Synthesis and Characterization of $[NH_2C(I){=}NH_2]_2ASnI_5$ with A = Iodoformamidinium or Formamidinium: The Chemistry of Cyanamide and Tin(II) Iodide in Concentrated Aqueous Hydriodic Acid Solutions

David B. Mitzi,* Kangning Liang, and Shumin Wang[†]

IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

Received October 21, 1997

Crystals of the organic−inorganic compounds $[NH_2C(I){=}NH_2]_2ASnI_5$ ($A = NH_2C(I){=}NH_2^+$ and $NH_2CH{=}NH_2^+$) have been grown in an inert atmosphere from slowly cooled aqueous hydriodic acid solutions, each with the same starting concentration of dissolved cyanamide and tin(II) iodide. Each compound can be achieved in high purity and yield simply by varying the thermal history of the solution during cooling. If one starts from lower temperatures, cyanamide rapidly undergoes an addition reaction to generate the iodoformamidinium cation, yielding crystals of $[NH_2C(I){=}NH_2]_3SnI_5$. At higher temperatures, iodoformamidinium is reduced to formamidinium and is ultimately hydrolyzed if heated further or left for long periods of time. When the solution is subjected to an intermediate thermal treatment of 24 h at 80 °C before slow cooling, both cations can be stabilized in the solid-state compound $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$. The $[NH_2C(I){=}NH_2]_3SnI_5$ structure has recently been reported in the monoclinic space group $P2_1/c$ and consists of highly distorted SnI_6 octahedra which share opposite corners to form extended one-dimensional chains separated by iodoformamidinium cations. The new mixed-cation compound adopts a very similar triclinic ($P1$) structure, with the lattice parameters $a = 6.3635(3)$ Å, $b = 8.8737(5)$ Å, $c = 10.8782(6)$ Å, $\alpha = 111.616(5)°$, $\beta = 92.938(4)°$, $\gamma = 95.358(4)°$, and $Z = 1$ and with much less distorted SnI_6 octahedra and shorter average Sn−I bond lengths. The different local coordination translates into a substantially darker coloration for crystals with A = formamidinium relative to those having A = iodoformamidinium (dark red versus orange). In addition to examining the stability of cyanamide and derivative species in aqueous hydriodic acid solutions, thermal analysis indicates that in an inert atmosphere the iodoformamidinium cation decomposes exothermally in the solid state at approximately 178(2) °C. Ultraviolet illumination studies on the title compounds also demonstrate the photosensitivity of the iodoformamidinium cation within the tin(II) iodide framework.

Introduction

Recently, we reported the synthesis and crystal structure of the compounds $[NH_2C(I){=}NH_2]_3MI_5$ (M = Sn, Pb).[1] These compounds are closely related to the layered organic−inorganic perovskites $[NH_2C(I){=}NH_2]_2(CH_3NH_3)_mSn_mI_{3m+2}$, which consist of "$m$" <110>-oriented $CH_3NH_3SnI_3$ perovskite sheets, separated by a layer of iodoformamidinium cations.[2] In fact they can be considered the $m = 1$ member of this family, with the substitution of $NH_2C(I){=}NH_2^+$ for $CH_3NH_3^+$ within the perovskite layers. Whereas for m ≥ 2, this family is two-dimensional, becoming more three-dimensional with increasing "m", for $m = 1$ the structure reduces to a layer of one-dimensional chains consisting of corner-sharing MI_6 octahedra. A remarkable feature of this family then is the ability to progress from one-dimensional "perovskite chains" ($m = 1$), to two-dimensional "perovskite sheets" ($m \geq 2$), to the three-dimensional cubic perovskite structure, $CH_3NH_3SnI_3$ ($m \rightarrow \infty$), all within a single structural family.

The effective dimensionality of the extended inorganic anion has a significant impact on the physical properties. For the tin(II) compounds, the system undergoes a transition from electrically insulating behavior for $m = 1$, to semiconducting behavior for $m = 2$, to metallic behavior for thicker perovskite sheets.[1−3] A similar trend is observed with increasing "n" in the related series of layered <100>-oriented perovskites $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_nI_{3n+1}$.[4] In addition to the unusually high conductivity in the tin(II) iodides,[2−5] both the tin(II) and lead(II) halide organic−inorganic perovskites exhibit enhanced exciton binding energies due to a dielectric confinement effect (with an associated intense luminescence peak in the visible spectral range at room temperature),[6−9] nonlinear optical properties with the potential for third harmonic generation,[10,11] and electroluminescence.[12] Examination of the optical properties as a function of decreasing thickness of the perovskite sheets

---

* Author to whom correspondence should be addressed.

[†] Present address: Cabot Corp., 500 Commons Drive, Aurora, IL 60504.

(1) Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. *J. Am. Chem. Soc.* **1995**, *117*, 5297.

(2) Mitzi, D. B.; Wang, S.; Feild, C. A.; Chess, C. A.; Guloy, A. M. *Science* **1995**, *267*, 1473.

(3) Mitzi, D. B.; Feild, C. A.; Schlesinger, Z.; Laibowitz, R. B. *J. Solid State Chem.* **1995**, *114*, 159.

(4) Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. *Nature* **1994**, *369*, 467.

(5) Mitzi, D. B. *Bull. Am. Phys. Soc.* **1993**, *38*, 116.

(6) Ishihara, T.; Takahashi, J.; Goto, T. *Solid State Commun.* **1989**, *69*, 933.

(7) Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B* **1992**, *45*, 6961.

(8) Papavassiliou, G. C.; Koutselas, I. B. *Synth. Met.* **1995**, *71*, 1713.

(9) Mitzi, D. B. *Chem. Mater.* **1996**, *8*, 791.

(10) Xu, C.; Kondo, T.; Sakakura, H.; Kumata, K.; Takahashi, Y.; Ito, R. *Solid State Commun.* **1991**, *79*, 245.

(11) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328.

S0020-1669(97)01332-3 CCC: $15.00

in the family $(C_6H_5C_2H_4NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ demonstrates a substantial increase in the band gap, the lowest exciton energy, and the exciton binding energy, as a result of quantum confinement or dimensionality effects.[13] Recently, the absorption and photoluminescence of $[NH_2C(I){=}NH_2]_3PbI_5$ and other related one-dimensional lead halide compounds have been examined and suggest a substantial further increase in band gap, lowest exciton energy, and exciton binding energy relative to the two-dimensional systems.[14] The $m = 1$ compounds therefore appear to be interesting one-dimensional quantum well structures.

The synthesis of $[NH_2C(I){=}NH_2]_3MI_5$ (M^{2+} = Sn, Pb) in aqueous solutions involves the somewhat surprising reaction between cyanamide and HI to form the iodoformamidinium cation. While anhydrous addition reactions between nitriles and hydrogen halides generally result in the imidyl halides, in aqueous acid solutions cyanamide generally hydrolyzes to give urea.[15] Stephen[16] has also shown that under anhydrous conditions imidyl halides are reduced by tin(II) chloride, in the presence of HCl, to form the aldimine tin(IV) chlorides. Addition of warm water readily leads to hydrolysis of the salt, with the formation of the aldehyde having the same number of carbons as the original nitrile. Consequently, the chemistry of cyanamide and tin(II)/lead(II) iodide in aqueous acidic solutions is expected to be more complicated than might be deduced from our earlier study.[1]

Here, we have focused on the tin(II) system and varied the thermal processing of the concentrated aqueous acidic solution before slow cooling to see what effect this might have on the formation of the iodoformamidinium cation and the resulting compound formation. During the course of this study, we have determined synthetic conditions for the synthesis of single-phase $[NH_2C(I){=}NH_2]_3SnI_5$. The new compound $[NH_2C(I){=}NH_2]_2[NH_2CH{=}NH_2]SnI_5$ has also been isolated in high yield as a distinct phase and examined structurally using single-crystal X-ray crystallography. Comparison of these two similar structures demonstrates the influence that the organic cation within the perovskite chain layers has on the degree of distortion of the SnI_6 octahedra. The compounds isolated during the course of this study also provide insight into the chemistry of cyanamide and tin(II) iodide in aqueous hydriodic acid solutions under various thermal conditions. In addition, thermal analysis and ultraviolet irradiation studies on the title compounds, as well as on $[NH_2C(I){=}NH_2]I$, enable a characterization of the stability of the iodoformamidinium cation in the solid state.

Experimental Section

Synthesis. Three reactions were carried out with the same starting solution composition. For each, 1.490 g (4.0 mmol) of SnI_2 was dissolved in 24 mL of concentrated (57% by weight) aqueous hydriodic acid at 70 °C, in a flowing argon atmosphere (approximately 80 cm^3/min flow). A 0.252 g (6.0 mmol) amount of cyanamide was added to the solution, resulting in a lightly colored precipitate which slowly dissolved over several hours. In contrast to our earlier study,[1] excess tin(II) iodide was used because of the much better solubility of tin(II) iodide relative to the organic salts formed in the hydriodic acid solution. This led to higher purity products for the synthesis of the title compounds.

Reaction "A" was immediately cooled at 2 °C/h from 70 to −20 °C. Reaction "B" was heated to 80 °C, after the initial precipitate had dissolved, and allowed to sit for 24 h, before being cooled at 2 °C/h to −20 °C. Reaction "C" was heated to 90 °C and maintained at this temperature for 24 h, before being cooled at 2 °C/h to −20 °C. In each case, the reactions were carried out in flowing argon with a flow rate of approximately 80 cm^3/min. The resulting crystals were filtered in a nitrogen atmosphere, dried under vacuum at room temperature, and transferred to a drybox with oxygen and water levels maintained below 1 ppm.

Solution "A" was a light transparent yellow in appearance before being cooled and resulted in approximately 1.75 g (1.4 mmol; 69% yield) of orange, needlelike, $[NH_2C(I){=}NH_2]_3SnI_5$ crystals. The crystals were up to 15 mm long, but generally less than 1 mm across. A chemical analysis of the crystals, performed by Galbraith Laboratories, yielded C(2.81%), H(0.95%), and N(6.58%), in good agreement with the theoretical values, C(2.85%), H(0.95%), and N(6.64%). Infrared analysis of the crystals, performed using KBr pellets, yielded the following major peaks (cm^{-1}): 598 (m, br), 1388 (m), 1607 (m, sh), 1646 (s), a broad (not well resolved) region of peaks including 3113 (m), 3159 (sh), 3179 (m), 3237(m), 3261 (sh), and 3288 (m), and another fairly weak, broad (unresolved) band between approximately 1070 and 1195. These peaks were in good agreement with those observed for pure iodoformamidinium iodide (described below). However, the broad peak (possibly two peaks) around 598 cm^{-1} was shifted to somewhat higher wavenumber in iodoformamidinium iodide (637 cm^{-1}). In addition, there were subtle shifts in some components of the broad band around 3200 cm^{-1}, presumably as a result of differences in hydrogen bonding between the two compounds.

Solution "B" became red-brown (like the color of iodine in solution) during the 24 h dwell at 80 °C and upon cooling resulted in approximately 1.25 g (1.1 mmol; 55% yield) of nearly pure, dark red, rod- and platelike, $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ crystals. Chemical analysis yielded C(3.13%), H(1.15%), and N(7.29%), which agrees with the theoretical values, C(3.16%), H(1.15%), and N(7.37%). The infrared spectrum consisted of the following major peaks (cm^{-1}): 612 (m, br), 1357 (m, sh), 1392 (m), 1648 (s), 1711 (s), and a broad region of peaks including 3114 (m), 3160 (m), 3185 (m), 3239 (m), 3263 (sh), and 3292 (m). In addition, there was a weak, unresolved region of peaks between 1054 and 1200 cm^{-1}. This spectrum is similar to that observed for $[NH_2C(I){=}NH_2]_3SnI_5$ except that there is an additional strong peak at 1711 cm^{-1} and a shoulder peak at 1357 cm^{-1}. These additional peaks are characteristic of the formamidinium cation, as has recently been reported for $NH_2CH{=}NH_2SnI_3$[17] and $[NH_2CH{=}NH_2]_3FeCl_6$.[18]

Both the $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ crystals and, to a lesser extent, the $[NH_2C(I){=}NH_2]_3SnI_5$ crystals were found to be photosensitive, turning darkly colored if left under ambient fluorescent lighting (even while being kept in an argon-filled drybox). Sample degradation could be avoided by completely wrapping the sample container in tin foil to avoid exposing the crystals to light. The degradation could be enhanced by irradiating the materials with ultraviolet light (discussed below).

After being soaked at 90 °C for 24 h, solution "C" had a similar color as the "B" solution. However upon cooling, fibrous or needlelike yellow crystals were the primary phase present, along with a relatively small yield of the red $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ crystals. In some cases, orange SnI_4 crystals could also be detected. The yellow phase could be prepared in single-phase form by changing the starting stoichiometry of the solution to 1.490 g (4 mmol) of tin(II) iodide and 0.084 g (2 mmol) of cyanamide in 10 mL of concentrated aqueous hydriodic acid and following the same cooling sequence described above for the 90 °C reaction. The yield was 1.42 g of the yellow needles. Chemical analysis of these crystals yielded: C($<$0.5%), H(0.61%), and N(1.92%). Of particular interest is the absence of carbon in the sample. The infrared (IR) spectrum consisted of major peaks (cm^{-1}) as follows: 1128 (m, br), 1389 (s, sh), 1640 (m), 3169 (m, br),

---

(12) Hong, X.; Ishihara, T.; Nurmikko, A. V. *Solid State Commun.* **1992**, *84*, 657.
(13) Ishihara, T. *J. Lumin.* **1994**, *60/61*, 269.
(14) Koutselas, I. B.; Mitzi, D. B.; Papavassiliou, G. C.; Papaioannou, G. J.; Krautscheid, H. *Synth. Met.* **1997**, *86*, 2171.
(15) Zil'berman, E. N. *Russ. Chem. Rev.* **1962**, *31*, 615.
(16) Stephen, H. *J. Chem. Soc.* **1925**, 1874.
(17) Mitzi, D. B.; Liang, K. *J. Solid State Chem.* **1997**, *134*, 376.
(18) Demant, U.; Conradi, E.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1985**, *40b*, 443.

3466 (m, br). The spectrum was virtually identical to that observed for ammonium iodide, except for the extra broad peak at 3466 cm^{-1}, which is likely due to water. In fact, Karl Fisher water analysis of the yellow needles, performed by Galbraith Laboratories, resulted in 3.32% H_2O.

The yellow needles melted in an inert atmosphere at approximately 282 °C, with a few percent weight loss during the heating cycle. The X-ray diffraction pattern of the crystals, formed upon cooling the melt, indexed to a similar tetragonal cell as that observed for $InSn_2I_5$.[19] The X-ray powder patterns before and after melting were different, indicating a structural change, probably as a result of water loss from the sample. Recrystallization of the original yellow needles in a nonaqueous solution also led to crystals which, upon preliminary analysis with single-crystal X-ray diffraction,[20] yielded the same basic structure as $InSn_2I_5$, with however ammonium replacing indium in the lattice. The tetragonal lattice parameters for the $NH_4Sn_2I_5$ crystals were $a = 8.9071(5)$ Å and $c = 15.569(1)$ Å (compared to[19] $a = 8.810(8)$ Å and $c = 15.24(3)$ Å for $InSn_2I_5$).

Finally, a sample of $[NH_2C(I){=}NH_2]I$, used in the thermal analysis and illumination experiments, was prepared by placing 0.4 g of cyanamide (Aldrich, 99%) in a test tube. While the sample was purged with nitrogen, 5 mL of concentrated aqueous hydriodic acid was added to the tube, resulting in a white solid. The reaction tube was maintained at 70 °C for 30 min, cooled to room temperature, and filtered under a nitrogen blanket. After the sample was dried under vacuum, 1.5 g (53% yield) of the white iodoformamidinium iodide solid was transferred to an argon-filled drybox. Chemical analysis yielded C(4.06%), H(1.46%), and N(9.48%), in reasonable agreement with the theoretical values, C(4.03%), H(1.35%), and N(9.40%). The infrared spectrum contained the following major peaks (cm^{-1}): 637 (m, br), 1392 (m), 1606 (m, sh), 1646 (s), a not well-resolved region of peaks including 3094 (m), 3148 (m), 3176 (m), 3227 (m), 3259 (m), and 3283 (m, sh), and a second region of weaker peaks including 1068 (w), 1107 (w), 1166 (w), and 1231 (w).

Illumination Studies. To test for photosensitivity, ground samples of the title compounds, as well as iodoformamidinium iodide, were subjected to UV light (366 nm) from a 4 W hand-held ultraviolet lamp for periods ranging up to 90 h. A control sample consisted of a similar ground powder placed in a container that was covered by aluminum foil to protect from light exposure. Exposed and unexposed powders were evaluated by infrared spectroscopy.

X-ray Crystallography. The crystal structure of $[NH_2C(I){=}NH_2]_3SnI_5$ has been reported previously,[1] and therefore no discussion will be given here regarding the data collection for this compound. For $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$, a suitable single crystal (with approximate dimensions 0.06 mm × 0.12 mm × 0.36 mm) was selected under a microscope, while in an argon filled drybox, and sealed in a glass capillary. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα (0.7093 Å) radiation. The unit cell parameters and the crystal orientation matrix were obtained by a least-squares fit of 25 reflections with $16° < 2\theta < 32°$. Three intensity control reflections were monitored every 5000 s during the data collection and decreased an average of 18% over the 54 h of X-ray exposure. In addition to the decay correction, empirical absorption corrections based on several azimuthal ψ scans were also applied, yielding transmission factors ranging from 0.217 to 0.302. The NRCVAX 386 PC version[21] program was used for the structural solution and refinement. Selected data collection parameters and structural refinement results are presented in Table 1. A more complete listing is given in the Supporting Information (Table S.1).

Table 1. Data Collection and Structure Refinement Parameters.

formula	$[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$
fw	1140.197
space group	$P1$
a, Å	6.3635(3)
b, Å	8.8737(5)
c, Å	10.8782(6)
α, deg	111.616(5)
β, deg	92.938(4)
γ, deg	95.358(4)
V, Å^3	566.14(6)
Z	1
ρ_{calcd}, g/cm^3	3.344
radiation (λ, Å)	Mo Kα (0.7093)
abs coeff (μ), cm^{-1}	105.78
R_f [a]	0.034
R_w [b]	0.045
goodness of fit (GoF)[c]	1.65

[a] $R_f = \sum(F_o - F_c)/\sum(F_o)$. [b] $R_w = \{\sum w(F_o - F_c)^2/\sum(wF_o^2)\}^{1/2}$. [c] GoF $= \{\sum w(F_o - F_c)^2/(n - m)\}^{1/2}$, where n = number of reflections and m = number of refinement parameters.

While the structure could be successfully refined in both the centrosymmetric ($P\bar{1}$) and the noncentrosymmetric ($P1$) space groups, the noncentrosymmetric space group was ultimately adopted since the refinement in the $P1$ space group produced a significantly better fit (for $P1$, $R_f = 0.034$, $R_w = 0.044$, and GoF = 1.65, while, for $P\bar{1}$, $R_f = 0.039$, $R_w = 0.056$, and GoF = 2.08). While the heavy atom bond lengths and angles were similar for the two space groups, there was a significant difference in the refinement of the formamidinium species between the tin(II) iodide chains. In $P1$, the bond angles and the average distance between the carbon and the two nitrogens were consistent with sp^2 bonding, whereas, for the $P\bar{1}$ model, the refinement produced a less reasonable linear molecule with C−N bond lengths of only 1.15(2) Å. This is necessarily the case in the $P\bar{1}$ space group, since there is only one formamidinium cation per unit cell and the general site in the $P\bar{1}$ space group has a multiplicity of 2. Consequently, the single carbon from the formamidinium cation must sit on a special site (0.5, 0.5, 0.0) and the nitrogens must be associated with one general position. The alternative is that the carbon can be moved off the special site and given an occupancy of less than one. Refinement of this disordered formamidinium model yields little improvement in the R-factors or GoF relative to the ordered $P1$ model. The $P1$ space group was therefore ultimately adopted because this structural model did not require organic cation disordering, and the $P1$ model produced relatively better R-factors and GoF even after considering disorder in the $P\bar{1}$ refinement. To further confirm the choice of the noncentrosymmetric space group, measurement of optical activity, piezoelectricity, or other phenomena which are sensitive to center of symmetry is needed.

The positions of the heavy atoms (Sn and I) were determined by direct methods, while the remaining non-hydrogen atomic positions were picked up from Fourier difference maps. Locating the hydrogen atoms was not attempted. All the heavy atoms were refined anisotropically, while the carbon and nitrogen atoms were refined isotropically. The final structural model was refined using the counting statistics weighting scheme, with a weight modifier in the KF_o^2 term of $K = 0.0003$. The minimum and maximum electron densities in the final difference Fourier synthesis were −0.82 and 1.59 e/Å^3, with the two largest residual peaks falling within approximately 1 Å of the iodoformamidinium cation I(6) and I(7) atoms. There were no significant residual peaks near the formamidinium cation. The atomic positions and isotropic thermal parameters for $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ are presented in Table 2, while the anisotropic temperature factors are supplied as Supporting Informations (Table S.2).

Thermal Analysis. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed, using a Seteram TAG 24 thermal analysis system, to examine the thermal stability of the title compounds and, in particular, the thermal stability of the iodoformamidinium cation. Measurements were made both on the iodoformamidinium iodide salt, $[NH_2C(I){=}NH_2]I$, as well as on samples of the two title compounds, $[NH_2C(I){=}NH_2]_2ASnI_5$, with A = iodoformamidinium and formamidinium. For comparison, thermal analysis was also performed on the related perovskite compound $NH_2CH{=}NH_2SnI_3$, which does not contain the iodoformamidinium cation. Approximately 60−70 mg of sample was loaded into a tantalum container for each run. The thermal cycling was performed using a 2

---

(19) Beck, H. P. *Z. Anorg. Allg. Chem.* **1986**, *536*, 45.

(20) Mitzi, D. B.; La Placa, S. Unpublished results.

(21) Gabe, E. J.; Le Page, Y.; Charland, J. -P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Table 2. Positional and Thermal Parameters[a] for $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$

atom	x	y	z	B_{iso} (Å^2)
Sn	0.0604(9)	0.2690(7)	0.1862(6)	3.28(4)
I(1)	0.5652	0.2705	0.1877	5.57(5)
I(2)	0.0588(9)	0.4198(6)	0.9652(6)	4.8(1)
I(3)	0.0076(8)	0.9149(6)	0.9589(6)	4.9(1)
I(4)	0.0680(9)	0.1194(6)	0.4067(6)	4.7(1)
I(5)	0.1151(8)	0.6212(6)	0.4123(5)	4.1(1)
I(6)	0.6769(8)	0.0329(6)	0.5947(5)	5.2(1)
I(7)	0.4458(9)	0.4986(6)	0.7759(5)	5.0(1)
N(1)	0.870(3)	0.541(2)	0.688(2)	5.0(4)
N(2)	0.614(3)	0.560(2)	0.543(2)	4.7(3)
N(3)	0.261(2)	0.053(2)	0.705(2)	3.7(3)
N(4)	0.529(4)	0.062(3)	0.848(2)	7.4(5)
N(5)	0.401(6)	0.822(4)	0.172(3)	10.8(9)
N(6)	0.678(4)	0.675(3)	0.142(2)	6.8(5)
C(1)	0.664(3)	0.503(2)	0.643(2)	2.3(3)
C(2)	0.440(5)	0.994(3)	0.723(3)	5.4(6)
C(3)	0.583(5)	0.814(3)	0.183(3)	6.4(5)

[a] Heavy atoms (Sn and I) are refined anisotropically. Anisotropic thermal parameters are found in Table S.2 (Supporting Information).

°C/min ramp rate in an argon atmosphere. Special care was taken to exclude oxygen from the apparatus by evacuating and back-filling the thermal analysis setup with argon. The temperature was calibrated using the melting transitions of indium (T_m = 156.6 °C) and tin (T_m = 231.9 °C) and using the same system configuration (crucible type, temperature ramp rate, gas type, gas flow, etc.).

Results and Discussion

Synthetic Issues. In a previous study,[1] $[NH_2C(I){=}NH_2]_3SnI_5$ crystals were isolated from a stoichiometric (3 mol of cyanamide to 1 mol of tin(II) iodide) concentrated aqueous hydriodic acid solution. The starting materials were dissolved in the acid solution at 80 °C and immediately cooled to −10 °C. However, in addition to the relatively small yield of orange needlelike $[NH_2C(I){=}NH_2]_3SnI_5$ crystals, a substantial yield of transparent colorless to pale yellow crystals of the organic iodide salt also formed. Since this secondary phase presumably separated out because of the lower solubility of the iodoformamidinium cation relative to tin(II) iodide, in the present study we used an excess of tin(II) iodide (3 mol of cyanamide to 2 mol of tin(II) iodide). In addition, given the expected thermal and chemical instability of the iodoformamidinium cation, the crystal growth was also carried out by slow cooling the transparent yellow solution from 70 °C, a starting point 10 °C cooler than for the earlier study. This procedure led to a good (69%) yield of the $[NH_2C(I){=}NH_2]_3SnI_5$ crystals, with the excess tin(II) iodide remaining in the solution and no evidence of the colorless crystals.

As mentioned in the intrcoduction, cyanamide generally hydrolyzes to form urea in aqueous acid solutions. Kilpatrick has demonstrated,[22] however, that while the rate of hydrolysis of cyanamide in aqueous nitric acid solutions increases continuously with increasing acid concentration, for hydrochloric and hydrobromic acids, the rate increases to a maximum with increasing concentration and above this point drops off as a result of the formation of competing less hydrolyzable species. In the current procedure, it is likely that the use of the concentrated aqueous hydriodic acid effectively avoids the hydrolysis of cyanamide through a similar process, with the rapid formation of the more hydrolysis-resistant iodoformamidinium cation through an addition reaction between the cyanamide and hydrogen iodide.

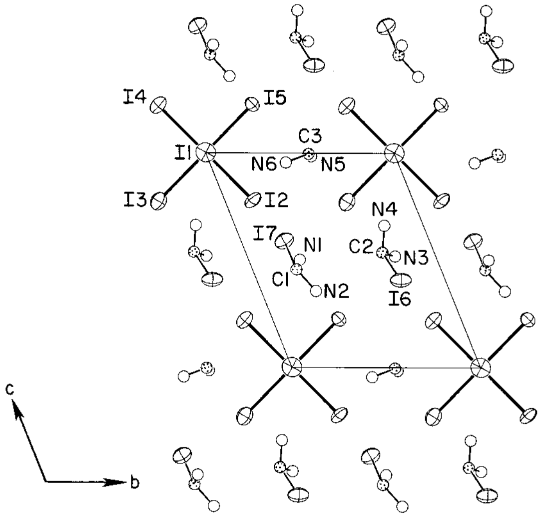


Figure 1. ORTEP drawing of the unit cell for $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$, viewed along the direction of chain propagation and with the unit cell outlined. The thermal ellipsoids for the tin (hidden behind the I1 atoms) and iodine atoms are drawn at 50% probability and represent their anisotropic thermal parameters. The carbon and nitrogen atoms are drawn as open and dot-filled circles and are drawn with an arbitrary scale factor.

To test the stability of the iodoformamidinium cation in the tin(II) iodide-containing concentrated aqueous hydriodic acid solution, additional reactions, using the same starting solution composition, were carried out at 80 and 90 °C. In contrast to the previous study, the 80 °C reaction was allowed to sit at this temperature for 24 h before cooling. After cooling, there were surprisingly no orange needlelike crystals of $[NH_2C(I){=}NH_2]_3SnI_5$ but rather a moderate yield (55% of theoretical) of dark red, slablike, crystals of $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$. The formation of iodoformamidine from cyanamide and the subsequent reduction to formamidine in the presence of divalent tin constitute the first two steps of the well-known Stephen reduction[16] of a nitrile to an aldehyde. The last step of this process (with cyanamide as the nitrile) would be the hydrolysis of formamidine, in the presence of water, to form formamide and ammonia or ultimately formic acid and ammonia. The fact that we achieved a high yield of crystals containing the formamidinium cation, despite the presence of water, suggests that the kinetics for the hydrolysis step are slow at 80 °C.

For the 90 °C reaction a multiphase product formed upon cooling, consisting primarily of fibrous yellow needles, along with a small yield of red $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ crystals, and in some cases small amounts of SnI_4. The yellow needles were identified by chemical analysis and IR spectroscopy to be an ammonium tin(II) iodide salt. It is clear from the isolation of SnI_4 that the reduction of the iodoformamidinium cation had progressed further than in the 80 °C reaction and from the significant yield of the ammonium salt that the formamidinium cation had substantially hydrolyzed.

Crystal Structure of the $[NH_2C(I){=}NH_2]_2ASnI_5$ Compounds. The unit cell for $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ is shown in Figure 1. Each tin atom adopts a slightly distorted octahedral coordination of six iodine atoms (Figure 2a), with the bond lengths ranging from 3.140(8) to 3.210(6) Å (Table 3). The tin(II) iodide octahedra share opposite corners to form one-dimensional chains extending down the crystallographic *a*-axis, with the 179.4(2)° I(1)−Sn−I(1)^a bond angle indicating that the chains are nearly linear. The formamidinium cations lie between the chains, forming nominally planar arrays of tin(II) iodide chains and formamidinium cations in the *a*−*b*

---

(22) Kilpatrick, M. L. *J. Am. Chem. Soc.* **1947**, *69*, 40.

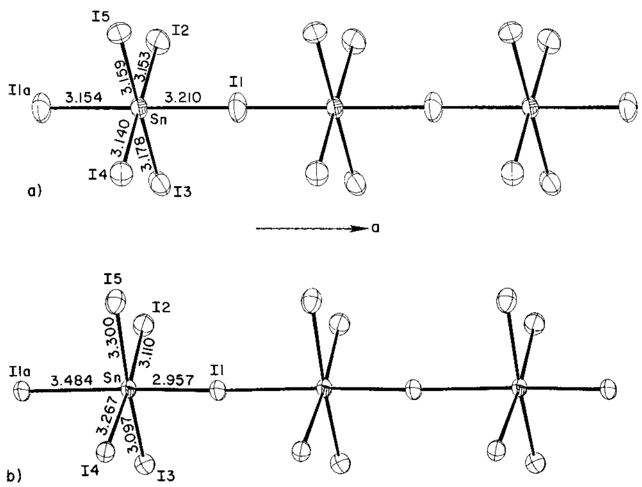


Figure 2. ORTEP drawings of the inorganic chains formed by the edge-sharing SnI_6 octahedra in $[NH_2C(I){=}NH_2]_2ASnI_5$, where "A" is (a) $NH_2CH{=}NH_2^+$ and (b) $NH_2C(I){=}NH_2^+$. The figure shows atom labeling, bond lengths, and anisotropic thermal ellipsoids, with the ellipsoids drawn at 50% probability.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$

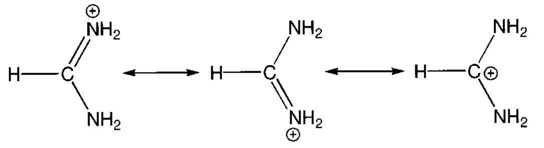
Sn−I(1)	3.210(6)	I(7)−C(1)	2.07(2)
Sn−I(1)^{a}	3.154(6)	N(1)−C(1)	1.34(3)
Sn−I(2)^{b}	3.153(8)	N(2)−C(1)	1.40(3)
Sn−I(3)^{c}	3.178(8)	N(3)−C(2)^{d}	1.33(3)
Sn−I(4)	3.140(8)	N(4)−C(2)^{d}	1.34(4)
Sn−I(5)	3.159(7)	N(5)−C(3)	1.17(5)
I(6)−C(2)^{d}	2.19(3)	N(6)−C(3)	1.36(3)
I(1)−Sn−I(1)^{a}	179.4(2)	I(2)^{b}−Sn−I(4)	179.3(3)
I(1)−Sn−I(2)^{b}	90.3(2)	I(3)^{c}−Sn−I(4)	91.1(2)
I(1)−Sn−I(3)^{c}	88.8(2)	I(3)^{c}−Sn−I(5)	179.8(2)
I(1)−Sn−I(4)	89.0(2)	I(4) −Sn−I(5)	88.9(2)
I(1)−Sn−I(5)	91.0(2)	I(6)^{e}−C(2)−N(3)^{e}	112(2)
I(1)^{a}−Sn−I(2)^{b}	89.9(2)	I(6)^{e}−C(2)−N(4)^{e}	108(2)
I(1)^{a}−Sn−I(3)^{c}	91.8(2)	N(3)^{e}−C(2)−N(4)^{e}	113(2)
I(1)^{a}−Sn−I(4)	90.8(2)	I(7)−C(1)−N(1)	118(1)
I(1)^{a}−Sn−I(5)	88.4(2)	I(7)−C(1)−N(2)	120(1)
I(2)^{b}−Sn−I(5)	91.0(2)	N(1)−C(1)−N(2)	112(2)
I(2)^{b}−Sn−I(3)^{c}	89.0(2)	N(5)−C(3)−N(6)	126(3)

^{a} −1 + x, y, z. ^{b} x, y, −1 + z. ^{c} x, −1 + y, −1 + z. ^{d} x, −1 + y, z. ^{e} x, 1 + y, z.

plane of the structure. Note that these arrays are what remain of the *m*-layer thick <110>-oriented perovskite sheets for the $m = 1$ end-member in the series $[NH_2C(I){=}NH_2]_2(CH_3NH_3)_mSn_mI_{3m+2}$, with the formamidinium cation replacing the methylammonium cations between the chains. Rather than two-dimensional "perovskite sheets" for $m \geq 2$, the structure has been reduced to an array of one-dimensional "perovskite chains". There are two distinct iodoformamidinium cations separating the layers of perovskite chains, with the orientation of the cation alternating between one in which the iodine points along the positive *c*-axis and one in which it points in the opposite direction (Figure 1).

The bonding geometry within the organic cations is for the most part consistent with earlier studies. The average C−N bond length within the formamidinium cation is 1.27(1) Å, very similar to the length observed in $[NH_2CH{=}NH_2]_3FeCl_6$ (1.28(1) Å)[18] and in $[NH_2CH{=}NH_2]Zn(HCO_2)_3$ (1.286(4) Å).[23] The N(5)−C(3)−N(6) bond angle of 126(3)° is also consistent with sp^2 hybridization and agrees with the values, 121(9) and 125.6(3)°, observed in the iron- and zinc-based formamidinium compounds, respectively.[18,23] It is somewhat surprising that the two C−N bond lengths within the formamidinium cation refine to different values (1.17(5) and 1.36(3) Å). While it is true that the formamidinium cation formally should have one single and one double C−N bond, in the situation where the imine is protonated, the symmetrical formamidinium cation should be stabilized by conjugation, as shown in Scheme 1, leading to essentially identical C−N bond lengths. Differences in hydrogen bonding and the potential double protonation of the formamidinium cation in strong acidic media[24] are two influences which could lead to distinct C−N bond lengths. It should be noted, however, that as a result of the relatively large errors in the positions of the light atoms in this heavy atom-containing structure, the two lengths are separated by less than 5 standard deviations (i.e. the difference is only marginally statistically significant). Detailed bond lengths and angles for both the formamidinium and the iodoformamidinium cation are given in Table 3.

Scheme 1



While the overall framework of the two compounds $[NH_2C(I){=}NH_2]_2ASnI_5$, with A = formamidinium and iodoformamidinium, are very similar, there are some important structural distinctions between the two. Whereas for A = formamidinium, the SnI_6 octahedra are only slightly distorted (Figure 2a), leading to well-defined inorganic chains, for A = iodoformamidinium the Sn−I bond lengths within the octahedra range from 2.957(1) to 3.484(1) Å, indicating a much more distorted SnI_6 octahedron (Figure 2b) with nominally three long and three short Sn−I bonds. The longest (3.484 Å) and shortest (2.957 Å) Sn−I bond lengths alternate down the length of the inorganic chain, thereby disrupting the connectivity of the chain. It is expected that the tin(II) lone pair orbital is stereochemically active in this structure, extending approximately along the axis between the three longest Sn−I bonds. For A = formamidinium, the tin(II) lone pair is presumably less stereochemically active since the octahedral geometry is more nearly perfect. In addition to the bond length differences, for the formamidinium system, the I−Sn−I bond angles within the SnI_6 octahedra are all within ±2° of the 90° angles expected for a perfect octahedron. For the iodoformamidinium system, these angles range from 82.87(4) to 94.23(4)°. The I(1)−Sn−I(1)^{a} bond angle of 177.30(5)° for the iodoformamidinium system also indicates that the tin(II) iodide chains are not as linear as for the A = formamidinium material.

Recently, a correlation has been drawn between the band gap of the Sn(II) iodide-based systems, the degree of distortion of the SnI_6 octahedra, and the average Sn−I bond length.[9,17] Namely, as the system becomes more conducting (smaller band gap), the average tin(II) iodide bond length decreases and the SnI_6 octahedra become less distorted. For the black cubic (at room temperature) perovskite $CH_3NH_3SnI_3$, for example, the system is metallic with a perfect SnI_6 octahedral coordination and an average Sn−I bond length of 3.121 Å.[3,17] In contrast, for the insulating low temperature (yellow) phase of $CsSnI_3$, the six Sn−I bonds range from 2.941 to 3.469 Å, with an

---

(23) Marsh, R. E. *Acta Crystallogr.* **1986**, *C42*, 1327.

(24) Häfelinger, G.; Kuske, F. K. H. In *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1991; p 5.

average of 3.210 Å.[25] In the insulating yellow crystals of $(CH_3)_2NH_2SnI_3$, the octahedra are similarly distorted with bond lengths ranging from 2.978 to 3.506 Å and an average Sn−I bond length of 3.225 Å.[26] Semiconducting compounds tend to fall between the two extremes with respect to both bond length and degree of distortion of the SnI_6 octahedra. $(C_4H_9NH_3)_2SnI_4$, for example, has a slightly distorted octahedral tin(II) coordination, with bond lengths ranging from 3.133 to 3.160 Å and an average of 3.144 Å.[9] Similarly for the $m = 2$ member of the $[NH_2C(I){=}NH_2]_2(CH_3NH_3)_mSn_mI_{3m+2}$ family, the Sn−I bonds range from 3.094 to 3.185 Å, with an average of 3.139 Å.[2]

For the current family of compounds, $[NH_2C(I){=}NH_2]_2ASnI_5$, the A = iodoformamidinium system is clearly insulating with a large band gap (transparent orange color). The octahedra are very distorted (Figure 2b), and the average Sn−I bond length is 3.202 Å, similar to that observed for other related insulating compounds. For A = formamidinium, the band gap appears to be significantly smaller since the color is much darker (dark red), the SnI_6 octahedra are significantly less distorted (Figure 2a), and the average Sn−I bond length is 3.166 Å. Consequently, with regard to both distortion of the octahedra and the average Sn−I bond length, this system appears to be approaching the range observed for semiconducting systems.

Photosensitivity. Samples of $[NH_2C(I){=}NH_2]_2ASnI_5$, with A = iodoformamidinium or formamidinium, rapidly darkened when placed under UV illumination. A powder of the A = iodoformamidinium material, illuminated for approximately 14 h, turned black (at least on the surface of the grains). The IR spectrum for the compound exhibited a pattern nearly identical to that of the unexposed material with the exception of a small new peak at 1713 cm^{-1}. Additional illumination led to this peak progressively increasing in intensity and an additional peak at 1353 cm^{-1} (shoulder peak to the 1388 cm^{-1} peak for the iodoformamidinium cation). These peaks are very similar to those observed for the formamidinium cation in $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ and $NH_2CH{=}NH_2SnI_3$. It is therefore likely that the darkening of the sample is the result of the photosensitivity of the carbon−iodine bond in the iodoformamidinium cation.

It is also interesting to note that a powder of $[NH_2C(I){=}NH_2]I$ exposed to the same 366 nm ultraviolet light, while slightly discoloring, showed no evidence of decomposition upon examination of the infrared spectrum. The spectra were virtually identical before and after irradiation (even after 60 h of exposure). While it is possible that the different photosensitivity behavior of the tin(II)-containing iodoformamidinium compounds and the non-tin(II)-containing salt could arise from a different configuration of the iodoformamidinium molecules in these structures, it is more likely that the tin(II) iodide matrix plays an active role in the photochemistry of the iodoformamidinium cation, perhaps by increasing the compound's ability to absorb in the visible and ultraviolet spectral range.

Thermal Stability of the Iodoformamidinium Cation. Figure 3 shows the simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves for the two title compounds (Figures 3a,b), as well as for iodoformamidinium iodide (Figure 3c). The most prominent feature of these measurements is the strong and relatively sharp exotherm that occurs at 179(2) °C for iodoformamidinium iodide and at 179(2) and 176(2) °C for $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ and $[NH_2C(I){=}NH_2]_3SnI_5$, respectively. This exotherm is also associated with the onset of significant weight loss from the sample and therefore corresponds to a decomposition reaction.

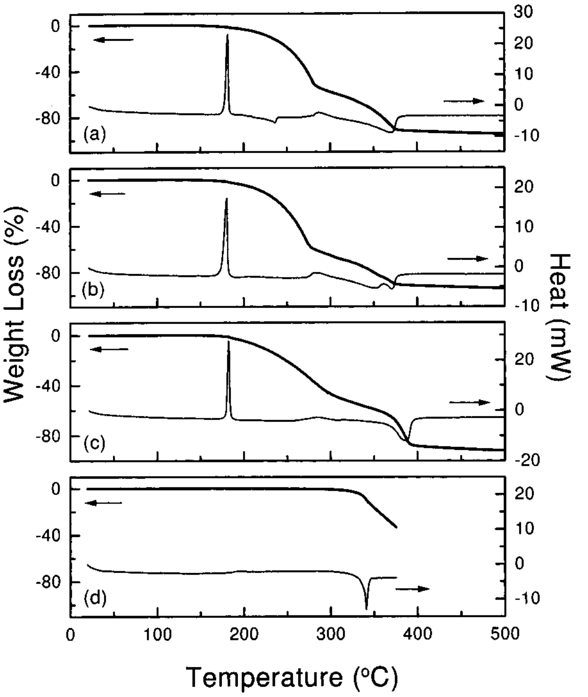


Figure 3. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) scans for (a) $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$, (b) $[NH_2C(I){=}NH_2]_3SnI_5$, (c) $[NH_2C(I){=}NH_2]I$, and (d) $NH_2CH{=}NH_2SnI_3$. Each scan was performed in flowing argon with a ramp rate of 2 °C/min. For clarity, only the heating portions of the curves are shown.

For comparison, the thermal analysis curves for $NH_2CH{=}NH_2SnI_3$ are also shown[17] (Figure 3d). No exotherm is apparent for this compound or for other related compounds which do not contain the iodoformamidinium cation. Consequently, the exotherm is assigned to the decomposition of the iodoformamidinium cation. Notice that, in the weight loss curve for iodoformamidinium iodide, the weight loss does not go to 100% at temperatures as high as 500 °C. This is unusual for pure low molecular weight organic salts, which are often volatilized by the time the samples reach these higher temperatures. In addition, the residue from thermal decomposition was black in appearance and insoluble in alcohols or a variety of other solvents examined. Along with the thermal stability, this suggests that the product had oligomerized or polymerized during the decomposition process.

A separate iodoformamidinium iodide thermal analysis run was made in which a sample was ramped up to 190 °C (just above the exotherm), maintained at this temperature for 30 min, and cooled to room temperature. The sample had lost 13.4% of its weight during the thermal cycle, and the product was a black tarlike compound. The IR spectrum was considerably different than the pattern for iodoformamidinium iodide. Although there was still a strong peak in the region of 1650 cm^{-1} and a moderately strong peak around 1394 cm^{-1}, there were a substantial number of new peaks, including a strong peak at 1712 cm^{-1}, medium-intensity peaks at 1683, 1530, and 1492 cm^{-1}, and a weak shoulder peak at 1335 cm^{-1}. In addition, while the broad region of relatively strong peaks between 3100 and 3300 cm^{-1} was still present, suggesting that the amine units were still at least partially intact, the peaks making up this band appeared to be broader and shifted from their positions in iodoformamidinium iodide. The growth of the peak at 1712

---

(25) Mauersberger, P.; Huber, F. *Acta Crystallogr.* **1980**, *B36*, 683.

(26) Thiele, G.; Serr, B. R. *Z. Kristallogr.* **1996**, *211*, 48.

cm^{-1} suggests that the C−I bond was broken during the exothermic process, since this peak is similar to the strongest peak observed for the protonated C═N group of the formamidinium cation. Further heating of the sample to 425 °C (in argon) resulted in approximately 90% of the original sample weight to be lost and provided a black product with a further substantial change in the IR pattern. Chemical analysis of this black powder led to the results C(37.6%), H(2.0%), and N(50.1%), indicating that most of the iodine had been lost from the sample.

Conclusion

While there have been numerous reports on the chemistry of simple aliphatic or aromatic ammonium cations in the <100>-oriented layered perovskites, the solid-state chemistry of the iodoformamidinium cation, which has proven useful for stabilizing the <110>-oriented family of lower-dimensional perovskites,[2] and the formamidinium cation, which recently has been found to substitute on the methylammonium site in the perovskite $(CH_3NH_3)_{1-x}(NH_2CH{=}NH_2)_xSnI_3$,[17] remains relatively unexplored. In this contribution we have discussed the synthesis and stability of two related crystal structures containing the iodoformamidinium and formamidinium cations, further demonstrating the potential usefulness of these cations for tailoring solid-state organic−inorganic hybrid materials.

Using aqueous hydriodic acid solutions, containing the same starting concentrations of dissolved tin(II) iodide and cyanamide, single-phase samples of the one-dimensional perovskites $[NH_2C(I){=}NH_2]_2ASnI_5$, with either A = $NH_2C(I){=}NH_2^+$ or $NH_2CH{=}NH_2^+$, have been stabilized simply by changing the thermal processing of the solution. For a solution which is immediately cooled from 70 °C, the iodoformamidinium cation is the dominant species in the solution, and therefore, $[NH_2C(I){=}NH_2]_3SnI_5$ crystals form during the cooling process. For a solution maintained at 80 °C for 24 h, some of the iodoformamidinium has been reduced to formamidinium, thereby favoring the crystallization of the mixed-cation compound, $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$. For solutions maintained at 90 °C for 24 h, more of the iodoformamidinium cations have been reduced and the formamidinium cations have been mostly hydrolyzed, leading to crystals of an ammonium tin iodide salt. Despite the relatively complex chemistry that occurs in these solutions, this study demonstrates a process for stabilizing the new compounds, in virtually single-phase form, by controlling the thermal processing of the solutions.

Both of the compounds $[NH_2C(I){=}NH_2]_2ASnI_5$, with A = $NH_2C(I){=}NH_2^+$ or $NH_2CH{=}NH_2^+$, are similar in structure, consisting of arrays of one-dimensional chains of opposite corner-sharing SnI_6 octahedra, separated by "A" cations within each layer of chains, and two crystallographically distinct iodoformamidinium cations between the layers. Of particular interest is the ability to use the organic cation separating the inorganic chains to control the degree of distortion of the SnI_6 octahedra and, therefore, the physical properties of the chains. For A = iodoformamidinium, the octahedra are highly distorted with bond lengths ranging from 2.957(1) to 3.484(1) Å, while, for A = formamidinium, the octahedra are only slightly distorted with all six Sn−I bonds falling in the range 3.140(8)−3.210(6) Å. Less distortion correlates with a shorter average Sn−I bond length and a smaller band gap.

In addition to the stability of cyanamide and derivative species in solution, we have also addressed the thermal stability and photosensitivity of the iodoformamidinium cation in the solid state. A strong exotherm, associated with substantial weight loss, is observed at temperatures between 176 and 179 °C for compounds containing this cation. The exotherm is associated with the decomposition of the iodoformamidinium cation by a process which involves breaking the C−I bond and which may also involve polymerization or oligomerization of the organic species. The two title compounds are also found to be light sensitive, with the decomposition apparently involving the tin(II) iodide framework and again the C−I bond within the iodoformamidinium cation.

Acknowledgment. The authors thank B. A. Scott for stimulating discussions and ARPA for partial support of this work under Contract DAAL01-96-C-0095.

Supporting Information Available: Tables showing the X-ray data collection and structural refinement parameters (Table S.1) and anisotropic temperature factors for the heavy atoms (Table S.2) for the $[NH_2C(I){=}NH_2]_2(NH_2CH{=}NH_2)SnI_5$ structure determination (3 pages). Ordering information is given on any current masthead page.

IC971332G