The Crystal Structure of $[(SnBr){\cdot}Ni(H_2O)(MeCN)(L)]^+Br^-$ (H_2L = *N,N′*-1,3-propylenebis-3-methoxysalicylideneamine): the First Authenticated Example of a Monohalostannate(II) Cation

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In the title compound each cation, $SnBr^+$, forms four Sn–O donor bonds to a nickel salicylideneamine molecule, while bromide ions alternate with water molecules in hydrogen bonded zig-zag chains.

The long-standing evidence for the existence of cations SnX^+ (X = halide) in solution[1] has stimulated a number of efforts to isolate these fundamental tin(II) cationic species in the solid state. SnF_2 reacts with the fluoride acceptors SbF_5, AsF_5 and BF_3 to yield 1 : 1 addition complexes which, on the basis of IR and Raman spectroscopic studies, appear to be best formulated as the salts $(SnF)(MF_6)$ (M = Sb and As) and $(SnF)(BF_4)$. However, the spectroscopic studies further reveal that these probably contain the polycations $(SnF)_n{}^{n+}$ rather than the simple cations SnF^+, and furthermore, the possibility of fluoride bridging between anions and cations cannot be ruled out.[2] More recently, the presence of cations $SnCl^+$ in the adduct $SnCl_2$–18-crown-6 ether (2 : 1) has been suggested on the basis of ^{119}Sn Mössbauer spectroscopy.[3] In neither of these cases, nor in any other case, has the existence of simple monohalostannate(II) cations been confirmed crystallographically. In actual fact, tin(II) appears to have a limited cationic chemistry and the only cationic tin(II) halo species which have been positively identified are polymeric tin(II) fluoro cations.[4] We have recently studied a reaction of diorganotin(IV) halides and pseudohalides with divalent metal salicylideneamines which strongly favours the formation of $SnR_2{}^{2+}$ and SnR_2X^+ cations (R = organo group; X = halide or pseudohalide) and it occurred to us that a similar reaction with tin(II) halides might favour the formation of the tin(II) ion (which has now been identified in the solid state[5]), or SnX^+ cations (X = halide). In view of the uncertainty surrounding the existence of these latter cations, the tin(II) halide reactions were investigated. Resulting from this investigation we now present the first positive identification of a monohalostannate(II) cation.

$SnCl_2$, $SnBr_2$ and $Sn(NCS)_2$ reacted with NiL (H_2L = *N,N′*-1,3-propylenebis-3-methoxysalicylideneamine) in

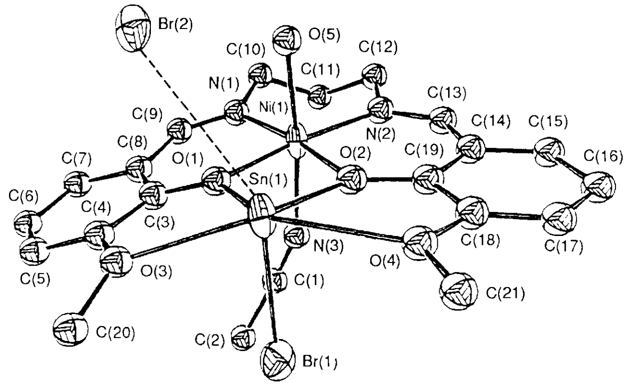

Fig. 1 ORTEP[10] plot of the asymmetric unit of **1**. Selected dimensions: Sn(1)–Br(1) 2.710(1), Sn(1)–Br(2) 3.724(1), Sn(1)–O(1) 2.189(4), Sn(1)–O(2) 2.199(4), Sn(1)–O(3) 2.642(5), Sn(1)–O(4) 2.650(5) Å. O(1)–Sn(1)–O(2) 70.9(2), O(2)–Sn(1)–O(4) 64.7(2), O(3)–Sn(1)–O(4) 151.8(2), O(1)–Sn(1)–O(3) 65.4(1), Br(1)–Sn(1)–O(1) 92.1(1), Br(1)–Sn(1)–O(2) 90.5(1), Br(1)–Sn(1)–O(3) 77.3(1), Br(1)–Sn(1)–O(4) 82.2(1), Br(2)–Sn(1)–O(1) 66.1(1), Br(2)–Sn(1)–O(2) 102.6(1), Br(2)–Sn(1)–O(3) 72.8(1), Br(2)–Sn(1)–O(4) 129.5(1), Br(1)–Sn(1)–Br(2) 148.3(1)°.

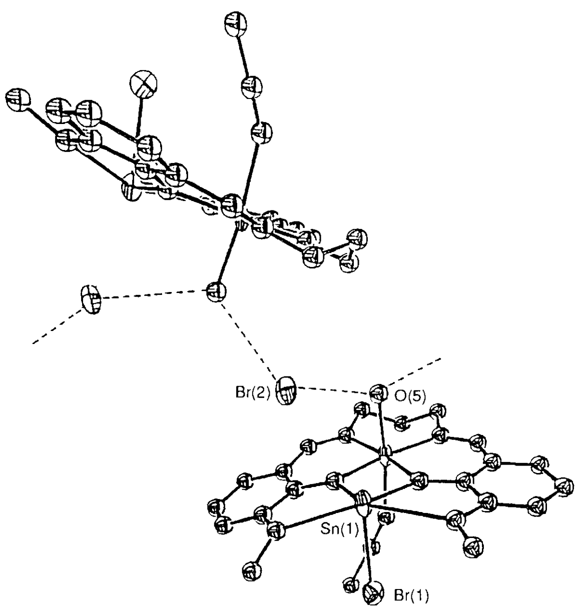

Fig. 2 Hydrogen bonding (represented by dotted lines) in **1**

MeCN to give paramagnetic 1 : 1 addition complexes. Mössbauer data[†] revealed that they were tin(II) complexes and magnetic data indicated that they contained octahedral nickel(II). The bromide (complex **1**) yielded pale blue crystals from MeCN under rigorously oxygen free conditions, and a crystal (which was air-stable when completely dry) was selected for a crystallographic study.

The asymmetric unit[‡] of the adduct is shown in Fig. 1. By far the most significant feature of this structure is the existence of one normal Sn–Br bond, 2.710(1) Å, while the next nearest Sn–Br contact of 3.724(1) Å is well beyond the sum of the covalent radii (2.77 Å) of the two atoms. Thus, this is unquestionably an ionic complex containing $SnBr^+$ cations and Br^+ anions. The tin atom of each cation forms two short and two long donor bonds to the phenolic and methoxy oxygens respectively of a salicylideneamine ligand. In fact, tin atoms of dialkyltin(IV) cations likewise form two short and two long donor bonds to the salicylideneamine oxygen atoms (this is explicable in terms of Kepert's theory[6,7]), but, on average, the Sn^{II}–O bonds are approximately 0.1 Å longer than the Sn^{IV}–O bonds. The immediate coordination geometry about tin (see Fig. 1) is best described as skew trapezoidal pyramidal, with the bromine atom occupying the apical position. The closest bromide ion, Br(2), contact to tin is from a direction approximately *trans* to the Sn(1)–Br(1) bond, but it is removed from the true *trans* direction so as to subtend two angles at tin, one with a methoxy and the other with a phenolic oxygen, which are substantially smaller than the other two Br(2)–Sn–O bond angles. Reference to bond length and bond angle data in Fig. 1 indicates that there is a considerable volume of the coordination sphere available for the non-bonding pair of electrons. Although the precise direction of the non-bonded pair cannot be specified, it is clear that it will be to the same side of the plane defined by the oxygen atoms as that occupied by Br(2). The fact that tin is removed from the plane (by 0.338 Å) to this same side rather than to the side containing the Sn–Br bond is undoubtedly a consequence of the lone pair presence.

Each bromide is within hydrogen bonding distance (3.276 Å) from oxygen of a water molecule coordinated to nickel (an MeCN molecule completes the octahedral geometry about nickel) within the asymmetric unit, while it is also within hydrogen bonding distance (3.219 Å) to a similar type of oxygen in a neighbouring asymmetric unit (see Fig. 2). In this way zig-zag chains of alternating oxygen atoms and bromide ions, linked by hydrogen bonds, are generated.

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[†] Mössbauer parameters for the title compound: δ = 3.39 (±0.03), Δ = 1.41 (±0.05) mm s^{-1}.

[‡] *Crystal data:* $C_{21}H_{25}O_5N_3Br_2SnNi$, M = 736.64, monoclinic, space group $P2_1/c$, a = 13.385(3), b = 9.813(3), c = 19.319(4) Å, β = 97.008(2)°, U = 2518.54 Å^3, D_c = 1.94 g cm^{-3}, μ(Mo-Kα) = 47.75 cm^{-1}, 3287 reflections with $I > 3\sigma I$, using a CAD4 diffractometer and Mo-Kα radiation, $2\theta_{max}$ = 48°. Data were collected at approximately 20 °C. The structure was solved by direct methods, SHELX86,[8] and refined with 208 variable parameters using SHELX76.[9] Following full matrix refinement with metal, bromine, oxygen, nitrogen and carbon (of methyl groups) atoms refined anisotropically, and no absorption correction applied (since the crystal had favourable morphology and the statistics of final refinement were satisfactory), R = 4.43 and R_w = 5.12%. Calculated hydrogen positions were included in the final refinement cycle. Maximum and minimum excursions in the final $F_o - F_c$ difference map were 0.84 and −0.58 e A^{-3} respectively. The ORTEP program[10] was used to produce the diagrams in Figs. 1 and 2. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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