Crystal and Molecular Structure, and Spectroscopic Characterization of Tetrakis(2-amino-1,3,4-thiadiazolium) Hexadecabromotetra-antimonate(III)†

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The compound $[HL]_4[Sb_4Br_{16}]$ (L = 2-amino-1,3,4-thiadiazole) was prepared and characterized by means of *X*-ray, i.r., and Raman measurements. Crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a = 10.995(2)$, $b = 11.950(2)$, $c = 9.830(2)$ Å, $\alpha = 112.92(2)$, $\beta = 96.23(2)$, $\gamma = 73.78(1)°$, and $Z = 1$. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final *R* value of 0.034 for 2 804 independent reflections. The crystal consists of a highly condensed $[Sb_4Br_{16}]^{4-}$ anion and four HL^+ cations. The anion has eight bromine atoms involved in hydrogen bonds with *N*-bonded H atoms. The metal atoms have distorted octahedral geometry.

The strong halide-ion acceptor behaviour of antimony trihalides has led to the isolation of a great number of complexes of the type $Sb_y^{III}R_xX_z$, where R = univalent cation and X = halide.[1] This kind of complex includes mono-, di-, and trimeric, but up to now tetrameric compounds only with chlorine atoms are known.[2] The co-ordination number, the more or less condensation of SbX_4^-, and hence the crystal structure of the compounds seem to be dependent on the nature of the counter ion.[2]

Experimental

All chemicals were reagent grade and used as received. The complex was prepared by adding a suspension of L•HBr (0.5 mmol) (L = 2-amino-1,3,4-thiadiazole) in dibromomethane and HBr (2 mmol) to a dibromomethane solution of $SbBr_3$ (1 mmol); methanol (2 cm^3) was then added to solubilize this mixture. From the solution, by slow evaporation over potassium hydroxide, transparent pale yellow crystals were collected (Found: C, 4.35; H, 0.80; N, 7.80; S, 5.85. Calc. for $C_2H_4Br_4N_3SSb$: C, 4.40; H, 0.75; N, 7.75; S, 5.90%).

The i.r. spectra were recorded with a Perkin-Elmer 180 spectrophotometer for the solid in a KBr disc (4 000—250 cm^{-1}) and for Nujol mulls of polythene (400—50 cm^{-1}). The Raman spectrum for the solid was recorded at room temperature with a Jobin-Yvon Ramanor HG 2S spectrometer, electronic spectra with a Shimatzu MPS 50L spectrometer.

Crystallography.—Crystal data. $C_8H_{16}Br_{16}N_{12}S_4Sb_4$, M = 2 174.1, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 10.995(2)$, b = 11.950(2), $c = 9.830(2)$ Å, $\alpha = 112.92(2)$, $\beta = 96.23(2)$, γ = 73.78(1)°, U = 1 142.2 Å^3, $Z = 1$, $D_c = 3.16$ ($D_m = 3.10$ by flotation) g cm^{-3}, $F(000) = 976.0$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 322.1 cm^{-1}, crystal dimensions *ca.* 0.10 × 0.10 × 0.35 mm.

The intensity data were collected at room temperature on a CAD 4 Enraf–Nonius automatic diffractometer with the ω—2θ scan technique in the range θ 2—27°, at scan speeds of 0.97—8.24° min^{-1}, with a scan width of 0.65° + 0.35 tanθ. Three standard reflections were measured every 3 h, but their intensities showed no significant changes. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on a ψ scan, was applied[3] (maximum, minimum transmission factors = 0.99, 0.29).

Table 1. Final positional parameters for $[HL]_4[Sb_4Br_{16}]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.751 06(5)	0.278 90(4)	0.250 11(6)
Sb(2)	0.862 92(5)	−0.024 60(4)	−0.188 15(6)
Br(1)	0.976 0(1)	0.200 01(8)	0.029 5(1)
Br(2)	0.663 5(1)	0.033 37(8)	0.005 5(1)
Br(3)	0.933 84(9)	0.096 15(8)	0.380 1(1)
Br(4)	0.780 41(9)	−0.210 18(7)	−0.364 0(1)
Br(5)	0.724 94(9)	0.122 75(8)	−0.315 0(1)
Br(6)	0.603 4(1)	0.420 03(9)	0.120 0(1)
Br(7)	0.835 8(1)	0.457 79(8)	0.430 4(1)
Br(8)	0.570 3(1)	0.305 52(8)	0.418 7(1)
S(1)	0.395 5(3)	0.249 2(2)	0.734 5(3)
S(2)	0.279 1(3)	0.553 6(2)	0.206 7(3)
C(1A)	0.372 5(9)	0.103 6(7)	0.701(1)
C(2A)	0.235(1)	0.310 1(8)	0.760(1)
N(1A)	0.250 7(8)	0.114 1(7)	0.713 0(9)
N(2A)	0.169 5(8)	0.234 9(7)	0.748 9(9)
N(3A)	0.462 2(8)	−0.001 2(7)	0.670(1)
C(1B)	0.255(1)	0.407 3(8)	0.154(1)
C(2B)	0.119(1)	0.614 1(9)	0.224(1)
N(1B)	0.132 2(8)	0.416 0(6)	0.153(1)
N(2B)	0.054 1(8)	0.533 9(8)	0.192(1)
N(3B)	0.343 5(8)	0.299 3(7)	0.114(1)

A total of 4 800 reflections were measured which, after merging ($R = 0.026$) equivalent data, gave 2 804 reflections with $I > 3\sigma(I)$ which were used in the refinement.

The structure was solved by conventional Patterson and Fourier methods and refined through full-matrix least-squares calculations. Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were included as fixed contributors at calculated positions assuming a bond distance of 1.0 Å and $B_H = B_C + 1.0$ Å^2 or $B_H = B_N + 1.0$ Å^2. This model converged to $R = 0.034$ and $R' = 0.032$ $\{w = 0.8/[\sigma^2(F) + 0.0004F_o^2]\}$ where $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. During refinement zero weights were assigned to two low-order reflections, which may be affected by secondary extinction.

Complex neutral-atom scattering factors[4] were employed throughout; major calculations were carried out on a Vax 11/750 computer, using the SHELX 76[5] program package and the ORTEP[6] plotting program.

Final fractional co-ordinates for non-hydrogen atoms are given in Table 1, bond distances and angles in Table 2.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Sb(1)–Br(1)	3.158(1)	Sb(1)–Br(2)	3.301(1)
Sb(1)–Br(3)	3.099(1)	Sb(1)–Br(6)	2.611(1)
Sb(1)–Br(7)	2.526(1)	Sb(1)–Br(8)	2.598(1)
Sb(2)–Br(1′)	3.136(1)	Sb(2)–Br(1)	3.185(1)
Sb(2)–Br(2)	2.818(1)	Sb(2)–Br(4)	2.555(1)
Sb(2)–Br(5)	2.601(1)	Sb(2)–Br(3′)	2.806(1)
C(1A)–S(1)	1.726(7)	C(1A)–N(1A)	1.33(1)
C(1A)–N(3A)	1.31(1)	C(2A)–N(2A)	1.27(1)
C(2A)–S(1)	1.72(1)	N(1A)–N(2A)	1.399(9)
C(1B)–S(2)	1.708(7)	C(1B)–N(1B)	1.32(1)
C(1B)–N(3B)	1.33(1)	C(2B)–N(2B)	1.27(1)
C(2B)–S(2)	1.71(1)	N(1B)–N(2B)	1.36(1)
Br(1)–Sb(1)–Br(2)	85.14(3)	Br(1)–Sb(1)–Br(3)	84.27(3)
Br(1)–Sb(1)–Br(6)	92.25(4)	Br(1)–Sb(1)–Br(7)	90.89(4)
Br(1)–Sb(1)–Br(8)	170.85(3)	Br(2)–Sb(1)–Br(3)	87.69(3)
Br(2)–Sb(1)–Br(6)	89.14(3)	Br(2)–Sb(1)–Br(7)	175.49(4)
Br(2)–Sb(1)–Br(8)	87.42(3)	Br(3)–Sb(1)–Br(6)	175.48(3)
Br(3)–Sb(1)–Br(7)	89.80(3)	Br(3)–Sb(1)–Br(8)	90.12(4)
Br(6)–Sb(1)–Br(7)	93.15(4)	Br(6)–Sb(1)–Br(8)	92.96(4)
Br(7)–Sb(1)–Br(8)	96.33(4)	Br(1)–Sb(2)–Br(1′)	89.96(3)
Br(1′)–Sb(2)–Br(2)	87.43(3)	Br(1′)–Sb(2)–Br(3′)	89.73(3)
Br(1′)–Sb(2)–Br(4)	88.55(3)	Br(1′)–Sb(2)–Br(5)	178.60(4)
Br(1)–Sb(2)–Br(2)	93.27(3)	Br(1)–Sb(2)–Br(4)	177.90(3)
Br(1)–Sb(2)–Br(3′)	88.43(3)	Br(1)–Sb(2)–Br(5)	89.98(3)
Br(2)–Sb(2)–Br(3′)	176.69(4)	Br(2)–Sb(2)–Br(4)	88.14(3)
Br(2)–Sb(2)–Br(5)	91.18(4)	Br(3′)–Sb(2)–Br(4)	90.08(3)
Br(3′)–Sb(2)–Br(5)	91.67(4)	Br(4)–Sb(2)–Br(5)	91.55(3)
Sb(1)–Br(1)–Sb(2)	88.85(3)	Sb(2)–Br(1)–Sb(2′)	90.04(3)
Sb(1)–Br(1)–Sb(2′)	89.20(3)	Sb(1)–Br(2)–Sb(2)	92.69(4)
Sb(1)–Br(3)–Sb(2′)	96.79(4)		
C(1A)–N(1A)–N(2A)	116.4(6)	N(1A)–C(1A)–S(1)	109.9(6)
C(1A)–S(1)–C(2A)	87.8(4)	N(2A)–C(2A)–S(1)	117.5(7)
N(1A)–N(2A)–C(2A)	108.4(7)	N(3A)–C(1A)–N(1A)	125.0(7)
N(3A)–C(1A)–S(1)	125.2(7)	C(1B)–N(1B)–N(2B)	116.1(7)
N(1B)–C(1B)–S(2)	110.0(6)	C(1B)–S(2)–C(2B)	88.2(4)
N(2B)–C(2B)–S(2)	115.6(7)	N(1B)–N(2B)–C(2B)	110.2(8)
N(3B)–C(1B)–N(1B)	123.8(8)	N(3B)–C(1B)–S(2)	126.2(7)

Primed atoms are related to unprimed by the symmetry transformation $-2 - x, -y, -z$.

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom co-ordinates and thermal parameters.

Results and Discussion

Description of the Structure.—The crystal structure is built up of discrete centrosymmetric $[Sb_4Br_{16}]^{4-}$ anions and two crystallographically independent HL^+ cations linked together by hydrogen-bonding interactions (Figure). The antimony atoms, all having distorted octahedral geometries, are linked by means of six bridging bromines, four of them are between two antimony atoms, while the other two bridge among three antimony atoms.

The Sb–Br bond lengths vary in the range 2.526—3.301 Å; the bridging Sb–Br bonds are clearly longer (2.818—3.301 Å) than the terminal ones (2.526—2.601 Å) with the average of 2.575 Å in good agreement with the average of 2.55(2) Å reported for other structures.[7–11]

It will be noted that the longest bridging is *trans* to the shortest terminal bond and, *vice versa*, that the shortest bridging bond is *trans* to the longest terminal bond. With regard to Sb(1), bond lengths of 2.526, 2.598, and 2.611 Å are found respectively for the terminal Sb–Br bonds which are *trans* respectively to bridging bonds with lengths of 3.301, 3.158, and 3.099 Å. In the case of Sb(2) the terminal Sb–Br bonds, 2.555 and 2.601 Å, are *trans* to the bridging bonds (3.185 and 3.136 Å), respectively. On the other hand, the lengths of the *trans* bridging bonds are similar, 2.818 and 2.806 Å. The sums of the *trans* terminal and bridging bonds are in the range of 5.710—5.827 Å.

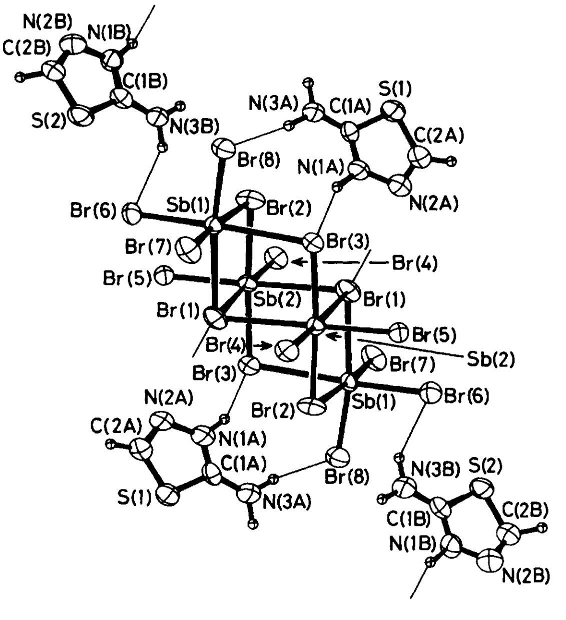
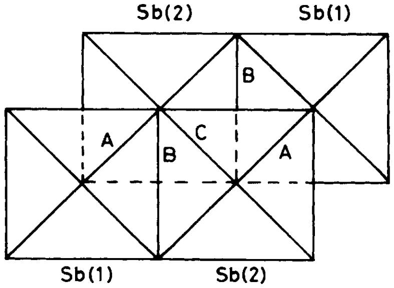


Figure. ORTEP View of the complex showing the atom numbering and thermal motion ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

The planes formed by four bromine atoms are planar within ±0.106 and ±0.013 Å and the deviations of the Sb atoms therefrom are within 0.130—0.001 Å. The strongest deviation from the octahedral geometry around each antimony atom, bond distances apart, can be found in the angle of 84.8° between the four-bromine atom plane and the Br–Sb axis, and in a dihedral angle of 91.7° between four-membered bromine planes.

From these data the octahedral co-ordination around the Sb atoms is seen not to be drastically distorted.

The packing of the anions can be represented as shown below.



From the model it is easy to see that the octahedra which contain the Sb atoms are linked together in two ways: those which contain Sb(1) share two edges (A,B) with the contiguous ones, while those which contain Sb(2) share three edges (A,B,C) with the contiguous ones. In the organic molecule the protonation has been fixed on the N(1) atom as suggested by a molecular-orbital calculation.

The preference of N(1) as protonation site can be explained by means of a semi-empirical all-valence-electron molecular orbital (m.o.) calculation, in the INDO approximation and parametrization.[12] The applicability and usefulness of INDO

Table 3. M.o. indices* of 2-amino-1,3,4-thiadiazole

Atom	q^{tot}	q	F_N
C(1)	0.4213		
C(2)	0.2316		
N(1)	−0.2350	−0.3291	0.5871
N(2)	−0.0928	−0.0919	0.1917
N(3)	−0.2302	0.1690	0.5699
S	−0.3603		

* Atomic units. F represents the frontier electron density of the h.o.m.o., q^{tot} represents the total ($\sigma + \pi$) net charge and q the π net charge of the non-hydrogen atoms of the ligand.

indices for the prediction of reactivity have recently been stressed.[13] The m.o. indices of L calculated in the present study are reported in Table 3. The indices chosen to represent the main features of the electronic structure of the ligand are the total ($\sigma + \pi$) net charge and the π net charge of the ring atoms and of the nitrogen atom of the NH_2 group, together with the frontier electron-density values of the highest occupied m.o. (h.o.m.o.) of the same atoms. From the analysis of the electron distribution and the h.o.m.o. which shows a strong localization on N(1), we may conclude that N(1) has the greatest chance of protonation. There are no significant differences between the corresponding bond distances and angles of the two crystallographically independent HL^+ ions. Their five-membered rings are planar within +0.001 Å and none of the exocyclic N atoms deviates more than 0.030 Å from the mean planes. Our bond distances and bond angles compare very well with those reported for 1,3,4-thiadiazole[14] and 2-amino-5-methyl-1,3,4-thiadiazole.[15]

Intermolecular hydrogen-bond contacts, on which the crystal packing depends, occur between NH_2 and NH groups and the bromine atoms, with N $\cdots$ H separations of 2.30, 2.51, 2.52, and 2.59 Å and subtended N–H $\cdots$ Br angles of 161, 157, 170, and 150° respectively.

I.r. and Raman Spectra.—In the i.r. and Raman spectra only three [223 (sh), 211 (sh), and 191vs cm^{-1}] and two (231s and 220vs cm^{-1}) bands, respectively, are observed and assigned to the Sb–Br$_t$ stretching vibrations. The $\nu(NH_2)$ ligand frequencies measured in $CHCl_3$ solution decrease significantly in the complex. This is not due to co-ordination of the amine group but to the hydrogen bonds still remaining in the solid state after complexation of the ligand.

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References

1 S. L. Lawton, D. M. Hoh, R. C. Johnson, and A. S. Knisely, *Inorg. Chem.*, 1973, **12**, 277 and refs. therein.
2 A. T. Mohammed and U. Müller, *Z. Naturforsch., Teil B*, 1985, **40**, 562.
3 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
4 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101 and 149—150.
5 G. M. Sheldrick, 'SHELX 76 Program for Crystal Structure Determination,' University Chemical Laboratory, Cambridge, 1976.
6 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
7 S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1966, **5**, 743.
8 C. R. Hubbard and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, 1968, **75**, 85.
9 M. K. Hackert, R. A. Jacobson, and T. A. Keiderling, *Inorg. Chem.*, 1971, **10**, 1075.
10 S. L. Lawton, R. A. Jacobson, and R. S. Frye, *Inorg. Chem.*, 1971, **10**, 701.
11 S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1968, **7**, 2124; 1971, **10**, 2813.
12 J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.
13 R. E. Brown and A. M. Simas, *Theor. Chim. Acta*, 1982, **1**, 62.
14 T. la Cour, *Acta Crystallogr., Sect. B*, 1974, **30**, 1642.
15 L. Antolini, A. Benedetti, A. C. Fabretti, A. Giusti, and M. C. Menziani, *J. Chem. Soc., Dalton Trans.*, 1988, 1075.

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