Some Organic-Inorganic Hybrid Compounds Based on \( \text{iso}-\)Thiuronium Cations and Lead Halide Anions

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Organic-Inorganic Hybrids, Low-Dimensional Semiconductors, Fluorescence

Using 1-chlorodecane (\( \text{C}_{10}\text{H}_{21}\text{Cl} \)), benzyl chloride (\( \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \)), a,a’-dichloro-p-xylene (\( \text{ClC}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_2\text{Cl} \)), 4-phenylbenzyl chloride (\( \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{Cl} \)), 2-bromomethyl-naphthalene (\( \text{C}_{10}\text{H}_{13}\text{Br} \)), 4-bromomethyl-7-methoxycoumarin (\( \text{C}_{10}\text{H}_7\text{O}\text{C}_6\text{H}_4\text{CH}_2\text{Br} \)), 2-bromomethyl-anthraquinone (\( \text{C}_{10}\text{H}_7\text{C}_6\text{H}_4\text{CH}_2\text{Br} \)), 9-chloromethyl-anthracene (\( \text{C}_{14}\text{H}_9\text{CH}_2\text{Cl} \)), thiourea and halides as starting materials, the organic-inorganic hybrid compounds \([\text{C}_{10}\text{H}_{21}\text{SC(NH}_2\text{)}_2]\text{PbI}_4 \), \([\text{C}_6\text{H}_5\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_3\text{I}_5 \), \([\text{H}_2\text{N}\text{C}_6\text{H}_4\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_1\text{I}_1 \), \([\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_1\text{I}_1 \), \([\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_1\text{I}_1 \), \([\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_1\text{I}_1 \), and \([\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_1\text{I}_1 \) were prepared and characterized analytically and spectroscopically.

Introduction

Organic-inorganic hybrid compounds (systems) of the general formula \([\text{RNH}_2\text{MYX}]_n \) (where \( R \) is an alkyl-group or a chromophore; \( M = \text{Pb}, \text{Sn}, \text{etc}; X = \text{I}, \text{Br}, \text{Cl}; x, y, z = 1, 2, 3, \ldots \) ) have been prepared and investigated extensively (see [1 - 17] and refs therein, for some reviews see [1 - 3]). They behave as three dimensional or low dimensional semiconducting systems. It has been found that these systems could be used as elements in nonlinear optical devices [4], in light emitting diodes [5], in optical microcavities [6], and as channels in thin-film field-effect transistors [7]. However, little is known on the systems based on \( \text{iso}-\)thiuronium cations, i.e., on compounds of the general formula \([\text{RCH}_2\text{SC(NH}_2\text{)}_2]\text{LMX}_n \) [10, 13, 15, 18]. In this paper the preparation and characterization of the following compounds are reported:

\[
\begin{align*}
[\text{CH}_3\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{PbI}_4 \quad (1), \\
[\text{CH}_3\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{PbI}_3 \quad (2), \\
[\text{H}_2\text{NCS-CH}_2\text{SC(NH}_2\text{)}_2]_0.5\text{PbI}_3 \quad (3), \\
[\text{CH}_3\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{PbBr}_4 \quad (4), \\
[\text{CH}_3\text{CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_2\text{I}_3 \quad (5), \\
[\text{MeO-CH}_2\text{SC(NH}_2\text{)}_2]\text{Pb}_2\text{I}_3 \quad (6),
\end{align*}
\]

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Experimental

Starting materials and apparatus

The following starting materials were used without further purification: PbO (Ferak 01-881), hydroiodic acid 57% (Merck 341), hydrobromic acid 47% (Merck 304), H₃PO₄ 50% (Fluka 9421), 1-chlorodecane (Aldrich C₃,290-9), benzyl chloride (Aldrich 32,016-1), a, a'-dichloro-p-xylene (Aldrich 10,574-0), 4-phenylbenzyl chloride (Aldrich C₅,227-6), 2-bromomethyl-naphthalene (Fluka 17,617), 4-bromomethyl-7-methoxy coumarin (Fluka 17,623), 2-bromomethyl-anthraquinone (Fluka 17,560), 9-chloromethylanthracene (Aldrich 19,651-7) and thiourea (Ferak 01525). The optical absorption (OA) spectra of thin deposits on quartz plates were recorded on a Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer and the photoluminescence (PL) spectra on a Jobin Yvon-Spez model Fluorolog-3 spectrophotometer. Also, PL spectra were recorded on a Jobin Yvon model HG2S Raman spectrophotometer using an argon laser (457.9 nm excitation line). All measurements were performed at room temperature.

Preparation of compounds

The iso-thiouronium halides were prepared first by known procedures [18-21]. A typical procedure for 9-anthracenemethyl thiouronium chloride [C₁₀H₂₇CH₂SC(NH₂)₂]Cl is described here: To a solution of 9-chloromethyl-anthracene (0.5 g) in CH₃CN (30 ml), a solution of thiourea (0.152 g) in CH₃CN (30 ml) was added. The mixture was refluxed for 0.5 h. The yellow precipitate was filtered off and dried in air; yield 95%.

[C₁₀H₂₇SC(NH₂)₂]₂PbI₄ (1): To a solution of C₁₀H₂₇SC(NH₂)₂I (34.4 mg) in aq. HI 57% (0.5 ml) and CH₃OH (5 ml) a solution of PbO (22.3 mg) in aq. HI 57% (0.5 ml) and CH₃OH (5 ml) (i.e., a solution of PbI₂), in the presence of H₂PO₂, at reflux temperature, was added at once. After slow evaporation of the solvents, yellow plate-shaped crystals were obtained. They were filtered off and dried in air; yield 49 mg (43%), based on PbO. Analysis for C₁₀H₂₇SC(NH₂)₂I₂Pb. Calcd. C 43.68, H 2.82, I 39.49; found C 43.65, H 2.84, I 39.21.

[C₁₀H₂₇CH₂SC(NH₂)₂]₄PbI₁₀ (2): To a solution of PbO (66.9 mg) in aq. HI 57% (1.5 ml) and CH₃OH (1 ml), in the presence of H₂PO₂, C₁₀H₂₇CH₂SC(NH₂)₂I (117.6 mg) was added at once and the mixture was heated at reflux temperature. By slow cooling yellow plates were obtained. They were filtered off and dried at 100°C; yield 161 mg (63%). Analysis for C₁₀H₂₇N₂I₁₀Pb₅ (2559): calcd. C 15.00, H 1.72, N 4.37, I 49.57; found C 14.92, H 1.72, N 4.35, I 49.51.

[(H₂N)₂CSCSH₂C₆H₄CH₂SC(NH₂)₂]₄PbI₄ (3): To a solution of [(H₂N)₂CSCSH₂C₆H₄CH₂SC(NH₂)₂]Cl₂ (27.8 mg) in aq. HI 57% (0.5 ml) and CH₃OH (15 ml), a solution of PbO (22.3 mg) in aq. HI 57% (0.5 ml) and CH₃OH (1 ml), in the presence of H₂PO₂, at reflux temperature, was added at once. After slow cooling of the solution at room temperature, a precipitate consisting of thin needles was obtained. Filtration and drying in air gave the compound in a yield of 58 mg. (81%), based on PbO. Analysis for C₁₆H₁₄N₂I₆Pb (716): calcd. C 8.38, H 1.12, N 3.91; found C 8.46, H 1.15, N 3.79.

[C₁₆H₁₄C₆H₄CH₂SC(NH₂)₂]₄PbI₂ (4): To a solution of PbO (22.3 mg) in aq. HI 57% (ca. 1 ml) and CH₃OH (ca. 5 ml), in the presence of H₂PO₂, at reflux temperature, C₁₆H₁₄C₆H₄CH₂SC(NH₂)₂Cl (27.8 mg) was added at once. The solution was cooled slowly to room temperature, to give plate-like crystals. They were filtered off and dried in air; yield 66 mg (79.5%). Analysis for C₁₄H₁₂N₂I₃Pb (831): calcd. C 20.23, H 1.81, N 3.37, I 45.80; found C 19.79, H 1.63, N 3.48, I 45.21.

[C₁₀H₂₇CH₂SC(NH₂)₂]₂PbI₃ (5): To a solution of PbO (22.3 mg) in aq. HI 57% (0.5 ml) and CH₃OH (2 ml), in the presence of H₂PO₂, at reflux temperature, a solution of C₁₀H₂₇CH₂SC(NH₂)₂I (34.4 mg) in aq. HI 57% (0.5 ml) and CH₃OH (6 ml) was added at once. After slow evaporation of the solvents, yellow plates were obtained. They were filtered off and dried in air; yield 71 mg (88%). Analysis for C₁₀H₁₃N₂I₃Pb (805): calcd. C 17.88, H 1.61, N 3.47, I 47.33; found C 18.01, H 1.49, N 3.35, I 46.72.

[C₁₀H₂₇CH₂SC(NH₂)₂]₂PbI₄ (6): To a solution of PbO (22.3 mg) in aq. HI 57% (0.5 ml) and CH₃OH (2 ml), in the presence of H₂PO₂, at reflux temperature, a solution of C₁₀H₂₇CH₂SC(NH₂)₂Br (34.5 mg) in aq. HI 57% (0.5 ml) and CH₃OH (10 ml) was added at once. After slow cooling to room temperature, yellow needles were obtained. They were filtered off and dried in air; yield 56 mg (66%). Analysis for C₁₀H₁₃N₂I₃Pb (853): calcd. C 16.88, H 1.54, N 3.28; found C 16.62, H 1.55, N 3.40.

[C₁₆H₁₄O₂CH₂SC(NH₂)₂]₂PbI₃ (7): To a solution of PbO (22.3 mg) in aq. HI 57% (0.5 ml) and CH₃OH (2 ml), in the presence of H₂PO₂, at reflux temperature, a solution of C₁₆H₁₄O₂CH₂SC(NH₂)₂Br (37.7 mg) in aq. HI 57% (0.5 ml) and CH₃OH (12 ml) was added at once. After cooling, a yellow-brownish precipitate was obtained. It was filtered off and dried in air; yield 69 mg (78%). Analysis for C₁₄H₁₂N₂O₃I₃Pb (885): calcd. C 21.69, H 1.47, N 3.16; found C 21.80, H 1.42, N 3.04.

[C₁₆H₁₄O₂CH₂SC(NH₂)₂]₂PbI₃ (8): To a solution of PbO (22.3 mg) in aq. HI 57% (1 ml), in the presence of H₂PO₂, at reflux temperature, a solution of C₁₆H₁₄O₂CH₂SC(NH₂)₂I (39.5 mg) in acetone (5 ml) was added at once. After slow evaporation of the solvents, yellow plate-like crystals were obtained. They were filtered off and dried in air; yield 57 mg (67%). Analysis for C₁₆H₁₄N₂I₃Pb (855):
Fig. 1. OA (a, b) and PL (a') spectra of \([\text{C}_{10}\text{H}_{21}\text{SC-}(\text{NH}_2)_2]\text{PbI}_4\), (a, a') and \([\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2]\text{I}\) (b). Excitation 457.9 nm.

Calcd. C 22.47, H 1.76, N 3.27, I 44.51; found C 22.52, H 1.87, N 2.97, I 44.28.

\([\text{C}_{14}\text{H}_{9}\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{PbBr}_4\) (9): To a solution of PbO (22.3 mg) in aq. HBr 47% (0.5 ml), a solution of \([\text{C}_{14}\text{H}_{9}\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{Cl}\) (30.3 mg) in aq. HBr 47% (0.5 ml) and CH$_3$OH (2.5 ml) at reflux temperature, was added at once. After slow cooling, yellow plates were obtained. They were filtered off and dried in air; yield 47 mg (44.3%) based on PbO. Analysis for C$_{32}$H$_{30}$N$_4$Br$_4$S$_2$Pb (1061): calcd. C 36.20, H 2.84, N 5.27, Br 30.11; found C 36.06, H 2.99, N 5.27, Br 29.87.

The crystals of the new compounds were not good enough for X-ray crystal structure solution.

**Optical Properties and Discussion**

Fig. 1 shows the OA and PL spectra of \([\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2]\text{PbI}_4\) as well as the OA spectrum of \([\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2]\text{I}\) for comparison. One can see that the OA spectrum exhibits an excitonic peak at 474 nm, while the PL spectrum exhibits an excitonic peak at ca. 492 nm. Both peaks occur at longer wavelengths than the first singlet level of the organic component, as it is seen in the OA spectrum of \([\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2]\text{I}\).

The stoichiometry and the excitonic peak position indicate that \([\text{C}_{10}\text{H}_{21}\text{SC}(\text{NH}_2)_2]\text{PbI}_4\) is a two-dimensional system, similar to that of \([\text{PhMe}_5\text{N}]_4\text{Pb}_3\text{Br}_{10}\) [17].

The OA spectra of \([[(\text{H}_2\text{N})_2\text{CSCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{PbI}_3\)]_0.5\text{PbI}_3\) and \([\text{C}_{6}\text{H}_5\text{CH}_2\text{SC}(\text{NH}_2)_2]_4\text{PbI}_3\) exhibit excitonic peaks at ca. 399 nm, which lie at longer wavelengths than that of the first singlet energy level of the organic component. Also, the OA spectra of \([\text{C}_{10}\text{H}_2\text{O}_2\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{PbI}_3\) and \([\text{C}_{14}\text{H}_2\text{O}_2\text{CH}_2\text{SC}(\text{NH}_2)_2]\text{PbI}_3\) exhibit excitonic peaks at 399 and 390 nm, respectively. The OA spectra of the corresponding organic compounds (iodides) exhibit peaks at 338 and 336 nm, respectively; i.e. the excitonic peaks of the hybrids lie close to the first singlet level of the organic com-
Fig. 4. OA (a, b) and PL (a', b') spectra of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\], (a, a') and \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] (b, b'). Excitation 457.9 nm.

Fig. 5. OA (a, b) and PL (a', b') spectra of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbBr}_4\], (a, a') and \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbBr}_4\] (b, b'). Excitation 350 nm.

It is concluded that the organic-inorganic hybrid compounds based on iso-thiuronium cations and component. However, the PL spectra of these hybrids are weak. The stoichiometry and the excitonic peak positions of the last four hybrids indicate that they are one-dimensional systems like \[\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3\text{PbI}_3\] [10] and \[\text{H}_3\text{N(CH}_2)_6\text{NH}_3\text{PbI}_3\] [15].

Fig. 3 shows the OA and PL spectra of \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] as well as the spectra of \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\]. One can see that the position and shape of the PL spectrum are almost the same as for \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] except that the vibronic progression in the spectrum of \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] is weaker than that in the spectrum of \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] [10, 13]. This means that the energy transfer from the inorganic to the organic component [16] in \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] is weaker than in \[\text{C}_{10}\text{H}_7\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\].

Fig. 4 shows the OA and PL spectra of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] and the spectra of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbI}_3\] for comparison. The PL intensity of the inorganic network (PbI3) lies at 447 nm, corresponding to the prompt and the delayed fluorescence, as well as a broad band (perhaps phosphorescence, arising from the triplet) at longer wavelengths. The PL spectrum of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbBr}_4\] with 350 nm excitation exhibits shoulders at 450 and 530 nm, corresponding to the prompt and the delayed fluorescence. This behaviour is a consequence of the energy transfer from the inorganic to the organic component as in the case of \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbCl}_4\] [16]. The PL intensity in \[\text{C}_{14}\text{H}_9\text{CH}_2\text{SC(NH}_2)_2\text{I}\text{PbBr}_4\] is higher than that of 9-chloromethyl-anthracene (a fluorescent material) [23]. Moreover, an enhancement of the mobility is expected in the hybrid system, because of the incorporation of the inorganic semiconductor (PbBr-network) [7].

It is concluded that the organic-inorganic hybrid compounds based on iso-thiuronium cations and...
metal halide anions behave like the corresponding compounds with alkyl ammonium or aryl-alkylammonium cations. The preparations and the properties of similar compounds based on iso-selenuronium cations, such as \([\text{C}_{10}\text{H}_{21}\text{SeC(NH}_{2}\text{)}_{2}]\text{PbI}_{4}\), will be reported elsewhere.