THE MOLECULAR STRUCTURE OF [{SbEtBr(μ-Br)[SCN(Me)C_2Me_2N(Me)]}$_2$]

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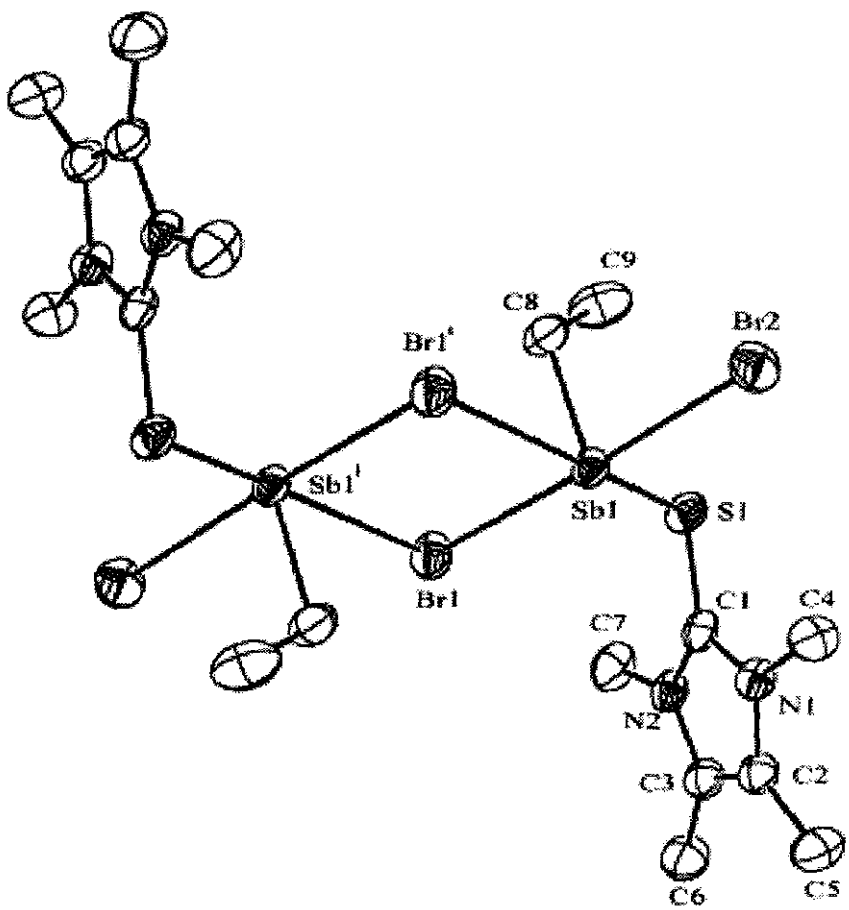

Figure 1. Molecular structure of [{SbEtBr(μ-Br)[SCN(Me)C_2Me_2N(Me)]}$_2$]. Selected bond lengths (Å) and angles(°): Sb(1)-C(8) 2.166(5), Sb(1)-S(1) 2.531(1), Sb(1)-Br(2) 2.7286(9), Sb(1)-Br(1) 2.8554(9), Sb(1)-Br(1)' 3.227(1), S(1)-C(1) 1.721(5), N(1)-C(1) 1.342(6), N(2)-C(1) 1.335(6), N(1)-C(2) 1.390(6), N(2)-C(3) 1.387(6), C(2)-C(3) 1.353(7), C(8)-Sb(1)-S(1) 91.5(2), C(8)-Sb(1)-Br(2) 86.7 (2), S(1)-Sb(1)-Br(2) 88.14(4), C(8)-Sb(1)-Br(1) 87.8(2), S(1)-Sb(1)-Br(1) 87.41(4), Br(2)-Sb(1)-Br(1) 172.81(2), Sb(1)-Br(1)-Sb(1)' 93.21(4), C(1)-S(1)-Sb(1) 102.9(2). Symmetry operator used to generate equivalent atoms: 1-x, 1-y, -z.

Comment

Prior to this work there were no crystallographically characterised examples of imidazolethione adducts of organoantimony compounds and only 3 examples of imidazolethione adducts of antimony trihalides [1-3]. The antimony centre in the present compound has a slightly distorted square based pyramidal geometry and a stereochemically active lone pair. The compound sits on an inversion centre and is dimeric through unsymmetrical Sb-Br-Sb bridges, both the longer and shorter interactions of which lie in the normal region for Sb-Br bonds [4]. The geometry of the imidazolethione ligand in the complex is similar to its geometry in the uncoordinated state [5].

Experimental

Preparation of [{SbEtBr(μ-Br)[SCN(Me)C$_2$Me$_2$N(Me)]}$_2$]:

A solution of SCN(Me)C$_2$Me$_2$N(Me) (1.0 g, 6.4 mmol) in THF (20 mL) was added over 15 minutes to a solution of SbEtBr$_2$ (2.0 g, 6.4 mmol) in THF (40mL) at –50 °C. The resulting yellow solution was warmed to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue recrystallised from CH_2Cl_2 to give the title compound as yellow prisms (2.15 g, 72%); m.p. 123-126 °C; ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 1.65 (6H, br., SbCH$_2$C*H*$_3$), 2.11 (12H, s, NCMe), 2.36 (4H, br., SbC*H*$_2$), 3.45 (12H, s, NMe); ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 9.1 (s, NC*C*H$_3$), 12.2 (s, SbCH$_2$*C*H$_3$), 27.3 (s, SbC*H*$_2$), 33.2 (s, NMe), 122.7 (s, *C*CH$_3$), 163.4 (s, CS); MS APCI m/z (%) 467 [M$^+$, 17], 156 [{CN(Me)C$_2$Me$_2$N(Me)}$^+$, 100]; IR (Nujol)ν/cm^{-1}: 1550 m, 1242 s, 115 m, 872 s.

Crystallography:

Table 1. Crystal data for [{SbEtBr(μ-Br)[SCN(Me)C$_2$Me$_2$N(Me)]}$_2$]

Formula	$C_{18}H_{34}Br_4N_4S_2Sb_2$	Formula weight	933.76
Crystal system	triclinic	Crystal size, mm	0.64x0.50x0.28
Space Group	$P\bar{1}$	*a*, Å	9.266(2)
b, Å	9.536(3)	*c*, Å	9.953(3)
α, °	113.96(1)	*β*, °	100.049(18)
γ, °	99.406(16)	*V*, Å^3	764.0(4)
Z	1	Diffractometer	CAD4
μ(Mo-K$_\alpha$), mm^{-1}	7.148	D_{calcd}, g cm^{-3}	2.029
F(000)	888	θ_{max}, °	25.0
Reflns meas.	2862	Reflns unique	2681
Reflns with $I > 2\sigma(I)$	2390	$R(F^2)$, $R_w(F^2)$ (all data)	0.037, 0.081
ρ, e Å^{-3}	0.96	G.O.F	1.03
No. parameters	142	Absorp. correct. [6]	Difabs
Programs used	SHELX-97 [7], Ortep-3 [8]		
Deposition number	CCDC 165463		

Acknowledgements

We gratefully acknowledge financial support from The Leverhulme Trust (SJB)

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