Synthesis and structure of [Sb{($Pr^iN)_2CNHPr^i$}{($Pr^iN)_2CNPr^i$}]; a distorted trigonal-bipyramidal antimony(III) complex with a helical hydrogen-bond network

Philip J. Bailey,*[a] Robert O. Gould,[a] Christopher N. Harmer,[b] Stuart Pace,[a] Alexander Steiner[b] and Dominic S. Wright*[b]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*

1,2,3-Triisopropylguanidine [($Pr^iNH)_2C{=}NPr^i$], reacts with antimony tris(dimethylamide) [$Sb(NMe_2)_3$] to provide [Sb{($Pr^iN)_2CNHPr^i$}{($Pr^iN)_2CNPr^i$}] 1, a heavily distorted trigonal-bipyramidal complex in which the Sb is chelated by a [$C(NPr^i)_3]^{2-}$ dianion and a [($Pr^iN)_2CNHPr^i]^-$ monoanion; in the solid state the complexes form helices by N–H···N hydrogen bonding of the single proton.

Our recent interest in trisubstituted guanidines and their anions as ligands has led to the characterisation of a number of new complexes which have demonstrated the flexibility of this new ligand system in both chelating and bridging coordination modes.[1–4] The ligands also exhibit a marked ability to stabilise higher oxidation states in transition-metal complexes.[4] The ability of the system to coordinate as a neutral (H_2L), monoanionic (HL^-) or dianionic (L^{2-}) ligand, and the presence of ionisable protons on the former two, adds to its flexibility. Hydrogen bonding plays an important role in much of the chemistry of guanidines and molecules containing the guanidine unit such as the nucleic acid base guanine, and we have thus become interested in the hydrogen-bonding properties of metal coordinated guanidines containing residual protons. Here we report a complex containing a single hydrogen which is formed by chelation of a trivalent metal by two trisubstituted guanidines, one a monoanion and the other a dianion, thus providing an N–H hydrogen-bond donor on one ligand and a imine nitrogen hydrogen-bond acceptor on the other.

Treatment of 1,2,3-triisopropylguanidine with 1 mol. equiv. of [$Sb(NMe_2)_3$][5] in toluene solution provides a yellow solution. Reduction of this solution to dryness in vacuum and dissolution of the residue in warm hexane followed by filtration, concentration and cooling provided highly air-sensitive crystals of [Sb{($Pr^iN)_2CNHPr^i$}{($Pr^iN)_2CNPr^i$}] **1** in 10% yield.† The presence of both the anion HL^- and dianion L^{2-} is confirmed by the ^1H NMR spectrum of **1** which shows that there are five independent isopropyl groups in the ratio 1 : 1 : 1 : 1 : 2, consistent with free rotation only about the uncoordinated C–$NHPr^i$ bond of the HL^- ligand whilst the C=NPr^i bond of the L^{2-} remains static. The formation of **1**, which retains an N–H hydrogen despite the presence of sufficient metallating agent in the reaction mixture to remove all such hydrogens, is worthy of note and may be a result of preferential crystallisation of the hydrogen-bonded partially metallated species, *vide infra*, and explain its low yield. Unfortunately, the extreme air sensitivity of **1** prevented the recording of any IR spectra.

Crystals of **1** are chiral with space group $P3_121$ or $P3_221$ and a low-temperature X-ray crystallographic study‡ shows that there are two independent, but chemically equivalent, molecules in the unit cell which differ only marginally in the conformations of their isopropyl groups and in their bond lengths and angles. One molecule lies on a twofold rotational axis relating the two ligands (Fig. 1), whilst the other (molecule 2, not shown) lacks this axis. The complex consists of [Sb{($Pr^iN)_2CNHPr^i$}{($Pr^iN)_2CNPr^i$}] molecules in which each Sb^{III} centre is formally chelated by a monoanion HL^- and a dianion L^{2-} ligand. The molecular structure of **1** is consistent with the ten-electron count of the Sb centre and can best be described as a heavily distorted trigonal-bipyramidal N_4Sb molecule with the fifth coordination site being occupied by the lone pair. In both independent molecules the Sb^{III} centres are asymmetrically coordinated by the two guanidine ligands [*e.g.* Sb(1)–N(11) 2.227(6) Å, Sb(1)–N(13) 2.069(6) Å]. This pattern of bond lengths is consistent with the description of the structure as distorted trigonal bipyramidal since in this geometry each ligand would be coordinated to an axial and an equatorial position. The nature of the distortion can be appreciated if it is considered that in this structure trigonal-bipyramidal geometry requires the chelating angle at the metal (N–Sb–N) to be 90°, whilst in **1** far more acute angles at Sb are found as a consequence of the geometric constraints arising from the chelation by the rigid guanidine ligands [*e.g.* N(11)–Sb(1)–N(13) 62.0(2)°]. The result of this is that the N–Sb–N angle between the axial N centres is distorted from the 180° [to

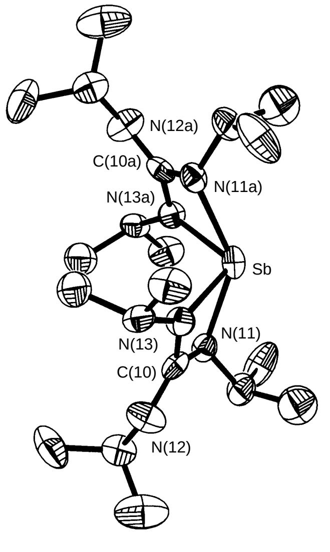

Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): molecule 1: Sb(1)–N(11) 2.227(6), Sb(1)–N(13) 2.069(6), C(10)∸N(11) 1.372(10), C(10)∸N(12) 1.311(11), C(10)∸N(13) 1.342(10); N(11)–Sb(1)–N(13) 62.0(2), N(11)–Sb(1)–N(11a) 140.3(3), N(13)–Sb(1)–N(13a) 104.5(3), N(13)–Sb(1)–N(11a) 93.1(2); N(12)···N(12a) 3.148(12), N(12)–H(12)–N(12) 160; molecule 2: N(31)–Sb(2) 2.320(6), N(33)–Sb(2) 2.098(6), N(41)–Sb(2) 2.133(6), N(43)–Sb(2) 2.050(5), C(30)∸N(31) 1.325(9), C(30)∸N(32) 1.353(9), C(30)∸N(33) 1.341(9), C(40)∸N(41) 1.402(9), C(40)∸N(42) 1.273(9), C(40)∸N(43) 1.381(9); N(31)–Sb(2)–N(33) 59.9(2), N(41)–Sb(2)–N(43) 63.9(2), N(41)–Sb(2)–N(31) 140.2(2), N(33)–Sb(2)–N(43) 104.2(2), N(33)–Sb(2)–N(41) 92.7(2), N(31)–Sb(2)–N(43) 93.4(2); N(32)···N(42) 3.125(12), N(32)–H(32)–N(42) 172, N(42)–H(42)–N(32) 144.

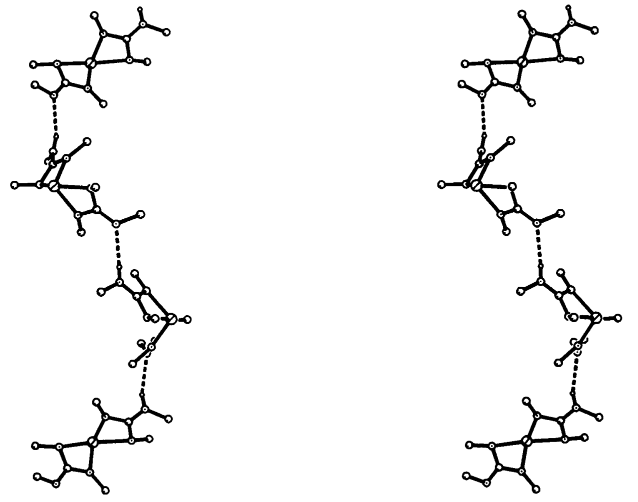

Fig. 2 Stereoview showing the association of molecules of **1** *via* N–H···N hydrogen bonds into helices. Symmetry transformations used to generate equivalent atoms a, *x–y*, *–y*, *–z* + 1/3.

140.3(3)° for N(11)–Sb(1)–N(11a)] and that for the equatorial N centres is distorted from the 120° [to 104.5(3)° for N(13)–Sb(1)–N(13a)] required for ideal trigonal-bipyramidal geometry. The distorted trigonal-bipyramidal geometries of the Sb^{III} centres of **1** are very similar to those observed for the central metal atom in the $[\{(Me_2N)_2Sb(NC_6H_{11})_2\}_2Sb]^-$ monoanion,[6] which is the only other structurally characterised unit containing an Sb^{III} centre four-coordinated by nitrogen ligands.

Although the ligands in each molecule of **1** must formally be a monoanion and a dianion to provide the necessary trianionic ligand set for the Sb^{III} centre, in the crystal they cannot be distinguished in this way since each of the uncoordinated NPr^i groups is involved in hydrogen bonding to an adjacent molecule with an N···N distance of 3.184(12) Å and N–H···N angle of 160°. As a consequence of the alignment of these groups, which is dictated directly by the distorted trigonal-bipyramidal geometry present in the molecular units of **1**, the resulting hydrogen-bonded H···L–Sb–L–H···L–Sb–L–H··· chains form left-handed helices through the crystal studied with three molecules of **1** per 360° turn (Fig. 2). It is probable that other crystals have the opposite chirality and hence right-handed chirality. Helical association of monomer units has been identified in a few polymeric phosphido and amido lithium complexes[7] and packing of molecules of $[Ru_3(CO)_9\{\mu\text{-NCH}(SiMe_3)_2\}(\mu\text{-N}(C_6H_2Pr^i{}_3\text{-}2,4,6)_2]$ exclusively into β helices occurs in the solid state.[8] However, helical packing or association of molecules is extremely rare in transition and main group metal compounds and, to our knowledge, the helical hydrogen-bonded association found in **1** is unprecedented for any metallo-organic complex.

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Footnotes

* E-mail: philip.bailey@ed.ac.uk

† 1,2,3-Triisopropylguanidine (0.928 g, 5.0 mmol) was dissolved in toluene (10 cm^3) and 2.6 cm^3 of a 1.93 M solution of $[Sb(NMe_2)_3]$ in toluene (1.275 g, 5.02 mmol) was added by syringe under argon. Over a period of 2 h the solution became yellow and the solvent was then removed *in vacuo*. The residue was dissolved in warm hexane (25 cm^3) and filtered through Celite to give a clear yellow solution. The volume was reduced to *ca.* 5 cm^3 and the resulting microcrystalline precipitate redissolved by warming. Gradual cooling in a water bath over two days provided X-ray quality crystals of **1** (*ca.* 10%). (Found: C, 48.2; H, 8.81; N, 16.4. $C_{20}H_{43}N_6Sb$ requires C, 49.1; H, 8.80; N, 17.1%). ^1H NMR (250 MHz) in $[^2H_6]$benzene: δ 0.7–1.6 [m, 36 H, $CH(CH_3)_2$], 3.34 [br, 2 H, $CH(CH_3)_2/NH$], 3.72 [spt, 2 H, $CH(CH_3)_2$], 4.12 [spt, 1 H, $CH(CH_3)_2$], 4.35 [spt, 1 H, $CH(CH_3)_2$], 4.83 [spt, 1 H, $CH(CH_3)_2$].

‡ *Crystal data* for **1**: $C_{20}H_{43}N_6Sb$, M_w = 489.35, trigonal, space group $P3_221$, a = 17.356(2), b = 17.356(2), c = 21.919(4) Å, U = 5718(2) $Å^3$, Z = 9, λ = 0.710 73 Å, D_c = 1.279 Mg m^{-3}, μ(Mo-Kα) = 1.101 mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated crystal[8] of dimensions 0.2 × 0.2 × 0.2 mm using the θ–ω method (4.04 ⩽ θ ⩽ 22.73°). Of a total of 6438 reflections collected, 4985 (R_{int} 0.026) were independent. The crystal studied was intimately twinned, giving a diffraction pattern approximating to 6/*mmm* (D_{6h}) symmetry. Twin refinement in space group $P3_221$ with $[1\bar{1}0]$ as the twin axis gave 56.46(9)% as the contribution of the major component and 0.03(3) as the Flack *x*-parameter, indicating that both twins have the same correct absolute structure. No conclusons may be drawn about the chirality of the other crystals in the batch. The structure was solved by Patterson methods, and refined by full-matrix least squares on F^2 to final values of R_1 = 0.027 [for 4985 data with $F > 4\sigma(F)$] and wR_2 = 0.070 (all data) [$R_1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)]^2/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 4.26P]$, $P = (F_o^2 + 2F_c^2)/3$].[10] Largest difference between peak and hole in the final difference map, 0.42, −0.38 e $Å^{-3}$. The hydrogen-bonded N–H hydrogens were placed in calculated positions and allowed to ride between their respective nitrogen atoms with a site occupancy of 0.5. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/460.

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