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Preparation, Characterization, and Crystallographic Data of Some Substituted-Pyridinium Antimony(III) Bromide Salts^{1,2}

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Structures of a wide variety of antimony(III) anions with fluoro and chloro ligands and differing in stoichiometry have been characterized, yet structures of only two involving bromo coordination, *viz.*, SbBr_6^{3-} ⁵ and $\text{Sb}_2\text{Br}_9^{3-}$ ⁶ have been determined. Formation of other bromo-coordinated ions in the crystalline state, such as SbBr_4^- or SbBr_5^{2-} or their polymeric forms, should be possible. Indeed, by using 17 different aliphatic amines and three aromatic amines, Whealy and Yeakley⁷ succeeded in synthesizing $\text{R}_x\text{Sb}_y\text{Br}_z$ salts having R:Sb:Br ratios of 2:1:5, 3:1:6, and 3:2:7; all were yellow, varying only in shade. We decided to explore the synthesis of $\text{R}_x\text{Sb}_y\text{Br}_z$ salts by considerably expanding the choice of aromatic amines, particularly in view of increasing structural evidence that (aromatic)N-H...X (X = Cl or Br) hydrogen bonds are capable of inducing significant deformation of halogen-coordinated anions. We succeeded in synthesizing a variety of salts, some intensely colored, ranging from deep yellow to orange and red. R:Sb:Br ratios of 1:1:4, 2:1:5, and 3:2:9 were obtained. This note reports the preparation of these salts and some of their physical properties.

Experimental Section

Preparation. Each salt was prepared by allowing the appropriate amine to react with antimony tribromide in concentrated hydrobromic acid (48%). The antimony tribromide solution was first prepared by dissolving 0.0111 mol of reagent grade SbBr_3 in 10 ml of concentrated hydrobromic acid. To this was added an equimolar amount (0.0111 mol) of the amine. Liquid amines were added dropwise, with stirring, to the SbBr_3 -HBr solution at room temperature. Reaction mixtures resulting from the addition of solid amines were heated to effect reaction. The amine:SbBr₃ ratio of 1:1 was arbitrarily used for initial syntheses, giving high yields only for those salts having R:Sb:Br of 1:1:4; yields were improved for the other salts when stoichiometric amounts of the starting materials were used.

The bromide salt of 1-methylpyridine, $\text{C}_5\text{NH}_5^+\text{Br}^-$, was used as the starting material for the 1-methylpyridinium derivative; it was added directly to the SbBr_3 -HBr solution with heating. Preparation

of the 1-bromopyridinium derivative made use of crystalline pyridinium bromide hydrobromide, $\text{C}_5\text{NH}_5\text{Br}^+\text{Br}^-\text{HBr}$, (from K & K Laboratories) as the starting material.⁸ Direct addition of this orange-red solid to the SbBr_3 -HBr solution at room temperature produced a black crystalline product. The mixture was heated to drive off molecular bromine and then allowed to cool, yielding this time light orange crystals.

Addition of pyridine, quinoline, isoquinoline, and the alkyl-substituted pyridines to SbBr_3 in HBr yielded crystalline precipitates on contact; these were filtered and recrystallized from hot concentrated hydrobromic acid. Reactions involving the halogenated pyridines (except that of 1-bromopyridine, as noted above) produced crystals only on standing, usually within 0.5 hr. Because it was believed that chemically pure $\text{R}_x\text{Sb}_y\text{Br}_z$ salts formed in these latter cases, no recrystallizations were carried out. All 19 compounds, except the 2-fluoropyridinium derivative, crystallized as needles.

Physical and Crystallographic Measurements. The colors, melting points (in air), and observed densities (by flotation) are presented in Table I. Crystallographic unit cell data, also summarized in Table I, were determined using single-crystal Weissenberg and precession film techniques.

Empirical formulas for 17 of the 19 salts were derived by utilizing the relationship $d = ZM/N_0V$ (where d is the density, Z is the number of formula units of weight M per unit cell, N_0 is Avogadro's number, and V is the unit cell volume) in conjunction with elemental analysis⁹ and fluorescence spectroscopy. Because Z is restricted to certain values by space group requirements, this expression proved to be quite sensitive and useful. In only two cases, formulas consistent with the crystal data could not be derived. Until all the salts are fully characterized by single-crystal structure determinations, it is appropriate to regard the empirical formulas in Table I as only tentative assignments.

Infrared Measurements. Infrared spectra of the 19 $\text{R}_x\text{Sb}_y\text{Br}_z$ salts¹⁰ were recorded with Perkin-Elmer Model 457 and 467 instruments. Samples were run as KBr pellets (3-mg sample in 300 mg of KBr). Several samples were examined as mulls in Nujol and Fluorolube for comparison with the KBr preparations. No appreciable shifts were noted and it is believed that no interaction between sample and KBr occurred. Wavelength calibration scans were made routinely of a polystyrene film.

Discussion

Two significant results emerged from this investigation. First, we have found that when aromatic amines are used as cations, R:Sb:Br ratios of 1:1:4, 2:1:5, and 3:2:9 can be obtained. Second, we have succeeded in identifying a variety of aromatic amines capable of forming antimony(III) bromide salts which are more deeply colored than those synthesized with nonaromatic cations. Whealy and Yeakley have noted that the 20 salts they synthesized were all yellow, varying only in shade. The pyridinium salt, $(\text{C}_5\text{NH}_5)_2\text{Sb}_2\text{Br}_{11}$, which contains the $\text{Sb}_2\text{Br}_9^{3-}$ ion, is also yellow,^{6a} as are those with alkali cations. Table I shows that the most intensely colored salts contain the halogenated cations, notably the 1-bromo-, 2-fluoro-, 2-chloro-, 2-bromo-, and 3,5-dichloropyridinium derivatives, which range in color

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(5) (a) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, **5**, 743 (1966); (b) C. R. Hubbard and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, **75**, 85 (1968); (c) S. L. Lawton, R. A. Jacobson, and R. S. Frye, *Inorg. Chem.*, **10**, 701, 2813 (1971).

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(8) When recrystallized from concentrated hydrobromic acid, this compound has the following crystal data at room temperature: orthorhombic, space group *Pnma* or *Pna2*₁ with lattice parameters $a = 8.34$ (4), $b = 7.93$ (2), and $c = 13.67$ (4) Å.

(9) $\text{R}_x\text{Sb}_y\text{Br}_z$ complexes of known composition were initially used to evaluate analytical methods available to us for determination of bromine (by titration with AgNO_3) and antimony (by wet oxidation with acid, reduction with SO_2 , and titration with KMnO_4). Deviation of the measured from the calculated content averaged 3% for both elements. This deviation exceeded, by a factor of 1-3, the calculated range in Br and Sb content for $\text{R}_x\text{Sb}_y\text{Br}_z$ salts having Sb:Br ratios 1:4, 1:4.5, and 1:5. Major sources of error were poor solubility of the salts in toluene-propanol-water mixtures for the bromine determinations and, in general, the presence of small amounts of hydrobromic acid adhering to the crystal surfaces. Accordingly, while reliable elemental analyses would have been desired for all 19 salts in this series, they were performed on only those for which empirical formulas derived by the other methods were inconclusive. No elemental analyses were performed for C or N content.

(10) See paragraph at end of paper regarding supplementary material.

Table 1. Physical Properties and Crystallographic Data of 19 R_xSb_yBr_z Salts

Cation, R ⁺	Color	Mp, °C	Space group ^a	Lattice parameters					d, g/cm ³		Z	Proposed empirical formula		
				a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å ³			Obsd ^b	Calcd
Pyridinium	Pale yellow	216-217.5	C2/c	11.82 (4) ^c	13.06 (4)	7.69 (2)	90	93.9 (2)	90	1185 (11)	2.8	2.92	4	C ₅ NH ₆ SbBr ₄
1-Methylpyridinium	Pale yellow	156-158.5	P2 ₁ /c	12.73 (4)	13.54 (4)	7.59 (2)	90	107.3 (2)	90	1250 (11)	2.7	2.85	4	C ₆ NH ₈ SbBr ₄
2-Methylpyridinium	Pale yellow	149.5-151.0	P2 ₁ /c	12.84 (4)	13.31 (4)	7.65 (2)	90	106.6 (2)	90	1252 (11)	2.7	2.84	4	C ₆ NH ₈ SbBr ₄
3-Methylpyridinium	Pale yellow	149.5-151.0	P2 ₁ /c	12.51 (4)	13.64 (4)	7.72 (2)	90	106.9 (2)	90	1260 (11)	2.8	2.82	4	C ₆ NH ₈ SbBr ₄
2,6-Dichloropyridinium	Pale yellow	83-110	P2 ₁ /m	10.45 (3)	10.76 (3)	13.45 (4)	90	110.2 (2)	90	1419 (13)	2.6	2.76	4	C ₅ NH ₄ Cl ₂ SbBr ₄
Quinolinium ^d	Light yellow	242-243	Cc	15.28 (5)	14.04 (4)	7.44 (2)	90	118.3 (2)	90	1405 (13)	2.5	2.70	4	C ₉ NH ₈ SbBr ₄
Isoquinolinium	Light tan	260-263	P2 ₁ /a	13.11 (4)	14.14 (4)	7.57 (2)	90	91.4 (2)	90	1403 (13)	2.5	2.71	4	C ₉ NH ₈ SbBr ₄
4-Methylpyridinium	Lemon yellow	156-158	P1	10.66 (3)	10.86 (3)	9.30 (3)	108.8 (2)	97.7 (2)	99.2 (2)	985 (9)	2.4	2.39	2	(C ₆ NH ₈) ₂ SbBr ₅
2-Chloropyridinium	Orange	121-130	P2 ₁ /a	10.64 (3)	15.87 (5)	5.88 (2)	90	105.3 (2)	90	957 (9)	2.6	2.60	2	(C ₅ NH ₅ Cl) ₂ SbBr ₅
2-Bromopyridinium	Red	146-155	P2 ₁ /a	10.73 (3)	16.17 (5)	5.89 (2)	90	104.8 (2)	90	989 (9)	2.7	2.82	2	(C ₅ NH ₅ Br) ₂ SbBr ₅
3-Bromopyridinium ^e	Pale yellow	170-185	P2 ₁ /c	18.37 (6)	11.98 (4)	9.35 (3)	90	102.5 (2)	90	2009 (18)	2.7	2.77	4	(C ₅ NH ₅ Br) ₂ SbBr ₅
3-Iodopyridinium	Pale yellow	210-218	P2 ₁ /c	17.99 (5)	12.31 (4)	9.35 (3)	90	91.5 (2)	90	2070 (19)	3.0	2.99	4	(C ₅ NH ₅ I) ₂ SbBr ₅
3-Carboxypyridinium	Lemon yellow	194-205	C2/c	14.10 (4)	19.43 (6)	8.01 (2)	90	98.6 (2)	90	2169 (20)	2.5	2.36	4	(C ₆ NH ₆ O ₂) ₂ SbBr ₅
3,5-Dichloropyridinium	Deep yellow	158-174	Pbca	21.77 (7)	8.14 (2)	24.38 (7)	90	90	90	4320 (39)	2.4	2.52	8	(C ₅ NH ₄ Cl ₂) ₂ SbBr ₅
2,6-Dimethylpyridinium	Pale yellow	179-182.5	P2 ₁ /c	12.10 (4)	15.65 (5)	21.27 (6)	90	115.7 (2)	90	3629 (33)	2.3	2.36	4	(C ₇ NH ₁₀) ₃ Sb ₂ Br ₉
2,4,6-Trimethylpyridinium	Yellow-tan	193-199	P2 ₁ /n	10.36 (3)	42.36 (13)	9.09 (3)	90	100.2 (2)	90	3926 (35)	2.2	2.25	4	(C ₈ NH ₁₂) ₃ Sb ₂ Br ₉
2-Fluoropyridinium	Deep yellow	105-118	C2/c	21.85 (7)	21.15 (6)	13.82 (4)	90	104.6 (2)	90	6179 (56)	2.7	2.70	8	(C ₅ NH ₅ F) ₃ Sb ₃ Br ₉
2,4-Dimethylpyridinium	Yellow	157-164	Pmmm	12.06 (4)	12.97 (4)	11.49 (3)	90	90	90	1797 (16)	2.2			
1-Bromopyridinium	Light orange	218-225	C2/c	11.83 (4)	13.03 (4)	7.70 (2)	90	93.9 (2)	90	1183 (11)	2.4			

^a In those cases where more than one space group is possible for a given set of extinction conditions, that which corresponds to the highest possible symmetry consistent with the observed density is indicated. ^b Observed densities are accurate to only ±10%. The tendency of the crystals to react with the organic medium made it difficult to improve this accuracy. ^c Numbers in parentheses are estimated errors. ^d The unit cell parameters given in this table are related to those in footnote 22 of the text by the following I → C transformation matrix: (1, 0, 1)/(0, 1, 0)/(0, 0, 1). ^e The unit cell parameters in this table are related to those in footnote 21 of the text by the following B → P transformation matrix: (1/2, 0, 1/2)/(0, 1, 0)/(0, 0, 1).

from deep yellow to orange and red. It is suggested that these shifts in color from pale yellow result from anion deformation or from anion-cation charge transfer. Crystallographic studies have shown that (aromatic) $N-H \cdots X$ ($X = Cl$ or Br) interactions can significantly deform an anion.^{5c,11} Deformation of an ion may induce a perturbation of its energy levels causing absorption bands to shift in wavelength or causing one or more new bands to emerge. Presence of charge-transfer may be important in situations involving short van der Waals contacts between Br^- ligands and the cations. A short donor-acceptor distance, accompanied by specific spatial orientations, may provide a favorable situation for the transfer of electrons from a donor orbital of the halogen to the π -acceptor orbital of the pyridinium ring. An example of a closely related system is the black N,N' -dimethyl-4,4'-bipyridylium salt of $[CuCl_2]_n^{n-}$.¹²

In order to gain an insight into the various types of anions one might find in the $RSbBr_4$ and R_2SbBr_5 salts, it is profitable to examine structures of other group V nontransition metal halides having similar formulas. Five such compounds are $C_5NH_6SbCl_4$,¹³ $C_6NH_8BiBr_4$,¹⁴ $C_6NH_8BiI_4$,¹⁴ $(C_5NH_{11})_2BiBr_5$,¹⁵ and $(NH_4)_2SbCl_5$.¹⁶ In the first three examples MX_4^- anions (actually $M_2X_8^{2-}$ dimers) bind together *via* pairs of halogen bridges, linking neighboring metal atoms together. Such an arrangement enables the metal atom to adopt a distorted octahedral environment. In $(C_5NH_{11})_2BiBr_5$ a distorted octahedral configuration is also adopted by the central metal atom (Bi in this case) by forming infinite chains of $BiBr_5^{2-}$ ions *via* bromine bridges. By contrast, $SbCl_5^{2-}$ in $(NH_4)_2SbCl_5$ exists only as an isolated ion. It adopts an octahedral configuration of six electron pairs in which a lone pair of electrons occupies one of the octahedral sites in the antimony(III) coordination sphere. The same stereochemical configurations, including a hypothetical straight-chain polymeric variation of the observed zigzag $BiBr_5^{2-}$ form, are logical possibilities for the $RSbBr_4$ and R_2SbBr_5 series. There is a striking similarity in crystal data of the 2-methylpyridinium salts $C_6NH_8BiBr_4$,^{14,17} and $C_6NH_8BiI_4$,^{14,19} with the 1-methyl-, 2-methyl- and 3-methylpyridinium salts in Table I, indicating that all five structures are probably isomorphous.²⁰ Similar remarks cannot be made unequivocally about the pyridinium analogs $C_5NH_6SbCl_4$ ¹³ and $C_5NH_6SbBr_4$, however, owing to their dissimilar cell parameters.

The $Sb_2Br_9^{3-}$ ion is possibly present in the $R_3Sb_2Br_9$ series.

This anion has previously been found in the structures of $(C_5NH_6^+)_5(Sb_2Br_9^{3-})(Br^-)_2$ ^{6a} and $[(CH_3)_4N^+]_3(Sb_2Br_9^{3-})(Br_2)$.^{6b} It comprises two $SbBr_6^-$ octahedra sharing a face. Alternate considerations for $R_3Sb_2Br_9$ include $SbBr_4^-$ chains or discrete $Sb_2Br_8^{2-}$ dimers, with interstitial bromide ions for charge balance.

Of the 19 salts synthesized, nine fall into four sets of isomorphous groups having the following cations: (i) 1-methylpyridinium, 2-methylpyridinium and 3-methylpyridinium; (ii) 2-chloropyridinium and 2-bromopyridinium; (iii) 3-bromopyridinium²¹ and 3-iodopyridinium; and (iv) quolinium²² and isoquinolinium.

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Registry No. $C_5H_5NHSbBr_4$, 52279-30-8; $1-CH_3C_5H_5NSbBr_4$, 52279-29-5; $2-CH_3C_5H_5NHSbBr_4$, 50284-20-3; $3-CH_3C_5H_5NHSbBr_4$, 52279-31-9; $2,6-Cl_2C_5H_3NHSbBr_4$, 52279-32-0; $C_6H_7NHSbBr_4$, 52279-33-1; $i-C_6H_7NHSbBr_4$, 52279-34-2; $(4-CH_3C_5H_4NH)_2SbBr_5$, 52279-35-3; $(2-ClC_5H_4NH)_2SbBr_5$, 52279-36-4; $(2-BrC_5H_4NH)_2SbBr_5$, 52279-37-5; $(3-BrC_5H_4NH)_2SbBr_5$, 52279-38-6; $(3-IC_5H_4NH)_2SbBr_5$, 52279-39-7; $(3-HO_2CC_5H_4NH)_2SbBr_5$, 52279-40-0; $(3,5-Cl_2C_5H_3NH)_2SbBr_5$, 52279-41-1; $[2,6-(CH_3)_2C_5H_3NH]_2Sb_2Br_9$, 52486-72-3; $[2,4,6-(CH_3)_3C_5H_2NH]_2Sb_2Br_9$, 52486-73-4; $(2-FC_5H_4NH)_2Sb_2Br_9$, 52486-74-5.

Supplementary Material Available. A listing of infrared frequencies in the region 1700-250 cm^{-1} will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2767.

(21) The 3-bromopyridinium crystals contain a B-centered unit cell (dimensions $a = 35.90$ (11), $b = 11.98$ (4), $c = 9.35$ (3) Å; $\beta = 92.2$ (2)°) which, according to Weissenberg photographs, is similar in shape and orientation to the primitive unit cell in the 3-iodopyridinium analog (dimensions given in Table I), indicating that there exists a subtle similarity in ionic packing for the two materials.

(22) The quolinium crystals contain a body-centered unit cell (dimensions $a = 13.45$ (4), $b = 14.04$ (4), $c = 7.44$ (2) Å; $\beta = 90.8$ (2)°) which, according to Weissenberg photographs, is similar in shape and orientation to the primitive unit cell in the isoquinolinium analog (dimensions given in Table I), indicating that there exists a subtle similarity in ionic packing for the two materials.

(11) See, for example: M. L. Hackert and R. A. Jacobson, *Acta Crystallogr., Sect. B*, 27, 1658 (1971); S. Koda, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jap.*, 44, 1597 (1971); R. E. DeSimone and G. D. Stucky, *Inorg. Chem.*, 10, 1808 (1971); R. C. Gearhart, T. B. Brill, W. A. Welsh, and R. H. Wood, *J. Chem. Soc., Dalton Trans.*, 359 (1973); S. L. Lawton, E. R. McAfee, J. E. Benson, and R. A. Jacobson, *Inorg. Chem.*, 12, 2939 (1973).

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(17) Monoclinic, space group $P2_1/c$, with lattice parameters $a = 12.91$, $b = 13.40$, $c = 7.63$ Å, and $\beta = 107.2^\circ$.¹⁸

(18) Lattice parameters correspond to those reported in ref 14 but transformed with the matrix $(\frac{1}{2}, 0, \frac{1}{2})/(0, \bar{1}, 0)/(0, 0, \bar{1})$.

(19) Monoclinic, space group $P2_1/c$, with lattice parameters $a = 13.65$, $b = 14.06$, $c = 8.03$ Å, and $\beta = 106.7^\circ$.¹⁸

(20) The structure of a sixth salt, $C_6NH_8SbI_4$, is isomorphous with the $C_6NH_8BiBr_4$ and $C_6NH_8BiI_4$ crystals, according to a preliminary study reported in ref 14.

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Atropisomerism in Aryl-Substituted Borazines¹

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There is much evidence^{2,3} to suggest that in the most stable conformation the aromatic rings of triaryl-substituted borazines are perpendicular to the plane of the borazine ring.

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

(2) E. F. Mooney, *Spectrochim. Acta*, 18, 1355 (1962), and papers quoted therein.

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