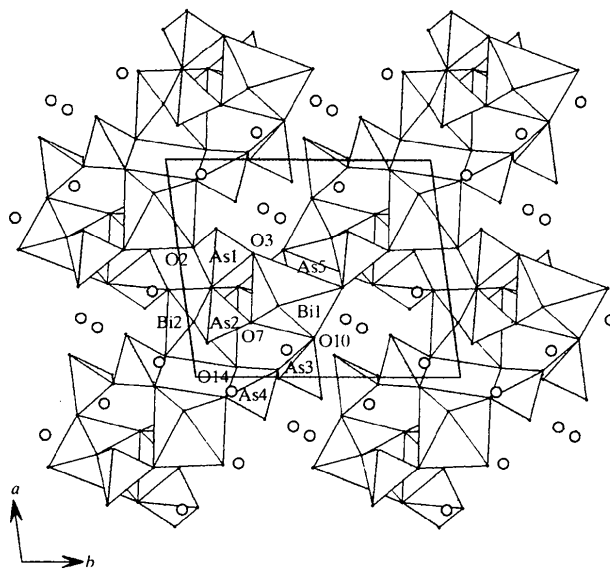


Fig. 1. Projection de la structure de $\text{Na}_5\text{Bi}_2(\text{AsO}_4)(\text{As}_2\text{O}_7)_2$ le long de l'axe c .

Les liaisons $\text{As}-\text{O}$ les plus longues correspondent aux oxygènes des ponts (O_b) dans les groupements diarsénates. Elles sont respectivement de 1,795 (8) et 1,719 (8) Å pour $\text{As}_1-\text{O}_4-\text{As}_2$, et 1,753 (9) et 1,744 (9) Å pour $\text{As}_3-\text{O}_{11}-\text{As}_4$. Bien qu'elles soient supérieures à la moyenne des distances $\text{As}-\text{O}_b$ (1,68 Å) dans les composés $M^I M^{III} \text{As}_2\text{O}_7$ (M^I : alcalin; M^{III} = Al, Fe) (Boughzala *et al.*, 1993; Driss & Jouini, 1994; Wang *et al.*, 1994; Boughzala & Jouini, 1995), elles restent comprises dans le domaine établi par Effenberg (Effenberg & Pertlik, 1993). Il en est de même pour les écartements angulaires des ponts $\text{As}-\text{O}_b-\text{As}$ atteignant respectivement 128,4 (5) et 132,0 (5)° pour $\text{As}_1-\text{O}_4-\text{As}_2$ et $\text{As}_3-\text{O}_{11}-\text{As}_4$.

Le polyèdre de coordination du bismuth est formé de six atomes d'oxygène à des distances interatomiques inférieures à 3 Å. L'utilisation de ces distances pour le calcul de la somme des valences (Brown & Altermatt, 1985) montre que les charges effectives relatives à Bi_1 et Bi_2 sont respectivement égales à 3,17 et 3,03. Les octaèdres BiO_6 sont très déformés, ainsi les angles définis par les sommets opposés et le centre d'un octaèdre sont de 151,9 (3)° pour $\text{O}_7-\text{Bi}_1-\text{O}_{17}^{\text{II}}$ et 162,4 (3)° pour $\text{O}_6-\text{Bi}_2-\text{O}_5^{\text{I}}$ (Tableau 1).

La série de Fourier finale révèle quatre pics résiduels situés dans l'environnement de Bi_1 et Bi_2 (0,93–1,07 Å). Ils peuvent être attribués à une éventuelle