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$[Sn_2(H_2O)_2Br_2(CH_3)_4\{\mu\text{-}(CH_2)_3\}\cdot 2bpy]$: A Layered, Hetero Bimolecular Composite (bpy=2,2′-bipyridine)

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Reaction of $(Me_2SnBr)_2\mu\text{-}(CH_2)_3$ with 2,2′-bipyridine (bpy) in benzene affords, in the presence of small amounts of water, crystals of the novel composite $[Sn_2(H_2O)_2Br_2Me_4\{\mu\text{-}(CH_2)_3\}\cdot 2bpy]$ (1). The crystal structure of 1 consists of alternating layers of either organotin bromide or bipyridine molecules, each bpy molecule being configured *cis*oid and linked with the organotin layer via one O–H···N hydrogen bond. The mutual disposal of the molecules in the bpy bilayer differs from that known for pure, crystalline bpy. Cell parameters: *a* 24.3499(1), *b* 6.5112(1), *c* 23.3262(1) Å; *β* 119.557(1)°. Monoclinic, space group *C*2/*c*, $D_{calc} = 1.750\,g/cm^3$, $Z = 4$; final *R*1: 0.0529; *wR*2 = 0.1374 for 3638 unique reflections [*R*(int) = 0.0676; $I > 2\sigma(I)$].

Keywords: *Cis*oid; 2,2′-bipyridine; Coplanar; O–H···N

In the absence of water, trimethyltin halides add readily one pyridine (py) molecule, affording $[Me_3SnX\cdot py]$ adducts of trigonal bipyramidal (tbp) configuration [1,2]. Corresponding binuclear derivatives $[(Me_2SnX\cdot B)_2(\mu\text{-}Y)]$ (X = halide, B = aromatic nitrogen base, Y = saturated hydrocarbon tether) involving two *tbp*-configured $[Me_2(Y)_{0.5}SnX\cdot B]$ fragments have also been reported [3]. However, when we attempted to arrive at corresponding crystalline products of the type $[(Me_2SnBr\cdot B)_2\mu\text{-}(CH_2)_3]$ with B = py, 0.5 bpy, 0.5 4,4′-bpy and 0.5 pyz, respectively (pyz = pyrazine), not strictly maintaining anhydrous conditions, single crystals resulted exclusively from a 1:2 mixture of $Me_2BrSn(CH_2)_3SnBrMe_2$ and bpy (product **1**).

The ^1H NMR spectrum of crystalline **1** dissolved in $CDCl_3$ revealed the presence of apparently free bpy and $Me_2BrSn(CH_2)_3SnBrMe_2$ in the anticipated ratio of 1:2. Although the NMR spectrum did not display any significant resonance to be ascribed to water, the crystal structure analysis of **1** strongly suggests that each tin atom carries one H_2O ligand instead of a nitrogen atom of the organic base. The $Me_2Br(H_2O)Sn(CH_2)_3Sn(H_2O)BrMe_2$ molecules actually present in the solid are C_2-symmetrical with respect to a C_2 axis perpendicular to the Sn···Sn vector, all C and Sn atoms lying approximately in one plane (see Fig. 1). Unlike in crystals of pure bpy [4,5] the two pyridyl units of each bpy molecule found in **1** are tilted by an angle of 33.5° and the two N atoms are *cis*oid configured. The local symmetry of the bpy molecule is only C_1 (vide infra). Selected interatomic distances and bond angles are collected in Table I. Most of the metrical parameters of the two molecular components of **1** seem to be unspectacular. The intramolecular Sn···Sn distance of 6.1714(7) Å compares well with corresponding data reported for various compounds involving likewise a $\{Sn(CH_2)_3Sn\}$ fragment [6–9]. While the Sn–Br distance lies at the upper end of the range so far reported for five-coordinated organotin(IV)bromide complexes [10], the Sn–O distance matches well with data known for various $[R_3SnCl\cdot H_2O]$ systems (R = aryl) [11]. On the other hand, unusually long Sn–N distances between 2.44 and 2.65 Å seem to be typical of complexes of the initially envisaged type $[R_3SnXB]$ [3,10],offering thus

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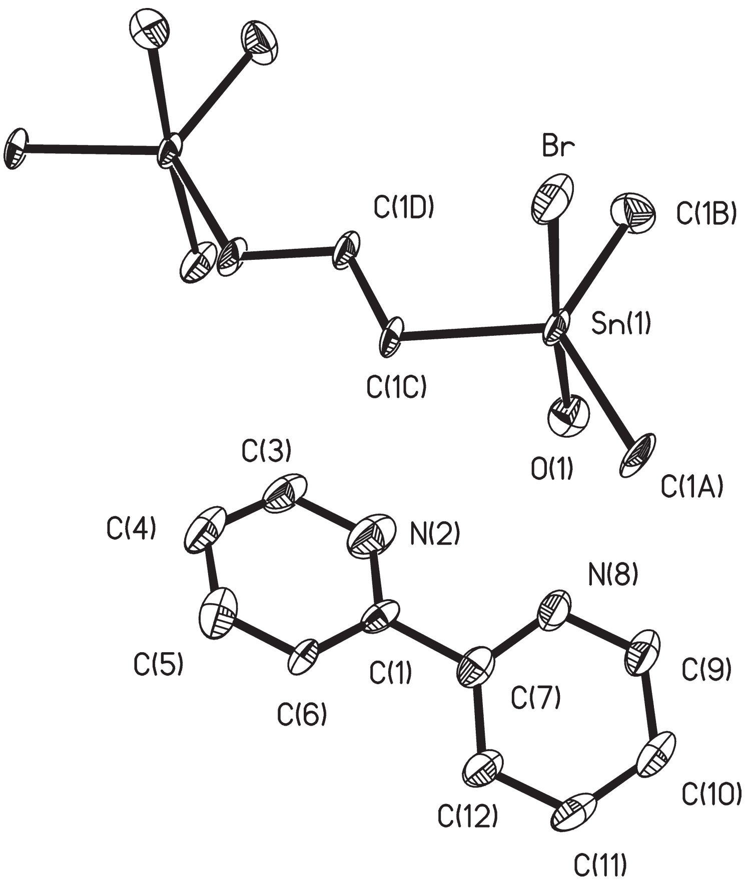

FIGURE 1 Asymmetric unit of the two components of **1**. To document the C_2-symmetry of the $[Sn_2(H_2O)_2Br_2(CH_4)_4\{\mu\text{-}(CH_2)_3\}]$ molecule, this component is drawn in full length. Space group: $C2/c$, $Z = 4$, $R1 = 0.0529$, $wR2 = 0.1374$.

promising conditions for a facile exchange of the nitrogen base by water molecules.

Quite unexpectedly, the two different molecular components of **1** are accommodated in alternating, parallel layers (Fig. 2). The bpy molecules are, moreover, aligned in bilayers (see Fig. 3), avoiding, however, eclipsed stacking. Interestingly, in crystals of pure bpy, the molecules are strictly coplanar-*trans*oid configured, and their packing resembles a herringbone pattern [4,5]. All the gaps between adjacent molecules (in each plane) are filled by bromine atoms. The shortest "interlayer" C···Br distance of 3.750 Å (involving C3 of 2,2′-bpy) seems, however, to be too long to reflect any weak, but non-negligible C–H···Br hydrogen bonding, [12] while direct Br···N interactions [13,14] can strictly be ruled out (shortest Br···N separation: 4.856 Å).

Notably stronger interlayer hydrogen bonding is, however, realized between each H_2O ligand and one of the two nitrogen atoms of each bpy molecule (distance: O···N8: 2.718(6) Å).

Ignoring here any C–H···Br interaction, this latter O–H···N hydrogen bond seems to be primarily responsible for the spontaneous formation of the layered composite. While **1** seems to be the first adduct of the series: {*trans*-$SnR_3Hal(OH_2)$(dibasic N-base)} with R = methyl, numerous examples with R = aryl and Hal = Cl are known, [11,15–17] wherein the respective nitrogen base is, however, found to use *both* of its N atoms for hydrogen bonding. Moreover, self-assembly according to a layered alignment has so far not been reported [15].‡

Recently, increasing interest in composites involving layers of two different compounds (one being an aromatic hydrocarbon) has emerged. Desiraju *et al.* have postulated [18] that planar aromatic hydrocarbons otherwise crystallizing in a herringbone fashion should be forced to adopt coplanar layers if they could be co-crystallized with strictly layered 1,3,5-tricyanobenzene. On the other hand, Zaworotko *et al.* have demonstrated [19] that "layers" of edge-to-face stacking pyrene molecules (not superimposable with those of pristine pyrene [20]) interpenetrate a framework of parallel, but staggered, $[Ni\{\mu\text{-}(4,4'\text{-bpy})\}^{2+}]_\infty$ layers. Our present results focus on a situation where the arrangement of the bicyclic π-electron system bpy has changed

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‡For instance the adduct $\{SnPh_3Cl(OH_2)\cdot 1,10\text{-phen}\}$ turns out to form a centrosymmetric dimer.

TABLE I Selected interatomic distances (Å) and angles (°) of **1**

Distance (Å)		Angle (°)	
Sn1–C1A	2.134(5)	C1A–Sn1–C1B	122.7(2)
Sn1–C1B	2.141(6)	C1A–Sn1–C1C	117.0(2)
Sn1–C1C	2.148(4)	C1C–Sn1–C1B	119.32(19)
Sn1–O1	2.359(4)	Sn1–C1C–C1D	114.1(4)
Sn1–Br	2.7037(7)	O1–Sn1–C1A/B/C	87.33(17)/82.90(17)/90.11(17)
C1C–C1D	1.521(6)		
01···N8	2.718(6)	Br–Sn1–C1A/B/C	94.92(14)/91.91(14)/93.07(13)
Sn1···Sn1′	6.1714(7)		
		O1–Sn1–Br	174.70(10)

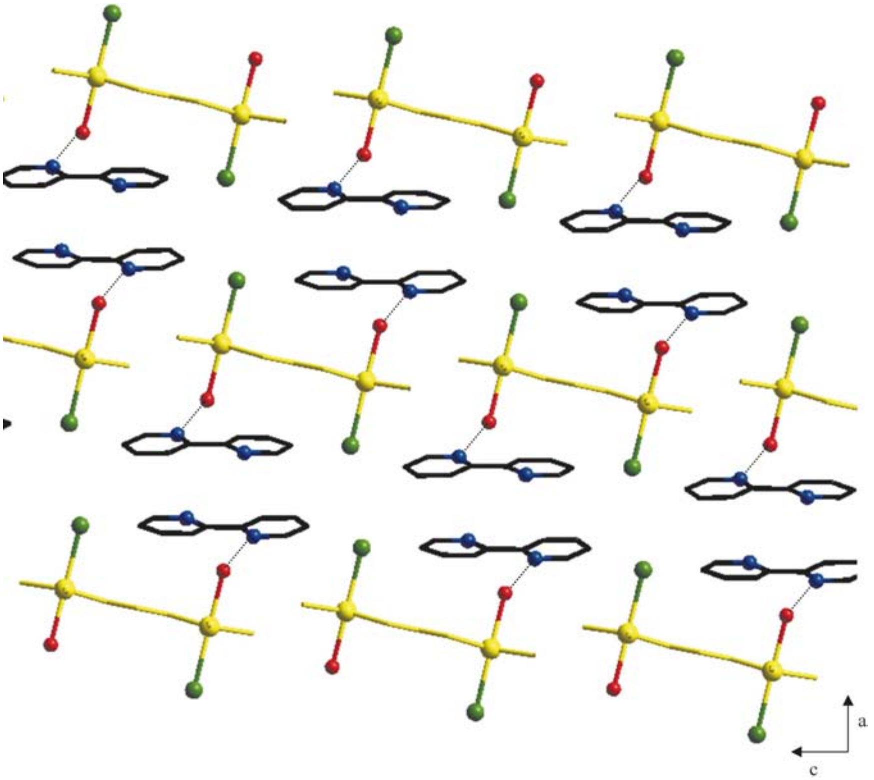

FIGURE 2 Perspective of the layered structure of **1** along *b*. Dotted line: O–H···N bridge. Colours: $(Me_2Sn)_2(CH_2)_3$ skeleton yellow, H_2O red, Br green and bpy blue/black. Hydrogen atoms have been omitted.

from herringbone-like [4,5] to quasi-coplanar without, however, any face-to-face stacking [21].

EXPERIMENTAL

Following essentially Ref. [3], $(Me_2BrSn)_2(CH_2)_3$ [22] (500.0 mg = 1.00 mmol) and 2,2′-bpy (312.4 mg = 2.0 mmol) were suspended in 2–3 ml of benzene (tech.). After short refluxing, a few drops of CCl_4 were added stepwise, until the initially clear solution became cloudy. Crystals of **1** suitable for crystallographic and NMR studies became available when the solution had been left in the refrigerator for ca. 90–100 days. Anal. calcd. for $C_{27}H_{38}Br_2N_4O_2Sn_2$ (847.82): C 38.25, H 4.51, N 6.60, found C 38.66, H 4.14, N 6.80%. Yield: 287 mg = 0.34 mmol (34.0%); decomp. temp. 58–59°C.

^{1}H NMR ($CDCl_3$, 360 MHz; δ/ppm): 0.71 s (12 H, $J = 54$ Hz, Me_2Sn), 1.41 t (4 H, CH_2Sn), 2.04 q (2 H, –CH_2–); 7.34 m (4 H, bpy), 7.68 t (4 H, bpy), 8.40 s (2 H, bpy), 8.44 s (2 H, bpy), 8.73 d (4 H, bpy). Crystallographic data for **1** (axs Smart-CCD diffractometer; temp. 173 K) have been deposited with the Cambridge Crystallographic Data Centre (CCDC-No.: 162337). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EC, UK. Fax: +44 122-333-6033. E-mail: eposit@chemcrys.cam.ac.uk.

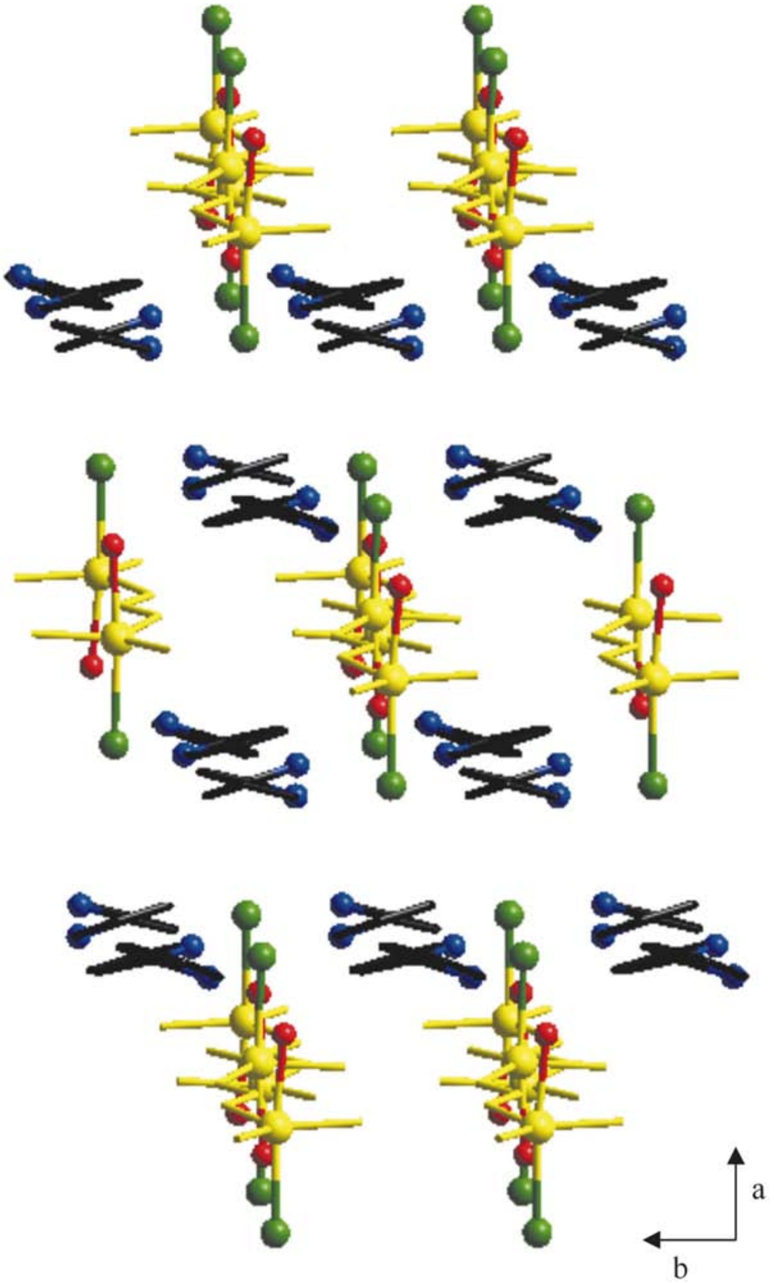

FIGURE 3 Perspective of the layered structure of **1** along *c*. Colours as in Fig. 2.

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