

- McCusker, J. K., Vincent, J. B., Schmitt, E. A., Mino, M. L., Shin, K., Coggin, D. K., Hagen, P. M., Huffman, J. C., Christou, G. & Hendrickson, D. N. (1991). *J. Am. Chem. Soc.* **113**, 3012–3021.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
- Siemens (1996a). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996b). *SAINT Software Reference Manual*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996c). *SHELXTL Reference Manual*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). **C55**, 905–907

Aminoguanidinium (ethylenediamine-*N,N,N',N'*-tetraacetato)antimonate(III) monohydrate

HOONG-KUN FUN,^a S. SHANMUGA SUNDARA RAJ,^a
IBRAHIM ABDUL RAZAK,^a ANDREY B. ILYUKHIN,^b
RUVEN L. DAVIDOVICH,^c JING-WEI HUANG,^d SHENG-ZHI HU^d AND SEIK WENG NG^e

^a*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia*, ^b*NS Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907, Russia*, ^c*Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok 690022, Russia*, ^d*Department of Chemistry, Xiamen University, 361005 Xiamen, People's Republic of China*, and ^e*Institute of Postgraduate Studies and Research, University of Malaya, 50603 Kuala Lumpur, Malaysia*. E-mail: h1nswen@umcsd.um.edu.my

(Received 29 September 1998; accepted 4 February 1999)

Abstract

In the title complex, (CH₇N₄)[Sb(C₁₀H₁₂N₂O₈)]·H₂O, the lone-pair electrons of the Sb atom occupy an axial site in the ψ -pentagonal bipyramidal polyhedron [Sb—N 2.265 (2)–2.507 (2) and Sb—O 2.144 (1)–2.543 (2) Å]. The (ethylenediaminetetraacetato)antimonate anion, the aminoguanidinium cation and the lattice water are linked by hydrogen bonds into a two-dimensional network structure.

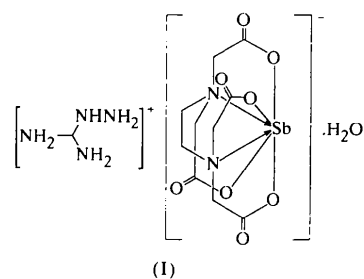
Comment

For six-coordinate antimony(III) compounds, the VSEPR (valence-shell electron-pair repulsion) model (Gillespie, 1992) predicts a ψ -pentagonal bipyramidal geometry at the metal atom in which the lone pair of electrons occupies an axial site, a feature that has been docu-

mented in, for example, the tris(oxalato)antimonate(III) ion (Poore & Russell, 1971). Hexacoordination can be forced on the Sb atom by the use of a single diaminetetracarboxylate polyanion, which chelates to the Sb atom through four carboxyl O and two amino N atoms; polyanions that have been used for this purpose include the ethylenediaminetetraacetate (edta), propylenediaminetetraacetate and *trans*-cyclohexanediaminetetraacetate tetraanions (Hu *et al.*, 1998).

Among the ethylenediaminetetraacetate complexes, the lone pair is axially positioned in [(CH₃)₄N][Sb(edta)]·2H₂O (Ilyukhin & Davidovich, 1999), as predicted by the VSEPR model. However, the lone pair is equatorially positioned in [NH₄][Sb(edta)]·H₂O (Ilyukhin & Davidovich, 1999) and in neutral [Sb(Hedta)]·2H₂O (Shimoi *et al.*, 1980). The difference in the geometry of the metal atom in the two salts can be ascribed to the more polarizable nature of the ammonium cation compared with that of the tetramethylammonium cation, since polarizability discourages localization of the lone pair. In the sodium salt Na[Sb(edta)]·3H₂O, the [Sb(edta)][−] ion lies on a twofold axis, and the pentagonal plane that is formed by the two O atoms, the two N atoms and the lone pair is planar. From its equatorial position, the lone pair distorts the axial O—Sb—O skeleton [O—Sb—O = 145.3 (2)°; Xie & Hu, 1991]. In the less polarizable guanidinium cation, the charge formally resides on the central C atom; a study of [CH₆N₃][Sb(edta)]·2H₂O has documented a ψ -pentagonal bipyramidal geometry in which the lone pair is axially disposed. The three amino groups of the cation are all bifurcated, and hydrogen bonds link the cation, the lattice water molecules and the anion into a one-dimensional chain structure. In addition, the crystal structure shows two weak Sb···O interactions (3.464 and 3.467 Å; Mistryukov *et al.*, 1987). The lone pair also lies in the equatorial position in [NH₄][Sb(cdta)]·[NH₄]Cl (H₄cdta = *trans*-cyclohexane-1,2-diaminetetraacetic acid; Hu *et al.*, 1998).

The introduction of another amino group to the guanidinium cation to give the title compound, (I), should lead to further delocalization of the positive charge; although (I) crystallizes with only one lattice water, the N-bonded amino group does not engage in hydrogen bonding with either the lattice water or any of the carbonyl O atoms. The N-bonded amino N atom is, in fact,



pyramidal, a feature that effectively rules out delocalization to this portion of the cation. The two C-bonded amino groups are bifurcated [N···O = 2.848 (3) and 2.860 (3), and 2.804 (3) and 3.081 (3) Å] and hydrogen bonds connect the ions and water into a two-dimensional network structure. The metal atom shows the expected ψ -pentagonal bipyramidal coordination (Fig. 1). Of the Sb—N bonds, the equatorial distance [2.507 (2) Å] significantly exceeds the axial distance [2.265 (2) Å]. Such a difference has also been noted in the guanidinium complex [2.516 (6) and 2.253 (6) Å]. On the other hand, the two Sb—N bonds are almost equivalent in the ammonium derivative [2.330 (3) and 2.398 (3) Å] (since the N atoms both lie in the equatorial plane), but are equal in Ti[Sb(edta)] (Ilyukhin & Davidovich, 1999). The equatorial plane is relatively flat [r.m.s. deviation 0.183 Å] in the aminoguanidinium complex; the metal atom is displaced by 0.434 (1) Å out of the plane in the opposite direction to the axial N atom, in agreement with the fact that the lone-pair-bonded-pair repulsion is greater than the bonded-pair-bonded-pair repulsion. The Sb atom forms a weak [3.283 (2) Å] bond with the carbonyl O atom of an adjacent anion across a centre of inversion. Consequently, the overall coordination polyhedron can be described as a distorted pentagonal bipyramid, with the N1 and O6ⁱ atoms taking the axial positions [symmetry code: (i) 1 - x, -y, -z].

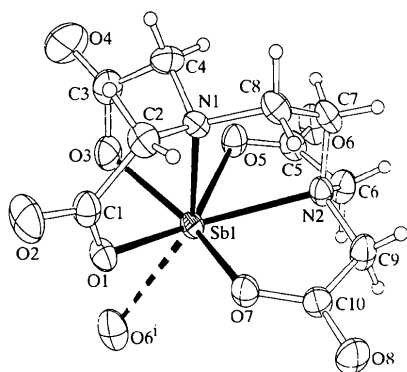


Fig. 1. ORTEP (Johnson, 1976) plot of the anion of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Intermolecular hydrogen bonding is indicated by a dashed line [Sb1···O6ⁱ = 3.283 (2) Å; symmetry code: (i) 1 - x, -y, -z].

Given that hard cations such as Na (Xie & Hu, 1991) and Li (Marrot *et al.*, 1996) induce an equatorial disposition of the lone pair, whereas polarizable cations, such as the dihydrated guanidinium (Mistryukov *et al.*, 1987) and the monohydrated aminoguanidinium in the title compound, should induce an axial disposition of the lone pair, the observed geometry reported for [Sb(Hedta)]·2H₂O appears to be an anomaly, since the compound, as formulated, has no ions in the crystal structure. The H atoms were not located in the structural

determination, so the acidic H atom was placed on the carboxyl O atom on the basis of a long C—O distance [1.316 (8) Å]. Of the two water O atoms, one is linked to two doubly bonded carbonyl O atoms [O···O = 2.550 (8), 2.714 (8) and 2.764 (6) Å], as well as to the second water O atom [O···O = 2.95 (1) Å; Shimoi *et al.*, 1980]. However, the configurations of antimony(III) complexes with flexible edta-type ligands are also affected by packing forces other than the hardness of the counter-ions. The packing in this class of complex is dominated by hydrogen-bonding interactions, so that the position of the lone pair in the coordination polyhedron of the Sb atom is intimately related to the strength of these interactions, which can be estimated by molecular mechanical calculations (Fu *et al.*, 1997).

Experimental

A quantity of (hydrogen ethylenediaminetetraacetato)antimonate(III) dihydrate, which was synthesized by the reaction of antimony(III) oxide with ethylenediaminetetraacetic acid (Shimoi *et al.*, 1980), was dissolved in the minimum volume of boiling water. Aminoguanidinium hydrocarbonate was added until the solution was almost neutral. The solution was filtered and concentrated to a third of its original volume, prior to crystallization at room temperature. Elemental analyses of the resulting crystals gave values in agreement with those calculated for (CH₇N₄)[Sb(C₁₀H₁₂N₂O₈)]·H₂O.

Crystal data

(CH₇N₄)[Sb(C₁₀H₁₂N₂O₈)]·
H₂O
M_r = 503.09
Monoclinic
*P*2₁/*n*
a = 8.2202 (3) Å
b = 18.2074 (6) Å
c = 11.9429 (4) Å
 β = 93.079 (1)°
V = 1784.9 (1) Å³
Z = 4
D_x = 1.872 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
Cell parameters from 5822
reflections
 θ = 2.81–27.50°
 μ = 1.607 mm⁻¹
T = 298 (2) K
Block
0.58 × 0.36 × 0.14 mm
Colourless

Data collection

Siemens SMART CCD area-
detector diffractometer
 ω scans
Absorption correction:
empirical (SADABS;
Sheldrick, 1996)
T_{min} = 0.595, *T_{max}* = 0.798
11 377 measured reflections
4081 independent reflections

3674 reflections with
I > 2σ(*I*)
R_{int} = 0.021
 θ_{\max} = 27.49°
h = -10 → 8
k = -23 → 23
l = -14 → 15

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.021
wR(*F*²) = 0.051

(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.55 e Å⁻³
Δρ_{min} = -0.58 e Å⁻³

$S = 1.087$
 4081 reflections
 328 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 0.6103P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Sb1—N1	2.265 (2)	Sb1—O3	2.198 (2)
Sb1—N2	2.507 (2)	Sb1—O5	2.543 (2)
Sb1—O1	2.144 (1)	Sb1—O7	2.254 (1)
N1—Sb1—N2	74.7 (1)	N2—Sb1—O7	70.0 (1)
N1—Sb1—O1	78.2 (1)	O1—Sb1—O3	76.2 (1)
N1—Sb1—O3	74.3 (1)	O1—Sb1—O5	146.1 (1)
N1—Sb1—O5	86.3 (1)	O1—Sb1—O7	73.1 (1)
N1—Sb1—O7	82.4 (1)	O3—Sb1—O5	70.7 (1)
N2—Sb1—O5	64.8 (1)	O3—Sb1—O7	144.5 (1)
N2—Sb1—O1	136.4 (1)	O5—Sb1—O7	134.7 (1)
N2—Sb1—O3	126.4 (1)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N6—H6A \cdots O8 ⁱ	0.89 (3)	2.34 (3)	3.119 (3)	146 (3)
N3—H3B \cdots O8 ⁱⁱ	0.86 (4)	2.01 (4)	2.860 (3)	170 (3)
N6—H6B \cdots O2 ⁱⁱⁱ	0.87 (3)	2.29 (3)	3.107 (3)	157 (3)
N4—H4B \cdots O9	0.84 (3)	2.04 (3)	2.804 (3)	150 (3)
N5—H5 \cdots O7 ⁱⁱⁱ	0.87 (3)	2.29 (3)	3.117 (3)	160 (3)
N3—H3A \cdots O6	0.82 (3)	2.05 (3)	2.848 (3)	166 (3)
N4—H4A \cdots O5	0.83 (3)	2.27 (3)	3.081 (2)	168 (3)
O9—H9A \cdots O6 ⁱⁱⁱ	0.85 (4)	1.90 (4)	2.741 (3)	172 (4)
O9—H9B \cdots O4	0.97 (5)	2.06 (5)	2.947 (3)	151 (5)

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different ψ angle (0, 88 and 180°) for the crystal and each exposure of 10 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -35° . Coverage of the unique set was over 99% complete. Crystal decay, monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, was found to be negligible.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINTE* (Siemens, 1996). Data reduction: *SAINTE*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97* and *PARST96* (Nardelli, 1995).

We thank the National Science Council for R&D, Malaysia (IRPA 09-02-03-0371, R&D No. 190-9609-2801), Universiti Sains Malaysia, the Russian Foundation for Basic Research (project code 96-03-32255a) and Xiamen University for supporting this work. SSSR thanks the Universiti Sains Malaysia for a Visiting Post-doctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1177). Services for accessing these data are described at the back of the journal.

References

- Fu, Y.-M., Xie, Z.-X., Hu, S.-Z., Xu, B., Tang, W.-D. & Yu, W.-J. (1997). *Jiegou Huaxue* (*Chin. J. Struct. Chem.*), **16**, 91–96.
- Gillespie, R. J. (1992). *Chem. Soc. Rev.* pp. 59–69.
- Hu, S.-Z., Fu, Y.-M., Toennesen, L. E., Davidovich, R. L. & Ng, S. W. (1998). *Main Group Met. Chem.* **21**, 501–505.
- Ilyukhin, A. B. & Davidovich, R. L. (1999). *Kristallografiya*, **44**, 238–246. (In Russian.)
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Marrot, B., Brouca-Cabarrecq, C. & Mosset, A. (1996). *J. Mater. Chem.* **6**, 789–793.
- Mistryukov, V. E., Sergeev, A. V., Mikhailov, Yu. N. & Shchelokov, R. N. (1987). *Koord. Khim.* **13**, 1129–1131.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Poore, M. C. & Russell, D. R. (1971). *J. Chem. Soc. Chem. Commun.* pp. 18–19.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Shimoi, M., Orita, Y., Uehiro, T., Kita, I., Iwamoto, T., Ouchi, A. & Yoshino, Y. (1980). *Bull. Chem. Soc. Jpn.* **53**, 3189–3194.
- Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Xie, Z.-X. & Hu, S.-Z. (1991). *Jiegou Huaxue* (*Chin. J. Struct. Chem.*), **10**, 129–131.

Acta Cryst. (1999). **C55**, 907–910

Diclofenac interactions: tetrakis[μ -2-(2,6-dichloroanilino)phenylacetato]-1:2 κ^8 O:O'-diacetone-1 κ O,2 κ O-dicopper(II)(Cu—Cu) acetaldehyde solvate

CARLO CASTELLARI,^a GIORGIO FEROCI^b AND STEFANO OTTANI^c

^aDipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, ^bIstituto di Scienze Chimiche, Università di Bologna, Via S. Donato 15, 40127 Bologna, Italy, and ^cCentro Studi Fisica Macromolecole, c/o Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: stefano@frodo.ciam.unibo.it

(Received 16 June 1998; accepted 3 February 1999)

Abstract

The structure of the centrosymmetric dimeric copper(II) title compound, $[\text{Cu}_2(\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NO}_2)_4(\text{C}_3\text{H}_6\text{O})_2] \cdot \text{C}_2\text{H}_4\text{O}$, has been determined and compared with the structures of analogous O-bridged Cu^{II} dimers. Polarographic experiments on aqueous solutions containing a mixture