

Synthesis of a stibindolyl anion from trimesitylantimony and potassium

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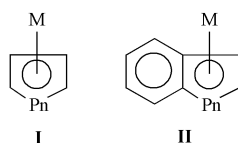
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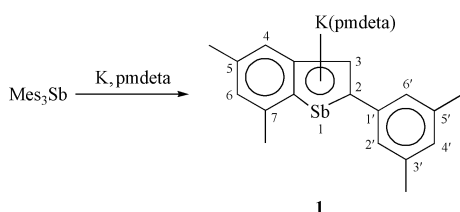
2-(3',5'-Dimethylphenyl)-5,7-dimethylstibindolyl potassium-pmdeta (**1**) (pmdeta = pentamethyldiethylenetriamine) is obtained from trimesitylantimony, potassium and the amine ligand in tetrahydrofuran; crystals of **1** consist of stacks of (pmdeta)K⁺ ions and stibindolyl anions with alternating Sb–K and η^5 -SbC₄–K interactions.

Alkali-metal complexes of cyclic hydrocarbons with delocalised π systems have been studied frequently because they are important as reagents for organometallic syntheses and their special bonding situation is remarkable. Among heterocyclic analogues with heavier pnictogen (Pn) atoms the complexes with anionic phospholyl and the phosphindolyl ligands (type I, Pn = P; M = Li,¹ Na,² K,^{2,3} Rb,⁴ Cs,⁴ and type II, Pn = P; M = Li,⁵ K,⁶) have received attention. With arsenic or antimony only two derivatives of type I (Pn = As, M = Li;⁷ Pn = Sb, M = K⁸) were described. Complexes with stibindolyl anions (type II, Pn = Sb) are not known, but neutral aryl or alkyl stibindoles have been described.^{9,10,11}



We report here the synthesis[†] and the crystal structure[‡] of 2-(3',5'-dimethylphenyl)-5,7-dimethylstibindolyl potassium-pmdeta (**1**) (pmdeta = pentamethyldiethylenetriamine), an antimony derivative of type II. **1** is a deep red solid which is soluble in tetrahydrofuran but not in hexane, petroleum ether, benzene or other organic solvents. In air it is self igniting and also very sensitive to traces of water, but stable in an inert atmosphere up to 176 °C. The synthesis of **1** is achieved in an one pot reaction of trimesitylantimony with potassium and pmdeta in tetrahydrofuran. After recrystallisation from tetrahydrofuran/toluene (1/3) **1** is obtained in 62% yield (Scheme 1).

The mechanism of the remarkably specific formation of **1** is not known. By analogy with the reaction of trimesitylantimony with lithium giving mesityllithium and lithium dimesitylantimonide¹² we propose the formation of MesK and Mes₂SbK in the first step. The following steps probably include the migration of an Sb–C bond, removal and shifting of hydrogen atoms and C–C coupling. It is noteworthy that the carbon framework in the stibindolyl anion corresponds to two mesityl moieties. Reactions of antimony compounds with migrations of



Scheme 1

the organosubstituents are not unusual and are observed in reactions of Ph₃Sb with Li¹³ or *cyclo*-(^tBuSb)₄ with K.¹⁴ For the complex sequence of transformations leading to **1** we found no exact match in the literature. Partially related are the multistep reactions of RP(H)Li with toluene leading to phosphindolyl anions.¹

The characterisation of **1** was achieved by X-ray diffractometry on single crystals obtained from thf–benzene and by NMR spectroscopy. Attempts to characterise **1** also by elemental analyses failed. The structure consists of stacks built of dimethyl(dimethylphenyl) stibindolyl anions and (pmdeta)K⁺ cations in bridging positions between each other. The repeating unit (Fig. 1) contains two pairs of anions and cations which are crystallographically independent but have very similar geometries.

An important structural feature of the stibindolyl anions is the perfect planarity of the condensed C₄Sb and C₆ rings, which corresponds to considerable delocalisation in the 10 π electron system where also one of the lone pairs of antimony is involved. Only between the rings there is subtle bending along the common C–C bond (dihedral angle 3°). Rotation of the

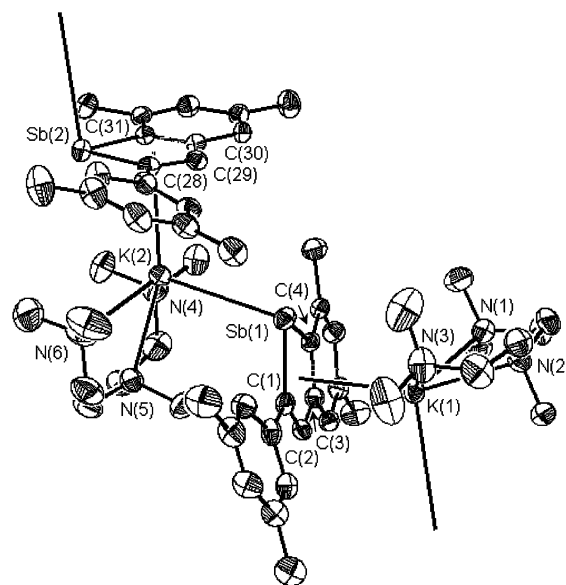


Fig. 1 Molecular structure and numbering scheme of **1**. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity. The centers of the five-membered rings in the stibindolyl anions are symbolised by Z(*n*) with *n* being the same number as for the corresponding Sb(*n*). Selected bond lengths (Å) and angles (°) for **1**: Sb(1)–K(2) 3.755(2), K(1)–Sb(1) 3.687(1), K(1)–C(1) 3.200(4), K(1)–C(2) 3.168(4), K(1)–C(3) 3.414(4), K(1)–C(4) 3.619(6), K(1)–Z(1) 3.11(5), Sb(1)–C(1) 2.121(4), Sb(1)–C(4) 2.128(4), C(1)–C(2) 1.394(5), C(2)–C(3) 1.443(5), C(3)–C(4) 1.390(5), Sb(2)–K(1) 3.743(2), K(2)–Sb(2) 3.687(1), K(2)–C(28) 3.209(4), K(2)–C(29) 3.168(4), K(2)–C(30) 3.417(4), K(2)–C(31) 3.622(6), K(2)–Z(2) 3.113(47), Sb(2)–C(28) 2.128(4), Sb(2)–C(31) 2.122(4), C(28)–C(29) 1.367(5), C(29)–C(30) 1.438(5), C(30)–C(31) 1.403(5), K–N 2.833(4)–2.889(4); C(1)–Sb(1)–C(4) 80.6(2), C(28)–Sb(2)–C(31) 80.53, Z(1)–Sb(1)–K(2) 98.99(2), K(2)–Z(2)–Sb(2) 93.72(2), Z(2)–K(2)–Sb(1) 105.79(2), Z(1)–K(1)–Sb(2)* 105.44(2).

dimethyl phenyl ring which is not involved in the 10π system leads to a dihedral angle between the C_6 - and the C_4Sb -planes of 16.8° . The Sb–C distances (2.121(4)–2.128(4) Å) in **1** are almost equal. They lie between the values for single and double bonds (cf. Sb–C: Mes_3Sb (2.181–2.185 Å),¹⁵ Sb=C: RC(O)Sb=C(OH)R (R = $tBu_3C_6H_2$) (2.078(3) Å)¹⁶ and compare well with the Sb–C bond lengths (2.085(8)–2.115(8) Å) in tetraethylstibolylpotassium-0.25thf.⁸ Also the SbC₂ angles in **1** (80.6(2), 80.5(2)°) are similar to the analogous values found in the stibolide (81.1(3)°).⁸ The C–C bond lengths in the stibindolyl ligand of **1** are not equal, they vary in the SbC₄ ring between 1.390(5) and 1.443(5) Å. The cations of **1** feature the tridentate coordination of the pmdeta ligands to the potassium centers where the K centres lie 1.27 and 1.30 Å above the N₃ planes.

In the repeating unit (Fig. 1) two different types of interactions between the cations and the anions can be distinguished. The position of K(1) above the C₄Sb ring of the stibindolyl anion containing Sb(1) or of K(2) relative to the anion containing Sb(2) corresponds to η^5 -coordination with K–Sb distances of 3.687(2) and 3.688(2) Å and K–C distances ranging between 3.168(4) and 3.688(2) Å. The distances between the K(1) or K(2) atoms and the centers (Z) of the C₄Sb(1) or C₄Sb(2) rings are both 3.11(5) Å. The η^5 coordination is slightly acentric with shorter distances between K and the peripheral carbon atoms C(2), C(3) or C(28), C(29). The angles between the Z–K vector and the C₄Sb plane are 79.3 and 79.6°. Another type of interaction exists between K(2) and the stibindolyl ion containing Sb(1). Here the geometric parameters (Sb(1)–K(2) 3.755(2); K–C distances >4 Å) correspond rather to an η^1 coordination through the p-orbital of the antimony atom of the stibindolyl ion than to η^5 interactions. We believe that repulsive steric interactions between the pmdeta ligands and between neighbouring stibindolyl anions which are almost perpendicular relative to each other are responsible for the pronounced bending and the alternation of the type of coordination in the stacks. A sterically less congested situation exists in the structure of the type I compound tetraethylstibolid-(0.25thf)⁸ where alternating cations and almost parallel anions with exclusive η^5 -coordination form a polydecker type structure which is much closer to linearity. In fact the modest bending in the stibolid structure is mainly related to Sb–K contacts between neighbouring stacks. In the structure of **1** there are no short contacts between the stacks.

Solutions of **1** contain only one type of stibindolyl groups. ¹H- and ¹³C-NMR spectra in thf-d₈ show one set of all the expected signals for the CH groups of the stibindolyl moiety. Signals for the methyl groups are partially overlapping with the methyl signals of the pmdeta ligand.

The facile synthesis and high thermal stability of **1** opens promising perspectives for the study of the chemistry of the stibindolide ion. Reactions with electrophiles or oxidising agents and the use as ligands in π -complexes are of particular interest.

Notes and references

† Addition of potassium pieces (0.32 g, 8.20 mmol) to a solution of Mes_3Sb (1.00 g, 2.08 mmol) in 20 mL tetrahydrofuran and stirring at room

temperature for 1 h results in a colour change to dark red. The remaining potassium pieces are removed by filtration and pmdeta (0.8 mL, 4.17 mmol) is added to the reaction mixture. After 1 h of stirring and removal of the solvent at reduced pressure a red powder remains which is washed twice with *n*-hexane; recrystallisation from tetrahydrofuran–toluene (3:1) gives **1** (0.73 g, 62%) as a red powder. Mp 176 °C (decomp.). ¹H NMR (200 MHz, C₄D₈O): δ 2.07 (12H, s, NCH₃), 2.10 (3H, s, NCH₃), 2.14 (6H, s, CH₃-C3' and C5'), 2.18–2.37 (14H, m, CH₃-C4, CH₃-C6 and NCH₂), 6.56 (1H, s, H-C4'), 6.66 (2H, s, H-C2' and H-C6'), 7.22 (1H, s, H-C4 or H-C6), 7.24 (1H, H-C4 or H-C6), 7.91 (1H, s, H-C3). ¹³C NMR (50 MHz, C₄D₈O): δ 13.88 (s, CCH₃), 22.97 (s, CCH₃), 31.98 (s, CCH₃), 42.71 (s, NCH₃), 45.65 (s, N(CH₃)₂), 56.85 (s, NCH₂), 58.28 (s, NCH₂), 117.69 (s, CH), 123.95 (s, CH), 124.34 (s, CH), 124.78 (s, CH), 125.96 (s, CH), 127.00 (s, CH), 128.54 (s, CH), 136.68 (s, CH), 137.49 (s, CH), 141.74 (s, CH), 148.26 (s, CH), 149.07 (s, CH).

‡ Crystal data for **1**: C₂₇H₄₁KN₃Sb, *M* = 568.48, *a* = 9.641(2), *b* = 13.243(3), *c* = 23.681(5) Å, α = 74.21(3), β = 89.60(3), γ = 89.99(3)°, *V* = 2909.3(11) Å³, *T* = 173(2) K, monoclinic, space group *P*2₁, *Z* = 4, μ (Mo–K α) = 0.71073 Å^{−1}, 40169 reflections collected (Stoe IPDS diffractometer), 10616 reflections [*I* > 2 σ (*I*)] were used in all calculations, *R* = 0.0346, *R*_w = 0.0645. The structure of **1** was refined anisotropically using full-matrix least square based on *F*². CCDC 198210. See <http://www.rsc.org/suppdata/cc/b2/b211177b/> for crystallographic data in CIF or other electronic format.

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