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Properties of Intervalence Antimony Bromides[1]

M. L. HACKERT, S. L. LAWTON[2] and R. A. JACOBSON

Abstract. Monovalent organic amines, R^+, have been used to synthesize 15 intensely colored salts of composition $R_xSb_yBr_z$. It is believed that the dark color may be due to the presence of mixed oxidation states of antimony or to some other type of charge transfer phenomena. Preliminary X-ray investigations and density measurements demonstrate that the ratio R:Sb:Br is cation dependent. Such ratios as 3:2:12, 4:2:12, and 2:1:9 have been observed and imply that the presumed Sb(III) and Sb(V) atoms do not necessarily occupy pseudo-equivalent positions in the unit cell. The temperature dependence of the color of these salts has also been studied. Many of these salts exhibit a color change from black or dark red at room temperature to orange at liquid nitrogen temperatures. The diffuse reflectance spectra of antimony bromide complexes diluted in KCl are reported for some of the cations. Resistivity measurements indicate that the salts, in general, are semiconductors having resistances in the range 10^9–10^6 ohm-cm.

It is well known that salts containing the same element or two similar elements in two different valence states are abnormally dark in color. Typical examples are halide systems of Fe(II)-Fe(III), Au(I)-Au(III), Ag(I)-Au(III), Pt(II)-Pt(IV), and Sb(III)-Sb(V) in which the ligands are chloride, bromide or iodide. The dark color arises through electron transfer transitions from the reduced state of the metal atom (an electron donor) to the oxidized form of the metal atom (an electron acceptor) and occurs *via* the van der Waals contacts of the halogen ligands. One of these systems, that of Sb(III)-Sb(V), has been under increasing investigation in recent years. Two significant papers of this system have appeared recently: a study of the charge transfer reflectance spectra of salts with constitution $Cs_4M^{III}Sb^VCl_{12}$ [M = Sb(III), Bi(III), In(II), and Tl(III)] by Day[3] and a single crystal X-ray structure determination of $(NH_4)_4Sb^{III}Sb^VBr_{12}$ by Lawton and Jacobson.[4] The structure determination of $(NH_4)_4Sb_2Br_{12}$ demonstrated that in this pseudo-K_2PtCl_6-type structure there are two oxidation states present, III and V, supporting Day's results. These different oxidation states are ordered in a tetragonal lattice (space group $I4_1/amd$) in which III and V alternate along just one unit cell axis and *not* in a cubic superlattice arrangement in which alternation along all three unit cell axes would occur. This ordering should be highly significant since charge transfer would be expected to play a key role in the crystallization of salts containing mixed Sb(III)-Sb(V) halide ions. Unfortunately, the X-ray investigation of

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this ammonium salt did not provide a direct unambiguous explanation for this ordering at the time of its completion. This point thus was still open to question and in general little was known concerning the charge transfer path and therefore the effect of charge transfer on packing in ionic structures of this type. Consequently, we have initiated such a study with the preparation of Sb(III, V) salts of monovalent cations in order to explore this influence structurally. To keep the number of variable parameters at a minimum, we have decided to study a series of bromide salts. This paper describes the preparation and properties of the salts we have studied.

In considering a series of related antimony bromide salts for such a study, we felt the following six points might have special importance in charge transfer salts and their structures: (i) the relative distribution of the mixed states in the unit cell, (ii) the halogen environment of antimony, both coordinated and uncoordinated, (iii) relative anion orientations and bond directions, (iv) the coordination number of both Sb(III) and Sb(V) and thus the charge carried by each halogen ligand, (v) variations in Sb(III)—X and Sb(V)—X(X = Cl, Br, I) bond lengths and X · · · X van der Waals contacts, and (vi) the influence of the cation on the structure and thus its role, directly or indirectly, in the charge transfer process.

A survey of the literature indicates that the group IA alkali metals and NH_4^+ cations are the most commonly used in the preparation of inorganic salts exhibiting charge transfer. Such ions, being of spherical electron density, usually result in the formation of crystals with fairly high symmetry. Unfortunately such symmetry is clearly capable of having an adverse affect on the amount of useful information which can be extracted. For example, ions likely to exhibit slight distortions in an isolated environment might go undetected in a cubic environment due to the presence of overriding crystal forces or to randomness in the orientation of the ion. A complete investigation therefore requires the preparation and analysis of low symmetry crystals as well, and it is this to which we decided to concentrate our attention. The method chosen for introducing low symmetry was through the use of non-spherical cations. Such cations would not give rise to dominant packing forces and therefore the formation of a stable ionic salt would be largely dependent on the packing of the mixed Sb(III)-Sb(V) ions. There is a wide variety of such cations available, such as substituted ammonium ions, carbonium ions, and saturated and unsaturated heterocyclic amines (phosphines or arsines), etc. We have decided to look at a series of monovalent organic amines.

The synthesis of compounds of the type $R_xSb_yBr_z$, where R represents either an aliphatic or aromatic amine, has been known since 1901 when Rosenheim and Stellman[5] reported the preparation of

[5]A. Rosenheim and W. Stellman, *Ber. Chem. Dtsch. Ges.* 34, 3377 (1901).

$(C_5H_5NH)_2SbBr_7$. Since then a wide variety of compounds have been reported[6]: (1) $RSbBr_4$, (2) $RSbBr_6$, (3) $RSbBr_7$, (4) R_2SbBr_5, (5) R_2SbBr_6, (6) R_2SbBr_7, (7) R_2SbBr_8, (8) R_2SbBr_9, (9) R_3SbBr_6, (10) $R_3Sb_2Br_9$, (11) $R_3Sb_2Br_{11}$, (12) $R_3Sb_2Br_{12}$, (13) $R_3Sb_2Br_{15}$, (14) $R_5Sb_3Br_{14}$, (15) $R_7Sb_3Br_{16}$, (16) $R \cdot SbBr_3 \cdot 3HBr$.

The size and charge distribution of the cation must also be considered in selecting suitable cations. The use of large bulky organic groups should give rise to lower density salts in which steric effects may be pronounced. Such effects could produce a marked change in the interhalogen distance of the Sb(III)-Sb(V) ions. Since it is believed that the charge transfer occurs *via* these ligands, the degree of absorption should be found to be a function of the size of the cation. The charge distributions of the cation may also give rise to distortions due to the relative orientation of electropositive and electronegative groups. The localization or delocalization of charge could also influence the charge transfer properties in that delocalized systems might provide an alternate path for the transfer to occur.

In our present investigation the following monovalent cations were selected: two quaternary ammonium ions, eight unsaturated heterocyclic amines, and five saturated heterocyclic amines. All 15 cations resulted in the formation of $R_xSb_yBr_z$ salts. Preliminary space group information is given for those compounds for which suitable single crystals could be obtained. The conductivity properties, stabilities, solubilities and color dependence with change in temperature have also been studied. The diffuse reflectance spectra of several of the salts are also reported.

EXPERIMENTAL

Preparation of Compounds

All compound were successfully prepared by the reaction of the amine and antimony tribromide in a hot solution of concentrated hydrobromic acid (48 percent) and liquid bromine. It was found that the preparation was relatively insentive to variations in the exact amounts used in the synthesis; however, the actual quantities used are listed in Table 1. The antimony solution was prepared first by dissolving reagent grade antimony tribromide in warm ($\approx 50°$ C.) concentrated hydrobromic acid (48 percent). Liquid bromine was then added as the oxidizing agent and finally the amine was added. Liquid amines were added directly, but solid amines were first dissolved in a minimum amount of the hydrobromic acid. Since some of the amines were found to react more vigorously than others, the amine was added slowly and with caution. In most cases the dark compound formed instantaneously. However, at times a thick yellow-

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[6]R. D. Whealy and R. L. Yeakley, *J. Inorg. Nucl. Chem.* 25, 365 (1963).

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brown paste formed instead of a dark crystalline salt, indicative of an insufficient amount of bromine. In those cases, additional bromine was added with stirring until the precipitate reverted to crystalline form. Each was filtered from the mother liquor by vacuum filtration through a sintered glass crucible, rinsed with a small portion of cold concentrated hydrobromic acid containing a few drops of liquid Br_2 and then dried in a desiccator containing concentrated sulfuric acid as a desiccant and a small partial pressure of bromine vapor.

Table 1

Summary of Quantities of Material Used in the Preparation of $R_xSb_yBr_z$ Salts

Cation, R^+	$SbBr_3$	HBr (48%)	Br_2	Amine
$N(CH_3)_4^+$	7.46 gm.	55 ml.	6.0 ml.	5.42 gm. tetramethyl-ammonium bromide
$C_5H_5NH^+$	2.50	10	0.5	1.0 ml. pyridine
$2\text{-}C_6H_7NH^+$	2.50	10	0.6	1.2 ml. α-picoline
$3\text{-}C_6H_7NH^+$	2.50	10	0.6	1.2 ml. β-picoline
$4\text{-}C_6H_7NH^+$	2.50	10	0.6	1.2 ml. γ-picoline
$4\text{-}C_7H_9NH^+$	2.50	10	0.5	1.5 ml. 4-ethylpyridine
$2, 4, 6\text{-}C_8H_{11}NH^+$	2.50	10	1.0	1.6 ml. γ-collidine
$C_9H_7NH^+$	2.50	12	1.0	1.3 ml. quinoline
$C_4H_9NH^+$	2.50	10	0.8	1.1 ml. pyrrolidine
$2\text{-}C_4H_7ONH^+$	2.50	5	0.5	0.95 ml. 2-pyrrolidone
$C_5H_{11}NH^+$	2.50	10	0.8	1.4 ml. piperidine
$4\text{-}C_4H_9ONH^+$	2.50	10	0.5	1.1 ml. morpholine
$C_7H_{13}NH^+$	2.50	10	0.8	0.9 gm. quinuclidine
$N(C_2H_5)_4^+$	2.50	10	1.5	2.0 gm. tetraethyl-ammonium bromide

Preparation of Single Crystals for X-Ray Study

Crystals suitable for single crystal studies were obtained by re-crystallizing the raw material from a small portion (2-3 ml.) of hot concentrated hydrobromic acid (48 percent). It was necessary to replenish the solution periodically with a few drops of bromine during the heating step. After dissolution was complete, the solutions were set aside to cool in a dessicator containing a small partial pressure of bromine vapor. The use of sulfuric acid (1 or 2 drops) as a "salting-out" agent was also tried and found to be of optional use. The size of the resulting crystals seemed to be governed mainly by the solubility of the raw material in hot concentrated hydrobromic acid (48 percent). Those of lower solubility giving rise to crystals that were of poorer quality and more plate-like in appearance. After crystal growth had ceased, an eye dropper was used to transfer a small portion of the crystals, together with the mother liquor, to flat filter paper for inspection under a microscope. The mother liquor on the paper served to delay debromination of the salt in order to allow sufficient time (approximately 5 to 10 minutes) for selecting and mounting the crystals

in open atmosphere. The black crystals were mounted and sealed within 0.3 mm. Lindemann glass capillaries. Once mounted, the crystals are apparently stable.
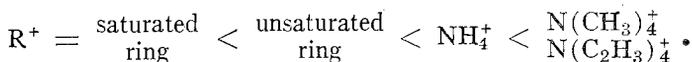
PHYSICAL AND CHEMICAL PROPERTIES

Solubility and Morphology

Like the ammonium salt these salts are moderately soluble in concentrated hydrobromic acid (48 percent), dissolution resulting in yellow solutions. Those salts containing the saturated ring cation were found to be more soluble than those with an unsaturated ring. Consequently, the salts of the unsaturated amines are soft plate-like needles while those of the saturated amines are hard, brittle needles. The salts are slightly soluble in methanol, less soluble in ethanol, and insoluble in nonpolar solvents like carbontetrachloride.

Stability at Room Temperature

The salts are comparatively stable in air, but on long exposure the crystals lose their luster through debromination. This is observed for all the salts except the tetraethylammonium salt which appears to be air stable indefinitely. The rate of debromination is apparently catalyzed by sunlight, i.e., compounds in open containers exposed to sunlight are found to debrominate more rapidly those those in open containers kept in the dark. The color of a fully debrominated product varies from salmon-red to tan to various shades of yellow. In the presence of bromine vapor these debrominated products again turn black in color. Reflectance spectra of the original, debrominated, and rebrominated species indicate that this rebromination is reversible. The relative order of stability toward debromination at room temperature was observed to be cation dependent, the over-all trend being:

$$R^+ = \begin{matrix} \text{saturated} \\ \text{ring} \end{matrix} < \begin{matrix} \text{unsaturated} \\ \text{ring} \end{matrix} < NH_4^+ < \begin{matrix} N(CH_3)_4^+ \\ N(C_2H_3)_4^+ \end{matrix} .$$

All the compounds except the tetraethylammonium salt were found to hydrolyze rapidly upon contact with water at room temperature. The colors of the hydrolyzed products are white or cream except for the quinolinum product which is yellow-orange. The stability of the tetraethylammonium salt cannot be accounted for at this time. Therefore, a structural investigation of this compound has been undertaken.

Color and Color Dependence on Temperature

All of the compounds prepared were intensely colored. All appear black under reflected light except for the tetramethyl and tetraethyl ammonium salts which are red and dark violet, respectively. However, in transmitted light the black salts appear to be deep red in color.

One of the interesting properties of this series of salts is their color dependence on temperature. As the temperature is lowered to liquid nitrogen temperature ($\approx 174°$ C.), some of the salts lose their black

Table 2A

Comparison of Melting Points and Colors at Various Temperatures for $R_xSb_yBr_z$ Salts

Cation	Color of Salt at 25° C.	Color of Salt at —174° C.	Melting Point Range, ° C.	Remarks Regarding Elevation in Temperature
$N(CH_3)_4^+$	Black	Black	> 300	Debrominates to red solid between 100-130°; at 290° starts to turn yellow
pyridinium	Black	Black	201-202	Turns crimson-red in color just before melting
quinolinium	Black	Violet-black	131-132	Partially melts at temperature indicated, then resolidifies
pyrrolidinium	Black	Black	> 300	Debrominates near 125° to yellow solid; turns black when reaches 280°
piperidinium	Black	Black	288-289	Debrominates at about 140° to a yellow solid; turns black when reaches 280°; melt is black in color
quinuclidinium	Black	Black	> 300	Debrominates to red solid beginning at 135°; entirely red at 152°; at 168° red solid begins to turn yellow; entirely yellow at 260-300°

Table 2B

Comparison of Melting Points and Colors at Various Temperatures for $R_xSb_yBr_z$ Salts

Cation	Color of Salt at 25° C.	Color of Salt at —174° C.	Melting Point Range, ° C.	Remarks Regarding Elevation in Temperature
α-picolinium	Black	Orange	116.5-117	Melt is black in color; no decomposition
β-picolinium	Black	Orange	119.5-120.5	Melt is black in color; no decomposition
γ-picolinium	Black	Red	135-138	Melt is black in color; no decomposition
4-ethyl pyridinium	Violet-black	Orange-red	94-95.5	Melt is black in color; no decomposition
2, 4, 6-methyl pyridinium	Violet-black	Orange-red	94.5-95.5	Melt is black in color; no decomposition
$N(CH_3)_4^+$	Red	Yellow-orange	> 300	Decomposes to grey solid above 340°
$N(C_2H_5)_4^+$	Violet-black	Orange	153-157	Melt is black in color
2-pyrrolidonium	Black	Orange-red	68-74	Melting point may be in error; solid is very deliquescent; color of liquid is black
morpholinium	Black	Red	105-107	Melts at temperature indicated if solid not allowed to debrominate before melting; if debrominates below 105°, m.p. > 130°

color. The color change is from black to red to orange as the temperature is lowered (Table 2). If the cation is a saturated ring system or an unsubstituted pyridinium ring, no color change is noticed. If the cation is a tetramethyl or tetraethyl ammonium ion, an unsaturated heterocyclic amine containing one or more substituted alkyl groups, or a saturated heterocyclic amine containing a ketone oxygen atom either incorporated in the ring or attached to it, the antimony halide salts exhibits color dependence on temperature. Experiments have shown that the degree of yellow or orange present at liquid nitrogen temperature is directly proportional to the temperature at which the black color begins to disappear.

The peculiar behavior of those salts which show color dependence with a decrease in temperature is also reflected in the behavior of the same salts as the temperature is raised to their melting points (Table 2). For those salts which exhibit this color dependence, the melt is dark in color with no evidence of decomposition or color change prior to melting. This appears to indicate unusual stability and the presence of strong charge transfer in the molten state.

To further characterize the unusual optical properties of these compounds, the diffuse reflectance spectra for several typical salts were taken. These are given in Figure 1. The spectra were taken using a Beckman DU spectrophotometer equipped with a reflectance attachment. A hydrogen source was used in the region 200-300 $m\mu$ and a tungsten lamp for the region 320-1200 $m\mu$. The samples were diluted with potassium chloride which was also used as a reference. Absorption occurring above 650 $m\mu$ is believed to be predominantly due to interspecies interactions in the crystal. The intense bands in the ultraviolet region arise from known transitions of antimony (III) and (V). Although it is impossible to draw definite conclusions from these few spectra, it is interesting to note some qualitative trends that are present. The amount of absorption which occurs beyond 650 $m\mu$ appears dependent on the size of the cation; an increase in size usually results in decreased absorption, as would be expected from the color dependence noted above. For example, compare pyridinium to α-picolinium, quinolinium to 2-methyl quinolinium, pyridinium to quinolinium, and ammonium to tetramethylammonium (spectrum given is for red form). These results, although inconclusive, do at least indicate that the degree of charge transfer is dependent on the cation size. This would appear reasonable if the charge transfer path is *via* the van der Waals contacts of the halogen ligands.

Conductivity Properties

Preliminary conductivity measurements[7] performed on a representative selection of four $R_xSb_yBr_z$ salts indicate that these compounds

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[7]Measured by B. A. Torp, Minnesota Mining and Manufacturing Company, Central Research Laboratories, St. Paul, Minnesota 55119.
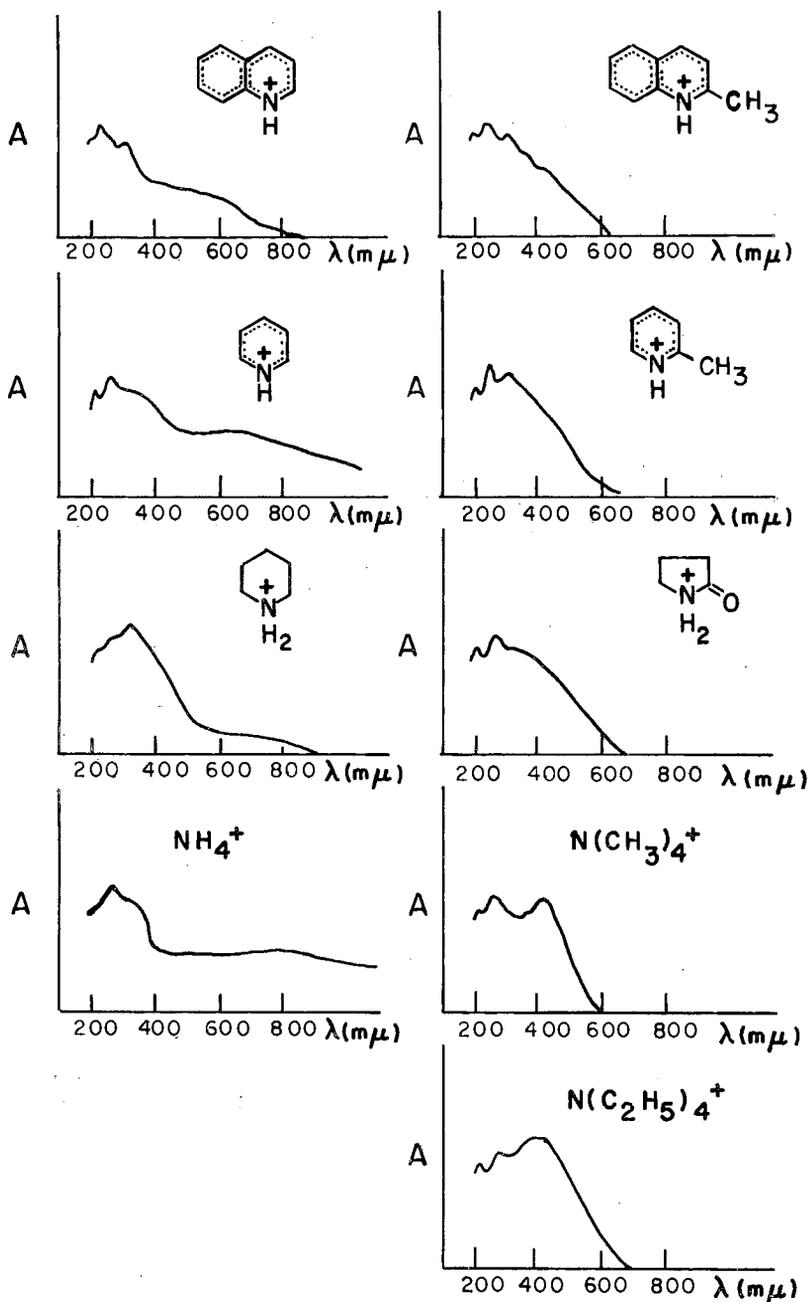
Figure 1.   Diffuse reflectance spectra of typical $R_xSb_yBr_z$ salts.

are semiconductors having resistances in the range 10^9–10^6 ohm-cm when pressed between gold electrodes and when 10-100 V are applied. They have been found to be slightly photoconductive at 1000 foot-candles when applying (visible) tungsten light. Higher photoresponse to near IR radiation is also found. A summary of the photoconductivity data is given in Table 3 for the conditions discussed above.

Table 3

Conductivity Data for Selected $R_xSb_yBr_z$ Salts

Sample	Form	$R_D,$[a]	R_D/R_L[a]	Rise-Decay[b]
		ohm-cm.		
$(NH_4)_4Sb_2Br_{12}$	Powder	2×10^6	1.1	Slow
$(pyr)_6Sb_4Br_{24}$	Powder	3×10^8	1.4	Slow
$(\alpha\text{-pic})_2SbBr_9$	Powder	8×10^7	1.1	Slow
$(pip)_4Sb_2Br_{16}$	Powder	4×10^8	1.6	Slow
$(NH_4)_4Sb_2Br_{12}$	Single crystal[c]	1×10^7	1.4	Fast

[a]R_D = dark resistance; R_D/R_L = dark resistance/light resistance = photoresponse.
[b]Rise-decay = photoconductivity rise and decay times.
[c]Silver electrodes applied to a single crystal. Measurements made at 10 V and $\simeq$ 100 foot-candles visible light.

The conductivity data could be explained on the basis of electron transfer from the ns^2 shell of Sb(III) to the ns^0 shell of Sb(V). Such a charge transfer mechanism was proprosed by Day[3] to account for the deep color of the salts at room temperature. The presence of a mixture of Sb(III) and Sb(V) has been confirmed for $(NH_4)_4Sb_2Br_{12}$[4] and $(pyr)_6Sb_4Br_{24}$[8] and may be suggested for $(pip)_4Sb_2Br_{16}$ and $(quinucl)_2SbBr_8$ on the basis of preliminary structural evidence for $(quinucl)_2SbBr_8$; the salt $(\alpha\text{-pic})_2SbBr_9$,[9] however, contains only Sb(V) and Br_3^- groups and so a different mechanism would have to be involved in this case. Regardless, the conductivity data indicate that interactions between $SbBr_6^{n-}$ ions do take place.

Crystal Data

Single crystals of 11 of the 15 salts were examined by X-ray diffraction techniques for preliminary crystal data using oscillation, Weissenberg, and precession film techniques. Zirconium-filtered molybdenum and nickel-filtered copper radiation were used. Lattice parameters and extinction conditions were determined from these photographs. Density measurements were made by the flotation method using organic liquids as the medium. Using these calculated lattice parameters and densities, the empirical formula for each salt was deduced. The results of this investigation are listed in Table 4.

[8]S. L. Lawton, R. A. Jacobson, and R. S. Frye, to be published.
[9]S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 7, 2124 (1968).

Table 4

Unit Cell Data for the $R_xSb_yBr_z$ Salts

Cation	Space Group	Lattice Parameters[c, d]	
pyridinium	orthorhombic[a] CmC2_1	$a = 17.51$ A $b = 23.77$ $c = 16.46$ (n) $V = 6851$ A^3	$\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
α-picolinium	triclinic[n, b] B$\bar{1}$	$a = 17.770$ $b = 9.750$ $c = 7.645$ (n) $V = 1232.5$	$\alpha = 90.074°$ $\beta = 96.767°$ $\gamma = 110.279°$
β-picolinium	monoclinic B2, Bm or B2/m	$a = 18.61$ $b = 9.69$ $c = 7.54$ (n) $V = 1249$	$\alpha = 90°$ $\beta = 90°$ $\gamma = 113° \ 17'$
γ-picolinium	monoclinic B2, Bm or B2/m	$a = 18.38$ $b = 9.83$ $c = 7.43$ (n) $V = 1234$	$\alpha = 90°$ $\beta = 90°$ $\gamma = 113° \ 08'$
4-ethyl pyridinium	orthorhombic Pna2_1	$a = 34.08$ $b = 7.67$ $c = 16.84$ (n) $V = 4402$	$\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
pyrrolidinium	monoclinic Cc or C2/c	$a = 31.4$ $b = 9.71$ (n) $c = 15.0$ $V = 4517$	$\alpha = 90°$ $\beta = 99° \ 00'$ $\gamma = 90°$
piperidinium	monoclinic C2, Cm or C2/m	$a = 28.8$ $b = 19.8$ (n) $c = 18.7$ $V = 9561$	$\alpha = 90°$ $\beta = 116° \ 17'$ $\gamma = 90°$
morpholinium	orthorhombic Pna2_1	$a = 28.01$ $b = 8.31$ (n) $c = 10.02$ $V = 2332$	$\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
quinuclidinium	cubic F432, F$\bar{4}$3m or Fm3m	$a = 13.88$ $b = 13.88$ $c = 13.88$ $V = 2674$	$\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$

[a]Space group confirmed by a single crystal X-ray structure determination; see Ref. 8 and 9.

[b]To enable a comparison of unit cells, the orientation of the triclinic B-centered cell of the α-picolinium salt listed corresponds to the same orientation of the related β-picolinium and γ-picolinium monoclinic unit cells. The parameters of the primitive reduced cell of the α-picolinium salt are: $a = 9.249 \pm 0.002$, $b = 9.750 \pm 0.001$, $c = 7.645 \pm 0.002$ A, $\alpha = 90.074 \pm 0.016°$, $\beta = 107.461 \pm 0.024°$, $\gamma = 70.520 \pm 0.016°$ (see Ref. 9).

[c]The letter (n) indicates the needle axis of the crystal.

[d]The estimated standard deviations in the unit cell parameters are as follows: pyridinium salt, a (0.02 A), b (0.03 A), c (0.02 A); α-picolinium salt, a (0.003 A), b (0.001 A), c (0.002 A), α (0.016°), β (0.024°), γ (0.014°); remaining salts, $\pm$ 0.15% in the cell edges and 10' in the cell angles not fixed by symmetry.

Of the salts investigated with X-rays, only the piperidinium salt gave rise to weak reflections in its reciprocal lattice of the type ob-

served for the ammonium salt, $(NH_4)_4Sb_2Br_{12}$. This indicates that the definite ordering of the antimony groups observed in the ammonium salt does not occur for all salts.

The α-, β-, and γ-picolinium are essentially isomorphous in structure, as indicated by similarities in their X-ray intensity patterns.

Table 5

Empirical Formulas for the $R_xSb_yBr_z$ Salts Based on Density Measurements and Unit Cell Data

Cation, R^+	Z^a	ρobs	ρcalc	Empirical Formula
pyridinium	8	2.66	2.80	$R_3Sb_2Br_{12}$[b]
α-picolinium	2	2.57	2.77	R_2SbBr_9[b]
β-picolinium	2	2.54	2.74	R_2SbBr_9
γ-picolinium	2	2.55	2.77	R_2SbBr_9
4-ethyl pyridinium	4	2.54	2.55	$R_3Sb_2Br_{14}$
pyrrolidinium	8	2.56	2.60	R_2SbBr_8
piperidinium	16	2.57	2.58	R_2SbBr_8
morpholinium	4	2.64	2.64	R_2SbBr_8
quinuclidinium	4	2.42	2.44	R_2SbBr_8

[a]The number of formula units per unit cell corresponds to the unit cell data listed in Table 4.

[b]Empirical formula confirmed by an actual single crystal X-ray structure determination. See also Ref. 8 and 9.

DISCUSSION

The use of organo-nitrogen cations in the synthesis of antimony bromide salts has resulted in a series of intensely colored salts of composition $R_xSb_yBr_z$. Examination of their physical properties indicates several basic similarities as well as striking differences within this series. Calculations of the empirical formula for each salt, based on unit cell data and density measurements, reveal changes of composition with change in cation. This dependence on R^+ was also observed by Petzold[10] although the exact formulas he obtained differ in some cases from ours. The presence of the unique set of weak reflections in the reciprocal lattice of the piperidinium salt strongly suggests the presence of Sb(III) and Sb(V) in an ordered array, but the lack of any such reflections in the other salts does not necessarily indicate the lack of an ordered mixture of III and V in them.

Examination of the data presented here raises numerous questions worthy of some comment. We find, for example, that upon cooling the salts to liquid nitrogen temperatures some salts lose their black color, whereas others do not. We also find that the substitution of a methyl group into pyridinium ring makes a considerable difference, not only on the structure, but, as the reflectance spectra indicate, in the charge

[10]W. Petzold, Z. anorg. Allgem. Chem. 215, 92 (1933).

transfer properties as well. The reflectance spectra also indicate that the size of the cation may be a major factor in determining charge transfer and other properties. The position of a nitrogen atom relative to a substituted methyl group in a picolinium ring also appears to have a significant effect on the charge transfer, as indicated by a comparison of the color change with decrease in temperature of the three picolinium salts. Even the presence of oxygen in a piperidinium ring seems to have a major effect on the structure; its influence is also worth investigating. These and other points are of considerable interest, but rather than speculate on their cause and effect at the present time, we wish to defer their discussion until representative structures are examined in more detail.

Acknowledgment