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Crystal Structure of Quinolinium Hexabromoantimonate(V) Tribromide, $(C_9H_7NH)_2Sb^VBr_9$

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Quinolinium hexabromoantimonate(V) tribromide, $(C_9H_7NH)_2Sb^VBr_9$, crystallizes as deep red plates in the monoclinic space group $P2_1/n$ (C_{2h}^5) with unit cell parameters $a = 7.518$ (4), $b = 11.316$ (10), $c = 16.351$ (2) Å, and $\beta = 97.41$ (2)°. The observed and calculated densities are 2.65 and 2.67 g/cm³, respectively, with $Z = 2$ formula weights per unit cell. Full-matrix least-squares refinement has led to a final value of the conventional discrepancy index (based on F) of 0.090 using three-dimensional X-ray diffraction counter data (2111 intensities). The structure consists of quinolinium, $Sb^VBr_6^-$, and Br_3^- ions, the packing of which is similar to that in the $(RH)_2Sb^VBr_9$ analogs with 2-methylpyridinium and 4-methylpyridinium cations. The slightly distorted octahedral $SbBr_6^-$ ion possesses crystallographic C_i symmetry with bond lengths ranging from 2.556 (3) to 2.581 (3) Å. The tribromide ion is also centrosymmetric with a bond length of 2.566 (3) Å. These two ions form nonlinear chains the backbones of which execute a zigzag configuration in which the anionic arrays $Br-Sb-Br$ and $Br-Br-Br$ are inclined 45.03 (6)° relative to each other. The bromine · · · bromine contacts along these chains, the shortest in the structure, are 3.607 (3) Å. Favorable orientation of the quinolinium cation allows N-H · · · Br hydrogen bonds to form with the $SbBr_6^-$ ions at an H · · · Br distance of 2.6 Å and making an N-H · · · Br angle of 176°; these moderately weak bonds are associated with the longest Sb-Br bonds.

Introduction

$R_xSb_yBr_z$ and $(RH)_xSb_yBr_z$ salts represent an area of current chemical interest because of the wide variety of complexes attainable in the solid state simply by varying the cation. Cations utilized in the syntheses of these salts whose structures have been determined include the following: the alkali series ammonium² and rubidium,³ the alkyl series tetramethylammonium,⁴ tetraethylammonium,⁵ and quinuclidinium,⁶ the aryl series pyridinium,^{7,8} 2-methylpyridinium,⁹ and 4-methylpyridinium.¹⁰ Anions which form have so far been limited to $Sb^{III}Br_6^{3-}$,^{2,3,6,8} $Sb^{III}_2Br_9^{3-}$,^{4,7} and $Sb^VBr_6^{2-}$,^{2,3,5,6,8-10} In some of these, however, bromide⁷ and tribromide^{9,10} ions as well as molecular bromine^{4,6} coexist, generating some rather usual solid-state structures. Curiously, of these three antimony anions, $Sb^{III}Br_6^{3-}$ has not yet been observed to occur alone but always occurs in association with the $Sb^VBr_6^-$ ion, so the color of this ion is not known. However, the complex containing $Sb^{III}_2Br_9^{3-}$ as the only anion (in the absence of molecular bromine) is light yellow.⁷ Those containing antimony in the pentavalent state are intensely colored, absorbing in the near-ultraviolet spectral region; in most cases, salts containing this ion appear black under reflected light.

One group of aryl salts, having the empirical formula $(RH)_2Sb^VBr_9$, consists of an equimolar mixture of $Sb^VBr_6^-$ and Br_3^- anions. Two of these, the 2-methylpyridinium and quinolinium analogs (referred to hereafter as 2-MPNA and

QNA, respectively) have been examined by diffuse reflectance spectroscopy.¹¹ Their spectra were found to be quite similar except for a displacement of the low-energy band(s) in QNA toward longer wavelengths. This relative displacement, or possible emergence of one or more additional bands, correlates with the color of the salt at the temperature of liquid nitrogen (-196°). At this temperature the 2-MPNA salt is orange,⁹⁻¹¹ whereas QNA exhibits no appreciable loss of coloration.^{10,11} Colors of others in this series have also been examined and tabulated,¹⁰ as expected, several display the intermediate colors red-orange and red. The transition temperatures at which all these salts begin to lose their intense coloration upon cooling have been measured¹⁰ and range from a high of *ca.* -20° for the salts which are orange at -196° to *ca.* -155° for that which is red at the same temperature. Three of these, *viz.*, 2-MPNA, 4-MPNA, and QNA, were subsequently selected for crystallographic study in an effort to relate differences in structure with differences in absorption. These three were chosen because they cover the full range of interest; at -196° 2-MPNA is orange, 4-MPNA is red, and QNA is black. More importantly, however, the tailing off of the absorption bands at room temperature for 2-MPNA and QNA differ by as much as 175 m μ ,¹¹ and it is precisely this difference which we hope to correlate with differences in structure. Details of the first two structures at room temperature have been published.^{9,10} We now wish to describe the third member, that of QNA, at the same temperature.

Experimental Section

Preparation. Crystalline $(C_9H_7NH)_2SbBr_9$, hereafter QNA, was prepared as described by Lawton and Jacobson.⁹ Crystals suitable for use in the X-ray investigation were obtained by recrystallization of the salt from concentrated hydrobromic acid (48%). The procedure involved first dissolving a small quantity of the compound in 4-5 ml of the acid at a temperature slightly below the boiling point of the solution and then allowing it to cool. Loss of bromine from the solution was prevented by continuously passing bromine vapor over the top of the beaker during all stages of dissolution and recrystallization. Upon cooling, deep red platelike crystals slowly formed.

Crystal Data. QNA, of formula weight 1101.3, is monoclinic with space group $P2_1/n$ (C_{2h}^5). The lattice parameters at 25° are $a =$

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7.518 (4), $b = 11.316$ (10), $c = 16.351$ (2) Å, $\beta = 97.41$ (2)°, and $V = 1391$ Å³; $d_{\text{obsd}} = 2.65$ g/cm³ (by flotation in a mixture of diiodomethane and methylene chloride) and $d_{\text{calcd}} = 2.67$ g/cm³ for $Z = 2$ formula weights per unit cell.

The preliminary crystal symmetry was determined from precession photographs which exhibited $2/m$ Laue symmetry with systematic extinctions ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with space group $P2_1/n$. The lattice parameters and associated errors (indicated as 2σ) were determined by a least-squares refinement¹² of 12 high-order reflections measured on a previously aligned Hilger-Watts four-circle diffractometer using a left-right, top-bottom beam-splitting technique.

Collection and Reduction of X-Ray Intensity Data. Complete three-dimensional X-ray diffraction data were taken at room temperature (approximately 25°) with zirconium-filtered molybdenum $K\alpha$ radiation from a platelike crystal of dimensions $0.32 \times 0.192 \times 0.096$ mm. The crystal was sealed in a 0.2-mm Lindemann glass capillary parallel with its longest dimension (a axis) and mounted on the diffractometer with a^* coincident with the ϕ axis. A fully automated Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to an SDS-910 computer in a real time mode was used for data collection. The stationary-crystal, stationary-counter measurement technique with a takeoff angle of 4.5° was employed to collect all data in the hkl and hkl octants within a 2θ sphere of 50°. The intensity of each reflection was derived from a 10-sec count measured at the peak maximum; background measurements were made on both sides of the peak. Three strong reflections, measured periodically as a check on electronic and crystal stability, showed essentially no variation. Approximately 100 reflections at various angular settings were also measured using step-scan techniques to construct an integrated intensity-peak height conversion curve. This curve was found to be dependent only on 2θ with step scan/peak height ratios ranging from 0.80 at low 2θ to 0.98 at large values of 2θ (26°).

The raw intensity of each reflection was corrected for background, Lorentz, polarization, and absorption effects. The transmission factors for the full set of three-dimensional data ranged from 0.27 to 0.46, based on a linear absorption coefficient of 142.08 cm⁻¹. Estimated standard deviations in the intensities were computed as described elsewhere.⁹ The estimated standard deviation in each structure factor was calculated by employing the method of finite difference.¹³ Using the arbitrary criterion $F_o < 3\sigma(F_o)$, 2111 independent reflections were considered as observed.

Solution and Refinement of the Structure

Solution of the structure was achieved by standard heavy-atom techniques. By virtue of the presence of only two $(C_6H_7NH)_2^+$ $SbBr_6^-$ groups per unit cell in a space group of order 4, the antimony atoms were assumed to lie on centers of symmetry. Accordingly, an electron density map computed with antimony at the origin revealed an octahedron of bromine atoms surrounding antimony (*viz.*, $Sb^V(Br_6^-)$) and a linear Br_3^- group centered at the inversion point $1/2, 1/2, 0$. A subsequent series of three-dimensional difference ($F_o - F_c$) electron density syntheses phased by these atoms, interspersed with several iterations of least-squares refinements, revealed the location of all ten nonhydrogen atoms in the cation.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$, with $|F_o|$ and $|F_c|$ being the observed and calculated structure amplitudes, respectively, and w is the weight defined as $1/\sigma^2(F_o)$. Atomic scattering factors for neutral atoms tabulated by Hanson, et al.,¹⁴ were used. Real and imaginary dispersion corrections¹⁵ for Sb and Br were applied to the calculated structure factors.¹⁶

The atomic positions and isotropic thermal parameters of antimony and bromine, along with the scale factor, were refined first,

(12) In addition to various local programs for the IBM 360 computer, local modifications of the following programs were used in the solution and refinement of the structure: Williams' LCR-2 lattice constant refinement program; Wehe, Busing, and Levy's ABCOR absorption correction program; Guggenberger's FOUR Fourier program; Doedens and Ibers' NUCLS crystallographic least-squares group refinement program; Busing and Levy's ORFFE function and error program; Johnson's ORTEP thermal ellipsoid plotting program.

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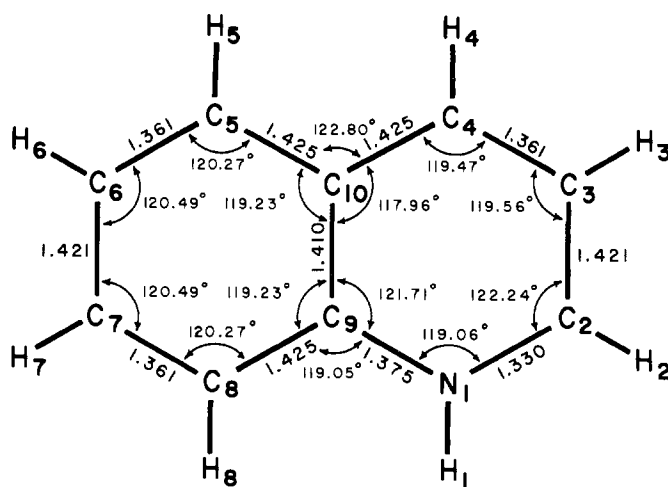


Figure 1. Idealized dimensions of the quinolinium cation.

resulting in a discrepancy index of $R_1 = \Sigma |\Delta| / \Sigma |F_o| = 0.21$. Contribution of the cation (excluding hydrogen) to the calculated structure factors was then included in the refinement, reducing R_1 to 0.127 and the weighted index to $R_2 = [\Sigma w\Delta^2 / \Sigma w|F_o|^2]^{1/2} = 0.149$. Additional cycles with anisotropic thermal parameters assigned to Sb and Br reduced R_1 and R_2 still further to 0.0914 and 0.1078.

Attempts were made at this stage to identify the nitrogen position in the cation by analyses of Fourier peak heights and inspection of the derived bond lengths and angles. Both procedures proved futile, however, owing to random errors in the intensity data, to libration of the cation, and to the relatively small scattering power of each light atom in a heavy-atom structure. A meaningful clue to nitrogen ordering was subsequently achieved by carrying out a series of least-squares refinements in which nitrogen was allowed to occupy, independently, each of four possible positions. Of the four positions one, hereafter N(1), was indicated as the most probable by producing an R_1 index of 0.0910 compared with 0.0914 for the other three positions. This particular site also appeared to be the most plausible of the four in terms of cation-anion interactions. Of all $H \cdots Br$ distances less than 3.2 Å an $H(1) \cdots Br(2)$ distance of ca. 2.6 Å was found to be the shortest in the structure. This distance, as well as the corresponding $N(1)-H(1) \cdots Br(2)$ angle of ca. 176°, provided convincing evidence for the presence of hydrogen bonding, albeit of only moderate strength, but bonding which is more likely to occur with nitrogen as a donor atom than with carbon.

Least-squares refinement was resumed, with the appropriate scattering factor now assigned to the nitrogen site and with anisotropic thermal parameters assigned to all ten nonhydrogen atoms in the cation. Analysis of the weights was also performed at this stage since maximum accuracy can only be achieved by the least-squares method when the weights assigned to the observations are valid. The requirement is the $w\Delta^2$ should be a constant function of $|F_o|$ and of $(\sin \theta)/\lambda$.¹⁷ Accordingly, analyses of these weighting schemes indicated that the strong reflections, as well as those at low $(\sin \theta)/\lambda$, were somewhat overweighted and the weights were subsequently adjusted. The condition that the strong low-angle data were systematically too weak was not satisfied, suggesting that secondary extinction was not a major problem. Subsequent iterations of refinement produced convergence to $R_1 = 0.087$ and $R_2 = 0.106$.

A second refinement was carried out in which the cation was geometrically constrained as a rigid group with C_8 symmetry using the least-squares group refinement procedure described by Ibers, et al.¹⁸ The variable parameters for the cation included an individual isotropic thermal parameter and three orientation angles. In keeping with the general observation that hydrogen thermal parameter B derived from X-ray diffraction studies tends to be too small, the isotopic B parameter of each hydrogen atom in this study was fixed throughout the refinement at $B = 5.0$ Å². Idealized dimensions of this group, summarized in Figure 1, were derived from a weighted average of

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Table I. Final Positional, Thermal and Group Parameters for $(C_9H_7NH)_2SbBr_6^a$

Anions										
Atom	x^b	y	z	β_{11}^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B, \text{\AA}^2$
Sb	0* ^e	0*	0*	1421 (23)	642 (10)	281 (5)	-30 (10)	40 (7)	-37 (5)	3.15
Br(1)	0.02800 (18)	-0.05780 (12)	0.15222 (8)	2272 (30)	813 (12)	299 (5)	-68 (14)	8 (9)	36 (6)	4.58
Br(2)	0.27463 (17)	0.13560 (13)	0.03191 (8)	1895 (29)	1034 (14)	402 (6)	-495 (14)	102 (10)	-107 (7)	4.43
Br(3)	-0.20214 (17)	0.17032 (12)	0.03130 (8)	1966 (28)	851 (13)	426 (6)	298 (14)	67 (10)	-72 (6)	4.16
Br(4)	0.5*	0.5*	0*	1976 (40)	863 (18)	501 (10)	-86 (19)	72 (15)	-192 (10)	4.72
Br(5)	0.54342 (21)	0.38675 (15)	0.13646 (10)	2506 (36)	1173 (17)	547 (8)	-118 (18)	-24 (13)	-48 (9)	5.85
Cation Group										
	x_c^f	y_c	z_c	δ	ϵ	η				
	0.4901 (7)	-0.0778 (5)	0.2659 (4)	2.401 (9)	-2.206 (4)	-2.088 (8)				
Derived Positional and Refined Thermal Parameters for Group Atoms										
Atom	x^g	y	z	$B, \text{\AA}^2$	Atom	x^g	y	z	$B, \text{\AA}^2$	
N(1)	0.397 (2)	-0.2209 (8)	0.2937 (6)	6.6 (3)	H(1)	0.346 (3)	-0.256 (1)	0.338 (1)	5.0	
C(2)	0.415 (4)	-0.2829 (8)	0.2262 (8)	7.9 (4)	H(2)	0.375 (5)	-0.366 (1)	0.223 (1)	5.0	
C(3)	0.490 (3)	-0.2336 (8)	0.1584 (6)	6.7 (4)	H(3)	0.501 (4)	-0.282 (1)	0.110 (1)	5.0	
C(4)	0.546 (2)	-0.1191 (7)	0.1619 (4)	5.5 (3)	H(4)	0.598 (2)	-0.084 (1)	0.116 (1)	5.0	
C(5)	0.583 (2)	0.0698 (7)	0.2416 (7)	6.4 (3)	H(5)	0.636 (3)	0.109 (1)	0.197 (1)	5.0	
C(6)	0.563 (4)	0.1311 (8)	0.3114 (8)	7.7 (4)	H(6)	0.605 (5)	0.214 (1)	0.317 (1)	5.0	
C(7)	0.487 (3)	0.0762 (8)	0.3769 (7)	7.5 (4)	H(7)	0.473 (4)	0.121 (1)	0.427 (1)	5.0	
C(8)	0.433 (2)	-0.0386 (8)	0.3707 (4)	7.1 (4)	H(8)	0.380 (2)	-0.076 (1)	0.416 (1)	5.0	
C(9)	0.452 (1)	-0.1050 (5)	0.2983 (4)	4.8 (3)						
C(10)	0.528 (1)	-0.0505 (5)	0.2334 (4)	4.9 (3)						

^a Numbers in parentheses in all tables and in the text are estimated standard deviations occurring in the least significant digit of the parameter. ^b Coordinates are based on positions $x, y, z; \bar{x}, \bar{y}, \bar{z}; 1/2 - x, 1/2 + y, 1/2 - z; 1/2 + x, 1/2 - y, 1/2 + z$. ^c The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β 's and their estimated standard deviations have been multiplied by 10^5 . ^d B 's are isotropic thermal parameters equivalent to the anisotropic tensors: W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959). ^e An asterisk denotes a parameter fixed by symmetry. ^f x_c, y_c, z_c are the fractional coordinates of the cation center, taken as the midpoint of the C(9)-C(10) bond. The angles δ, ϵ, η (in radians) are those described in ref 18. The origin of the internal system was taken as the group center with a_1' passing through the midpoints of bonds C(2)-C(3) and C(6)-C(7) and a_2' along the C(9)-C(10) bond. ^g The positional parameters and their estimated standard deviations for the group atoms were derived from the six group coordinates.

bond lengths and angles in previously determined structures¹⁹ and by utilization of known and theoretical molecular dimensions of naphthalene²⁰ and pyridine.²¹ Several iterations of least-squares refinement, using the original weights, resulted in reliability values of $R_1 = 0.091$ and $R_2 = 0.109$. A weighting scheme analysis, performed as previously described, revealed the same trend as before and was modified accordingly. After four additional cycles parameter shifts reduced to 1.1% of their standard deviations, indicating the refinement had converged. The final values of R_1 and R_2 were 0.090 and 0.108, respectively, and the final error of fit based on the 65 variables was 1.81. A final difference Fourier synthesis was featureless, indicating that all scattering matter had been accounted for.

Comparison of the results of the two refinements revealed that the parameters of the nongroup atoms are relatively insensitive to the geometrical restrictions imposed on the cation. In fact, shifts in the positional parameters were less than 1.5 standard deviations in every case but one and shifts in the thermal parameters were one standard deviation or less in all cases. Because it is our feeling that the results of the group refinement are to be preferred on physical grounds, in accord with views expressed by Eisenberg and Ibers,^{18b} we present in Table I the final positional, thermal, and group parameters derived from it, along with the associated standard deviations as estimated from the inverse matrix.²² Root-mean-square thermal displacements along the directions of the principal axes for those atoms refined anisotropically are given in Table II.

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

Table II. Root-Mean-Square Thermal Amplitudes of Vibration (\AA) of Atoms in $(C_9H_7NH)_2SbBr_6$

Atom	Min	Med	Max
Sb	0.186 (1)	0.204 (4)	0.209 (4)
Br(1)	0.196 (2)	0.228 (2)	0.260 (2)
Br(2)	0.191 (2)	0.232 (2)	0.289 (2)
Br(3)	0.204 (2)	0.233 (2)	0.269 (2)
Br(4)	0.205 (2)	0.239 (2)	0.283 (2)
Br(5)	0.244 (2)	0.280 (3)	0.290 (2)

Table III. Dimensions of the Anions in $(C_9H_7NH)_2SbBr_6$

Atoms	Dist, \AA	Atoms	Angle, deg
Sb-Br(1)	2.556 (1)	Br(1)-Sb-Br(2)	89.54 (5)
Sb-Br(2)	2.571 (2)	Br(1)-Sb-Br(3)	88.53 (5)
Sb-Br(3)	2.547 (2)	Br(2)-Sb-Br(3)	89.54 (6)
Br(4)-Br(5)	2.557 (2)		

Description of the Structure

Crystals of QNA consist of ordered monovalent quinolinium cations and centrosymmetric $Sb^V Br_6^-$ and Br_3^- anions, with the antimony anion displaying a slightly distorted octahedral configuration. The ionic packing is shown in Figure 2.

Dimensions of the anions and associated standard deviations are documented in Table III. The standard deviations were based on the final variance-covariance matrix containing the estimated uncertainties in lattice parameters. Analysis of the thermal motion²³ of the atoms in the $SbBr_6^-$ anion indicates that their motion can be approximated reasonably well to that of a rigid body. This motion has a significant effect on the bond lengths and the corrected values are given in Table IV. In making this correction the breadth parameter,

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Table IV. Comparison of Structurally Equivalent Distances (Å) and Angles (deg) in 2-MPNA, 4-MPNA, and QNA^a

Identification (Figure 2 and Table V of ref 10)	2-MPNA ^b	4-MPNA ^b	QNA ^c	
			Distances	
<i>a</i> (Sb-Br)	2.565 (3)	2.568 (3)	Sb-Br(1)	2.561 (2)
<i>b</i> (Sb-Br)	2.547 (3)	2.561 (2)	Sb-Br(2)	2.581 (3)
<i>c</i> (Sb-Br)	2.548 (3)	2.561 (2)	Sb-Br(3)	2.556 (3)
<i>d</i> (Br···Br)	2.554 (3)	2.561 (4)	Br(4)-Br(5)	2.566 (3)
<i>e</i> (Br···Br)	3.473 (3)	3.444 (4)	Br(1)···Br(5A)	3.607 (3)
<i>g</i> (Br···Br)	3.749 (3)	3.695 (4)	Br(2)···Br(4)	4.506 (5)
<i>h</i> (Br···Br)	3.709 (3)	3.695 (4)	Br(3B)···Br(4)	4.339 (4)
<i>i</i> (Br···Br)	3.717 (3)	3.857 (4)	Br(2)···Br(5)	3.759 (4)
<i>j</i> (Br···Br)	3.819 (3)	3.857 (4)	Br(3B)···Br(5)	3.661 (4)
<i>k</i> (Br···Br)	4.069 (3)	3.814 (4)	Br(2)···Br(3B)	3.941 (4)
Av Sb-Br ^d	2.553 (9)	2.563 (4)	Av Sb-Br	2.565 (13)
			Angles	
<i>ab</i> (Br-Sb-Br)	89.72 (5)	89.49 (6)	Br(1)-Sb-Br(2)	89.54 (5)
<i>ac</i> (Br-Sb-Br)	89.53 (6)	89.49 (6)	Br(1)-Sb-Br(3)	88.53 (5)
<i>bc</i> (Br-Sb-Br)	89.27 (5)	90.15 (8)	Br(2)-Sb-Br(3)	89.54 (6)
<i>ae</i> (Sb-Br···Br)	166.77 (8)	174.16 (9)	Sb-Br(1)···Br(5A)	166.04 (10)
<i>ed</i> (Br···Br-Sb)	164.88 (11)	171.63 (10)	Br(1)···Br(5A)-Br(4A)	136.63 (10)
<i>ad</i> (Br-[Sb,Br]-Br)	4.44 (6)	2.53 (8)	Br(1)-[Sb,Br(4A)]-Br(5)	15.61 (6)
			Br(1)-[Sb,Br(4A)]-Br(5C)	45.03 (6)

^a Distances and angles include a correction for libration (SbBr₆⁻) and thermal "riding" motion (Br₃⁻) (see text). The estimated standard deviations include an arbitrary uncertainty factor of 1.4 for this correction. ^b Taken from ref 10. ^c Key to symmetry operations in this table and Figure 3: (A) $1/2 - x, -1/2 + y, 1/2 - z$; (B) $1 + x, y, z$; (C) $-1/2 + x, 1/2 - y, 1/2 + z$; (D) $1/2 + x, 1/2 - y, 1/2 + z$. ^d The indicated value denotes the weighted average of all six Sb-Br bonds in the ion (corrected for librational effects) with the associated rms deviation given in parentheses, using formulas given in footnote *a* of Table VI in ref 8.

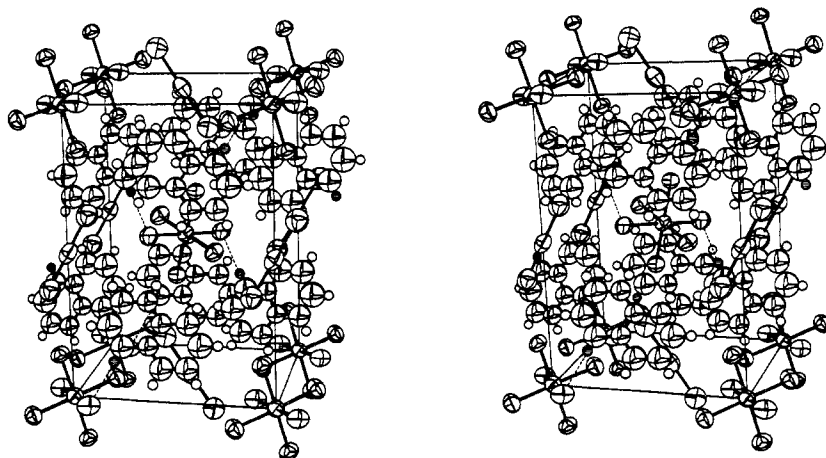


Figure 2. A stereographic view of the packing of ions in crystals of QNA. View depicts the contents of one unit cell, with the origin in the rear left with *a* directed toward the viewer, *b* horizontal, and *c* vertical. Ellipsoidal boundaries of all nonhydrogen atoms are at the 80% probability level. Acidic N-H···Br hydrogen bonds, displaying H···Br contacts of 2.61 Å, are denoted by dashed lines.

q^2 , was assigned a value of 0.12 Å². The fit of the rigid-body model to the thermal parameters can be gauged from the rms ΔU_{ij} of 0.0007 Å for U_{ij} not fixed by symmetry, where ΔU_{ij} is the difference between the individual atomic displacement tensors U_{ij} and those calculated from the rigid-body parameters. In every case but four individual ΔU_{ij} 's were 2.5 standard deviations or less, so the rigid-body approximation appears to be within the precision of the data. Increases in the lengths of the bonds display a slightly wider range (0.005–0.010 Å) than was observed for 2-MPNA (0.009 Å for all bonds) and 4-MPNA (0.007–0.008 Å), though the average (0.008 Å) is relatively unchanged. The average Sb-Br bond length for the ion, 2.565 (13) Å (Table IV), is in good agreement with values reported in other structures containing this ion.^{2,3,5,8–10} Correction of the Br-Br bond in the tribromide ion was based on the "riding" model in which the terminal atom was assumed to ride on the center atom. This bond, 2.566 (3) Å in length (Table IV), is comparable with values reported for centrosymmetric ions in other struc-

tures.^{9,10,24,25} Its increase in length (0.009 Å) is fully consistent with the increase found in 2-MPNA (0.011 Å) and 4-MPNA (0.010 Å). These corrected values will be used throughout our discussion which follows.

Despite an increase in the size of the cation, QNA adopts a structure remarkably similar to those of 2-MPNA and 4-MPNA. Interatomic distances and angles in the three analogs are compared for structurally equivalent bond lengths and angles (based on their environment) in Table IV. Those for the MPNA salts are identified by letters depicted in Figure 2 of ref 10; those for QNA are identified in Figure 3 of the present paper.

It is enlightening to examine first the anions themselves since these are responsible for the major components of the visible absorption spectrum. Of all three salts, none contains

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(25) O. Andresen and Chr. Romming, *Acta Chem. Scand.*, **16**, 1882 (1962).

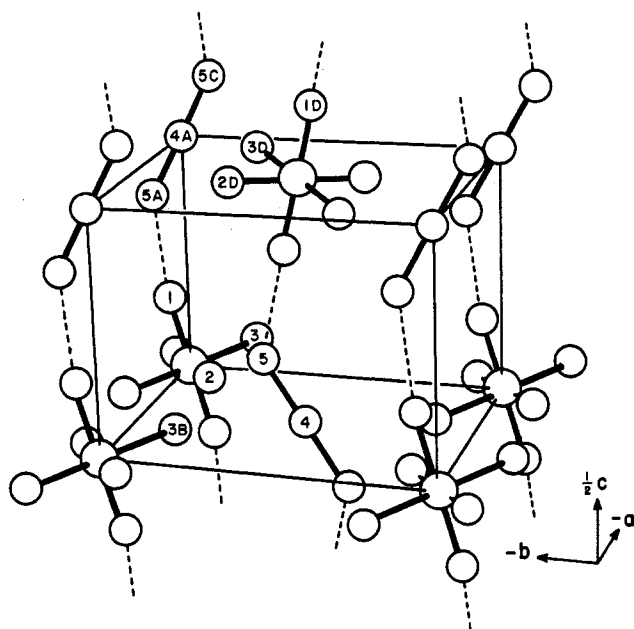


Figure 3. Crystal packing of SbBr_6^- and Br_3^- anions in QNA. Dashed lines connect bromine atoms along the $\text{SbBr}_6^- \cdots \text{Br}_3^-$ chains involving the $\text{Br} \cdots \text{Br}$ separations of 3.607 (3) Å. Other distances are documented in Table IV.

SbBr_6^- ions displaying full O_h symmetry, though the extent of deformation is small. Angular deviations from orthogonality do not exceed 1.5° and the bond lengths do not exceed 0.018 Å from their mean. Curiously, a trend has emerged, albeit small, in which there appears to be a gradual weakening of the bonds in both the SbBr_6^- and the Br_3^- anions in going from 2-MPNA to 4-MPNA to QNA. The maximum extent of the increase in bond lengths for both ions (between 2-MPNA and QNA) is 0.012 (3) Å, or four standard deviations.

In the MPNA series nearly linear $\text{SbBr}_6^- \cdots \text{Br}_3^-$ chains are sandwiched between planar cations. Bromine \cdots bromine contacts within these chains are 3.473 (3) Å in 2-MPNA and 3.444 (4) Å in 4-MPNA (Table IV). The Br-Sb-Br and Br-Br-Br bond arrays along the chains display relative twists of 4.44 (6) and 2.53 (8) $^\circ$, respectively, so that for all intensive purposes their axes may be considered parallel. In QNA similar chains also exist, as shown in Figure 3, are also "sandwiched" by planar cations, as shown in Figure 4, and also exhibit moderately short, though slightly greater, bromine \cdots bromine separations of 3.607 (13) Å. The Br-Sb-Br and Br-Br-Br bond arrays comprising the backbone of each chain are not collinear, however, but rather adopt a zigzag configuration in which the anionic axes are inclined 45.03 (4) $^\circ$ relative to each other. Only within a given level of z (*viz.*, $z = 0$ or $1/2$) do the Br-Sb-Br and Br-Br-Br axes assume the more nearly parallel orientations found in the MPNA salts; within these layers the relative inclinations are 15.61 (6) $^\circ$. Curiously, one angle is found to be somewhat invariant to the geometry of the aromatic cation and hence packing. This is the Sb-Br \cdots Br angle within the $\text{SbBr}_6^- \cdots \text{Br}_3^-$ chain itself. In 2-MPNA, 4-MPNA, and QNA this angle assumes values of 166.77 (8), 174.16 (9), and 166.04 (10) $^\circ$, respectively (Table IV). Such an orientation allows the p_z orbitals emanating from the axial bromine atoms in the SbBr_6^- ions to be directed toward the terminal bromine atoms in the tribromide ion. Figures 3 and 4 provide two views of this. It is unclear whether any real significance should be attached to this unless evidence is found which unequivocally supports the proposition that weak orbital interactions of two

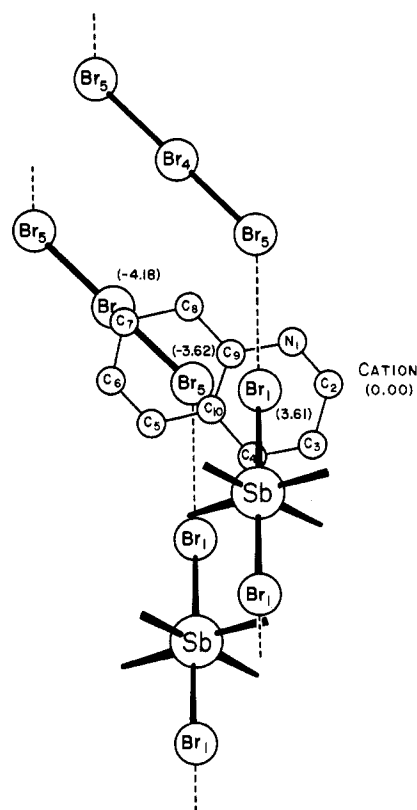


Figure 4. View normal to the plane of the quinolinium cation, depicting nearest neighbors of bromine atoms with π electrons of the aromatic ring. A number within parentheses refers to the perpendicular distance of the atom from that plane. The closest nonbonded contacts between nearest atoms shown in this figure are the following: Br(1) \cdots N(1), 3.84 Å; Br(1) \cdots C(9), 3.77 Å; Br(1) \cdots C(10), 3.82 Å; Br(5) \cdots C(5), 3.83 Å; Br(5) \cdots C(9), 3.80 Å; Br(5) \cdots C(10), 3.69 Å (all ± 0.01 Å).

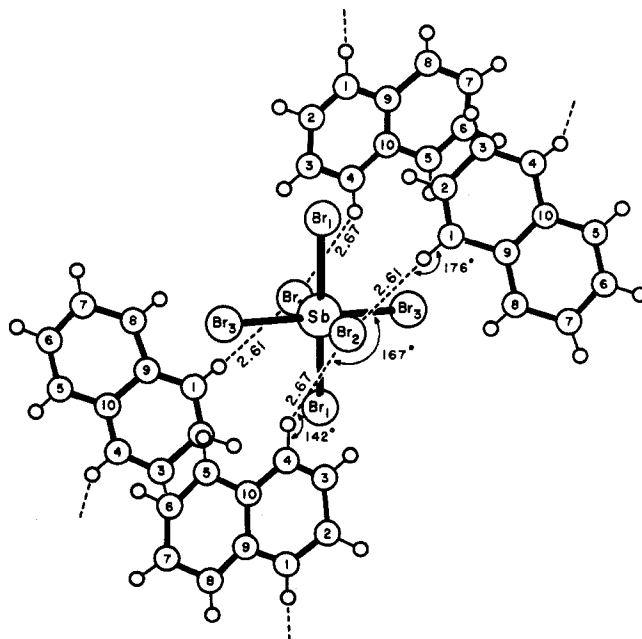


Figure 5. The short N-H \cdots Br and C-H \cdots Br contacts in QNA between the cation and Br(2) atoms in the SbBr_6^- anion. These contacts make H(1) \cdots Br(2)-Sb and H(4) \cdots Br(2)-Sb angles of 95.0 and 92.0° , respectively.

negatively charged ligands may contribute to an alignment of the ions at bromine \cdots bromine separations ranging from 3.4 to 3.6 Å. Indeed, these distances are appreciably shorter

than the expected van der Waals contact of 3.90 Å using Pauling's radius of 1.95 Å²⁶ for bromine or the 3.70-Å sum using Bondi's 1.85-Å radius.²⁷ But in accord with views previously expressed,¹⁰ this is insufficient evidence that the short Br···Br contacts are the result of weak donor-acceptor interactions. Until empirical or theoretical evidence can be developed to support such an interpretation, a more plausible consideration for the short anionic contacts and the angles along the chain is crystal packing forces.

The anionic environment of the tribromide ion is illustrated in Figure 3. As in the MPNA salts, these ions make contact with six surrounding SbBr₆⁻ ions, two along the axis at the short distance of 3.607 (3) Å and four approximately perpendicular to the axis at distances ranging from 3.661 (4) to 4.506 (5) Å. The shortest of these involve the terminal bromine atoms of the Br₃⁻ ion, in direct contrast with the MPNA salts in which the Sb-Br bonds are directed more toward the centers of the Br-Br bonds.

There is no structural evidence in QNA that the π electrons of the quinolinium ring participate in any donor-acceptor interactions of the type found in crystals of benzene with bromine²⁸ and *p*-xylene with carbon tetrabromide.²⁹ Figure 4 illustrates the arrangement of alternating layers of cations and the SbBr₆⁻··Br₃⁻ chains, a packing sequence duplicated in both 2-MPNA and 4-MPNA. Perpendicular distances between the cation and neighboring bromine atoms of these chains, 3.61 and 3.62 Å, are just slightly shorter than those in 2-MPNA (3.65 and 3.75 Å) and 4-MPNA (3.72 Å). All are equal to or greater than the expected van der Waals sum of 3.62 Å using Bondi's radius of 1.85 Å for bromine and 1.77 Å for aromatic carbon atoms.²⁷

(26) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

(27) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(28) O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, **12**, 1146 (1958).

(29) F. J. Strieter and D. H. Templeton, *J. Chem. Phys.*, **37**, 161 (1962).

In contrast with 2-MPNA and 4-MPNA in which the shortest H···Br distances, involving acidic hydrogen, are only 2.9 Å, a particularly favorable orientation of the quinolinium cation in QNA allows a considerably shorter distance of 2.6 Å to occur, as shown in Figure 5. This distance, as well as an N-H···Br angle of 176°, suggests the presence of an intermolecular N-H···Br hydrogen bond, there being two such interactions per SbBr₆⁻ anion. This contact is *ca.* 0.5 Å shorter than the sum of the appropriate van der Waals radii (3.15 Å²⁶ or 3.05 Å²⁷). By comparison, three other pyridinium complexes are also known to exhibit moderately strong N⁺-H···Br-(M) hydrogen bonds with H···Br separations ranging from 2.3 to 2.6 Å.^{8,30,31} As Figure 5 further illustrates, a pair of C-H···Br contacts at 2.7 Å also occurs with the SbBr₆⁻ anion. However, since C-H groups are highly improbable proton donors, crystal packing forces are likely responsible for these particular contacts. Finally, we note in passing that since the short N-H···Br contacts involve only the Br(2) atoms of the SbBr₆⁻ ion, it is not surprising to find that the Sb-Br(2) bonds have become the longest of the three independent Sb-Br bonds in the ion.

Registry No. QNA, 39394-71-3.

Supplementary Material Available. A listing of structure factor amplitudes 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, 20× reduction, negatives) containing all of 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-73-2939.

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(31) R. E. DeSimone and G. D. Stucky, *Inorg. Chem.*, **10**, 1808 (1971).

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Structure and Spectroscopic Properties of μ -(*o*-Tetrafluorophenylene)-diiron Octacarbonyl, C₆F₄Fe₂(CO)₈

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The known compound, μ -(*o*-tetrafluorophenylene)-diiron octacarbonyl, C₆F₄Fe₂(CO)₈, prepared by a rather unusual route, has been identified and characterized by mass, infrared, and ¹⁹F nmr spectroscopic techniques. The crystal and molecular structure has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes in the monoclinic space group *P2₁/n* with unit cell dimensions *a* = 6.739 (1), *b* = 26.966 (5), and *c* = 8.859 (1) Å, β = 93.78 (2)°, and *Z* = 4. The structure, solved by heavy-atom techniques, has been refined by full-matrix least-squares methods to a conventional *R* factor of 0.029 for the 1942 significant, independent intensities measured. Mo K α radiation was used. Solution of the structure has shown that C₆F₄Fe₂(CO)₈ is, in fact, the *o*-phenylene adduct originally proposed. The Fe-Fe distance is 2.797 (1) Å.

Introduction

In 1970 Roe and Massey¹ prepared the novel iron complex C₆F₄Fe₂(CO)₈ from the reaction of triiron dodecacarbonyl with tetrafluorobenzene (generated *in situ*). Based on in-

(1) D. M. Roe and A. G. Massey, *J. Organometal. Chem.*, **23**, 547 (1970).

frared and mass spectral data the four-membered cyclic structure I was proposed for this compound.¹ An alternative structure that is still consistent with the experimental data is II, in which tetrafluorobenzene is bonded to the two iron atoms in a manner similar to the dicobalt-acetylene linkage in the well-characterized (C₂H₂)Co₂(CO)₆ compounds.^{2,3}