Preparation and Characterization of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ and $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$

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Organometallic Compounds, Layered Compounds, Two-Dimensional Semiconductors

The title compounds were prepared in crystalline form and characterized analytically and spectroscopically.

Compounds $CH_3NH_3PbCl_3$, $CH_3NH_3PbBr_3$, $CH_3NH_3PbI_3$, $CH_3NH_3SnBr_3$, $CH_3NH_3SnI_3$, $CsSnI_3$ etc. have been known for a long time [1–4]. $CH_3NH_3SnI_3$ and $CsSnI_3$ are metallic [2], while the rest are (three-dimensional) semiconductors [1–4]. In the last years, compounds of the formulas $(C_6H_5CH_2CH_2NH_3)_2PbX_4$ and $(CH_3NH_3)(C_6H_5CH_2CH_2NH_3)_2Pb_2I_7$ (where X = Cl, Br, I) and similar with $C_nH_{2n+1}NH_3$ or $H_3NC_nH_{2n}NH_3$ (n = 4,6,8,9,10...) instead of $C_6H_5CH_2CH_2NH_3$, have been prepared and their two-dimensional semiconductor behaviour has been established (see [4–8] and refs. therein). In $(C_6H_5CH_2CH_2NH_3)_2PbI_4$, for example, the two-dimensional networks of PbI_4, forming perovskite-type components (anions), correspond to quantum wells, while alkylammonium chains (cations) play the role of barriers and sandwich the wells. Also, in $(CH_3NH_3)(C_6H_5CH_2CH_2NH_3)_2Pb_2I_7$ the cation/anion (CH_3NH_3/Pb_2I_7) layers alternate with cation $(C_6H_5CH_2CH_2NH_3)$ layers [7]. Recently, compounds of the formulas $(C_nH_{2n+1}NH_3)_2SnX_4$ and $(CH_3NH_3)(C_nH_{2n+1}NH_3)_2Sn_2I_7$ have been prepared in powdered form and their optical properties reported [4]. The narrow excitonic absorption and luminescence bands is a characteristic feature of this kind of materials. In this paper the preparation of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ and $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$, in pure crystalline form, as well as their analytical and spectroscopic data are reported.

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Experimental

Precursors and instrumentation

Precursors $C_6H_5CH_2CH_2NH_3I$ and $C_6H_5CH_2CH_2NH_3Br$ were prepared by treatment of $C_6H_5CH_2CH_2NH_2$ (2-phenylethylamine, Fluka 77900) with aqueous solution of HI and HBr, respectively. The excess of HI and HBr and H_2O as well as the impurities of Br and I were removed by heating the compounds at *ca.* 60 °C for several days. They were recrystallized from acetonitrile. SnI_2 and $SnBr_2$ were prepared and purified according to the literature methods [9–11]. Also commercial products (Ventron SnI_2, 71112 and Ventron $SnBr_2$, 71110) were used without purification. Absorption spectra were recorded on a Varian model 2390 spectrophotometer and luminescence spectra on a Jobin-Yvon model HG2S Raman spectrophotometer, using an argon laser (excitation line 454.4 nm).

Preparation of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ and $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$

A mixture of $C_6H_5CH_2CH_2NH_3I$ (540 mg, 2.16 mmol) and SnI_2 (373 mg, 1 mmol) in acetonitrile (10 ml) was heated at the reflux temperature with stirring under an argon atmosphere. A part of the solvent (*ca.* 4 ml) was removed with a stream of argon at *ca.* 75 °C and the remaining pale yellow solution was cooled slowly at 10 °C. The precipitate was filtered and dried at *ca.* 40 °C under an argon atmosphere to give 610 mg (70%) of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ as brown-golden crystalline plates, m.p. 210 °C.

Analysis: $C_{16}H_{24}N_2I_4Sn$

Calcd	C 22.07	H 2.78	N 3.22	I 58.30%,
Found	C 22.16	H 2.71	N 3.36	I 59.04%.

These crystals remain stable for a long time under an argon atmosphere.

$(C_6H_5CH_2CH_2NH_3)_2SnBr_4$ was prepared by the same method from $C_6H_5CH_2CH_2NH_3Br$ and $SnBr_2$; yellow crystalline plates; m.p. 183 °C.

Analysis: $C_{16}H_{24}N_2Br_4Sn$

Calcd	C 28.15	H 3.54	N 4.14	Br 46.82%,
Found	C 27.97	H 3.61	N 4.37	Br 46.90%.

These crystals are more stable in air than those of the SnI_4-analogs. The method can also be applied for the preparation of $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ in crystalline form. Attempts for the preparation of $(CH_3NH_3)(C_6H_5CH_2CH_2NH_3)_2Sn_2X_7$ in a pure crystalline form were unsuccessful. Instead, polycrystalline powders of the compounds were obtained by this method.

Results and Discussion

In contrast to the cases of Sn compounds containing long-chain anions, $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ and $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$ were obtained in pure crystalline form. X-ray powder-diffraction diagrams showed that $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ is isostructural with $(C_6H_5CH_2CH_2NH_3)_2PbI_4$ [7]. Also, there are similarities in the optical absorption and luminescence spectra. Fig. 1 a shows the optical absorption spectrum of a thin deposit of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ obtained by rubbing some crystals of the compound on a quartz plate, and Fig. 1 a shows the corresponding luminescence spectrum. The luminescence spectrum of a single crystal or of a polycrystalline pellet is the same as that of a thin deposit. Also, the spectra of deposits obtained by melting stoichiometric amounts of the corresponding precursors on a quartz or glass plate are the same as those of Fig. 1. The dc-conductivity on a compressed polycrystalline pellet was found to be at least one order of magnitude higher than that of the PbI_4-analogs. Similar results were obtained for $(C_6H_5CH_2CH_2NH_3)_2SnBr_4$; the absorption bands occur at shorter wavelengths than those of SnI_4-analogs. Details of the X-ray crystal structure determination and physical properties of these new semiconductor compounds will be reported elsewhere.

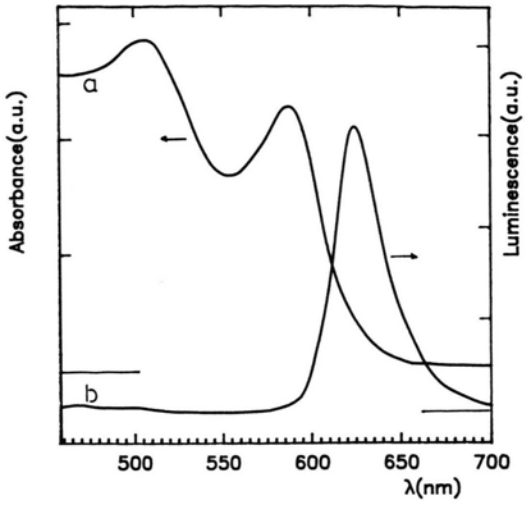

Fig. 1. Optical absorption spectrum (a) and luminescence spectrum (b) of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ at room temperature.

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