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Crystal Structure of 4-Methylpyridinium Nonabromoantimonate(V), $(4\text{-}C_6H_7NH)_2Sb^VBr_9$[1]

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4-Methylpyridinium nonabromoantimonate(V), $(C_6H_7NH)_2Sb^VBr_9$, crystallizes as deep red acicular crystals in the monoclinic space group $C2/m$ (C_{2h}^3) with unit cell parameters $a = 18.39$ (1), $b = 7.440$ (4), $c = 9.84$ (1) Å, and $\beta = 113.14$ (6)°. The observed and calculated densities are 2.64 and 2.760 (7) g/cm^3, respectively. The structure was refined by least-squares methods to a conventional discrepancy index of 0.050 using three-dimensional X-ray diffraction counter data. The structure is comprised of 4-methylpyridinium, $Sb^VBr_6^-$, and Br_3^- ions, the packing of which is similar to that in 2-methylpyridinium nonabromoantimonate(V). The $SbBr_6^-$ ion possesses crystallographic C_{2h} symmetry and has an average bond length of 2.563 (4) Å. The tribromide ion is centrosymmetric with a bond length of 2.561 (4) Å. These two ions form nearly linear chains displaying bromine · · · bromine contacts of 3.444 (4) Å. The shortest hydrogen · · · bromine separation, 2.9 (1) Å, involves the *N*-H proton of the cation with the $SbBr_6^-$ anion.

Introduction

The use of various cations, notably ammonium,[4] rubidium,[5] tetraethylammonium,[6] pyridinium,[7] 2-methylpyridinium,[8] and quinuclidinium,[9] in the synthesis of $R_xSb_yBr_z$ salts (where R = monovalent cations) has produced a variety of complexes containing $Sb^{III}Br_6^{3-}$, $Sb^VBr_6^-$, and Br_3^- anions as well as interstitial molecular bromine. At room temperature these materials range in color from deep red to black, a consequence, in part, of absorption by the $Sb^VBr_6^-$ anion. Below room temperature, those containing both trivalent and pentavalent antimony remain intensely colored, owing to the additional presence of intervalent electron-transfer absorption bands. Those having composition $(RH^+)_2 \cdot (Sb^VBr_6^-)(Br_3^-)$, however, become variably colored at −196° (the temperature of liquid nitrogen[10]). Upon cooling, their intense colors disappear, first changing from black to violet (reference here being to reflected light[11]), then progressively to red, red-orange, and orange, depending upon RH^+ and hence structure. This progression of color change is consistent with a sharpening of absorption bands in the near-ultraviolet region whose edges overlap the blue end of the visible spectrum. As is shown by Table I for a series of these salts, the higher the temperature at which the color change starts to occur for a given material the more orange it becomes at −196°. The different colors at any given temperature depend primarily on how far into the visible region the absorption bands extend before tailing off. This has been demonstrated for the 2-methylpyridinium and quinolinium salts by diffuse reflectance spectroscopy;[12] spectra of these two materials at room temperature reveal a decrease in absorption to near zero at 675 and 850 mμ, respectively.

The origin of these differences in the absorption spectra is not yet fully understood.[13] Variation in the energies of weak charge-transfer transitions, induced by close approach of the anions at moderately short Br · · · Br distances (*ca.* 3.5 Å), is one consideration. Perturbation of the energy levels within the anions themselves induced by bond length variations or, in the case of $SbBr_6^-$, deformation from O_h symmetry is another. Generally, the greater the perturbation, the greater the shift of an absorption band toward longer wavelengths (a red shift). Accordingly, those salts which exhibit the greatest absorption in the visible region (and subsequently remain the most deeply colored, *viz.*, red or black, at −196°) might then be expected to contain anions which undergo the greatest perturbations of their energy levels.

Before a rigorous theoretical interpretation of the observed spectral shifts can be made, a knowledge of several of their crystal structures is required, both at room temperature and at low temperatures. With this in mind, we undertook a structural investigation of the 4-methylpyridinium nonabromoantimonate(V) salt, $(4\text{-}C_6H_7NH)_2Sb^VBr_9$ (4-MPNA), at room temperature. This compound, which is red at −196°, complements the isomorphous 2-methylpyridinium salt (2-MPNA) previously reported to attain the orange color at −196°.[8,10,12] A third member, quinolinium nonabromoantimonate(V), exhibits no appreciable color change at

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(4) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 5, 743 (1966).

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(9) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 10, 709, 2813 (1971).

(10) In three earlier papers[7,8,12] reference was made to the temperature of liquid nitrogen as being −173 to −174°. This appears to be incorrect. The accepted literature value is −195.8°.

(11) Thin crystals appear deep red when light is transmitted through them. Reflected light gives the appearance of black crystals.

(12) M. L. Hackert, S. L. Lawton, and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, 75, 97 (1968).

(13) The three compounds $[(C_2H_5)_4N^+][Sb^VBr_6^-]$, $[(CH_3)_3NH^+]_2[Br_3^-][Br^-]$, and $[C_6H_5N_2^+][Br_3^-]$ at room temperature are dark red-brown,[6] red-orange,[14] and yellow-orange,[15] respectively, indicating that the $Sb^VBr_6^-$ and Br_3^- ions each have at least one absorption band in the near-ultraviolet region. Absorption spectra of the ions provide the relative locations of these bands. The diffuse reflectance spectrum of the $SbBr_6^-$ ion in the tetraethylammonium salt has a very high absorption band at λ_{max} between 375 and 420 mμ.[12] The spectrum of the tribromide ion in both acetonitrile and in ethylene dichloride has an intense absorption band at λ_{max} between 269 and 273 mμ and a second band of considerably lower intensity at 390 mμ.[16] In view of a coincidence of the bands for both ions at *ca.* 390 mμ, considerable masking will occur in absorption spectra of salts containing *both* ions, such as of the current $(RH)_2Sb^VBr_9$ series.

(14) C. Romers and E. W. M. Keulemans, *Proc., Kon. Ned. Akad. Wetensch., Ser. B*, 61, 345 (1958).

(15) O. Andresen and C. Romming, *Acta Chem. Scand.*, 16, 1882 (1962).

(16) A. I. Popov and R. F. Swensen, *J. Amer. Chem. Soc.*, 77, 3724 (1955).

Table I. Reflectance Data for a Representative Selection of $(RH)_2Sb^VBr_9$ Salts

RH^+	Reflected color at −196°	Black ⇌ violet transition temp, °C	Wavelength at which absorption in the visible region approaches zero,[a] mμ
2,4,6-Trimethylpyridinium	Orange[b]	−20	na[c]
2-Methylpyridinium	Orange	−40	675
3-Methylpyridinium	Orange	−40	na
2-Bromopyridinium	Red-orange	−85	na
2-Chloropyridinium	Red-orange	−95	na
2,4-Dimethylpyridinium	Red-orange	−95	na
4-Methylpyridinium	Red	−155[d]	na
Quinolinium	Black	<−196	850

[a] Room temperature data; from ref 12. [b] Revised from that reported in ref 12. [c] Not available. [d] Revised from that reported in ref 8.

−196° and its structure at room temperature is currently under investigation.[17]

Experimental Section

Low-Temperature Measurements. The eight $(RH)_2Sb^VBr_9$ samples presented in Table I were synthesized as outlined in ref 8 and 12. Isolation of the 2,4-dimethylpyridinium, 2,4,6-trimethylpyridinium, and quinolinium salts was achieved only when the mother liquor was *saturated* with bromine, a necessary step to prevent formation of a black salt having composition other than the desired $(RH)_2SbBr_9$ species. (It is noteworthy that the black salts of the 2,4-dimethylpyridinium and 2,4,6-trimethylpyridinium cations which crystallize from a solution *not* saturated with bromine do not exhibit the color changes noted in Table I but remain black down to −196°, a property previously observed for salts containing mixed $Sb^VBr_6^-$ and $Sb^{III}Br_6^{3-}$ ions.[4,5,7,9,12])

A Leeds and Northrup millivolt potentiometer, Model 8690, was used to measure the temperature at which each salt in Table I ceased being black (reflected color[11]) at temperatures below 25°. The reference junction temperature of the potentiometer was set for 0°, adjusted by use of an ice–water bath. The measurement procedure involved placing a small quantity of the sample at the base of a test tube into which was placed an iron *vs.* constantan thermocouple. The sample was cooled to −195.8° by lowering the base of the test tube into liquid nitrogen or to −78.5°, as in the case of the 2,4,6-trimethylpyridinium, 2-methylpyridinium, and 3-methylpyridinium salts, in a Dry Ice–acetone bath. The test tube was then removed from the bath and the orange or red color so obtained was monitored visually while the temperature of the solid was allowed to increase slowly. The instant when no perceptible violet coloration remained and the solid once again appeared black, the millivolt reading on the potentiometer was recorded. This procedure was repeated three or four times for each sample and the resultant readings were averaged and converted to degrees. The temperatures noted in Table I are given to the nearest 5° and are considered reliable to within ±15°. The alternate procedure of recording the temperature as the sample cooled, rather than warmed, was not employed owing to the fast nonuniform cooling rate which occurs when the sample is immersed in the coolant.

Preparation of $(4\text{-}C_6H_7NH)_2SbBr_9$. 4-Methylpyridinium nonabromoantimonate(V) was prepared by the method of Lawton, *et al.*,[8,12] using 2.1 g of 4-methylpyridine, 4.0 g of antimony tribromide, and 0.88 g of bromine in 12 ml of concentrated hydrobromic acid (48%). The material crystallized as deep red needles.[11]

Crystal Data. Weissenberg and precession X-ray photographs exhibited $2/m$ Laue symmetry with systematic extinctions $h + k = 2n + 1$ for hkl reflections, consistent with space groups $C2$, Cm, and $C2/m$. The centrosymmetric space group was subsequently confirmed by the successful refinement of the derived structure. The lattice parameters and their estimated standard deviations were obtained by a least-squares refinement[18] of 40 independent reflection angles measured in the angular region $34° < 2\theta < 52°$ on a Siemens diffractometer using Mo Kα radiation (λ 0.7107 Å) and a takeoff angle of 1°. Each measurement consisted of determining the 2θ value at half-peak-height on both sides of the peak in both the positive and negative 2θ regions and averaging. The lattice parameters at 23° so obtained were as follows: $a = 18.39$ (1), $b = 7.440$ (4), $c = 9.84$ (1) Å, $\beta = 113.14$ (6)°, and $V = 1238$ Å^3; indicated errors are 2σ. The observed density is 2.64 g/cm^3, measured by the flotation method using a mixture of 1,2-dibromoethane and diiodomethane; the density calculated for $Z = 2$ and a formula weight of 1029.2 was 2.760 (7) g/cm^3.

Collection and Reduction of X-Ray Intensity Data. Complete three-dimensional X-ray diffraction intensity data were taken at room temperature (23 ± 3°) with zirconium-filtered molybdenum Kα radiation from an acicular crystal 0.72 mm long and of cross section 0.11 × 0.20 mm. The crystal was mounted in a 0.5-mm Lindemann glass capillary parallel with its longest dimension (b axis) and mounted on the diffractometer with b^* coincident with the ϕ axis. The half-widths in degrees θ of a number of narrow-source, open-counter 2θ scans ranged from 0.07° (a^* and c^* vectors) to 0.25° (b^* vector), indicating that the crystal mosaicity was small, albeit somewhat anisotropic.[19] A General Electric quarter-circle Eulerian cradle mounted on a Siemens diffractometer equipped with a Siemens scintillation detector and pulse height discriminator was used to collect the intensity data with the moving-crystal, moving-counter measurement technique (θ, 2θ coupling) and a 3.5° takeoff angle. The crystal–source and crystal–counter distances were 17 and 18.5 cm, respectively. The receiving aperture size selected to minimize extraneous background was 5.0 mm wide × 6.0 mm high. The counter angle, 2θ, was scanned over 2° at a speed of 2°/min. Background counts of 12 sec were taken at each end of the 2θ scan. A total of 1531 independent reflections in the range $2\theta \leqslant 55°$ was collected. Three standard reflections were measured periodically as a check on electronic and crystal stability and no significant decrease in intensities was observed.

The raw intensity of each reflection was corrected for background, Lorentz, polarization, and absorption effects. Transmission factors were computed by the program ACACA,[20] based on an ellipsoidal model with minor and major diameters 0.1187 and 0.2010 mm, respectively; these diameters constituted a modification of those obtained by optical measurement and were derived by utilizing a method previously described.[7] The transmission factors for the full set of three-dimensional data ranged from 0.055 to 0.201, based on a linear absorption coefficient of 165.06 cm^{-1}. Estimated standard deviations in the intensities were computed as described elsewhere, using a value of 0.04 for the ignorance factor p.[21] The estimated standard deviation in each structure factor was calculated by employing the finite-difference method of Williams and Rundle.[22] Using the arbitrary criterion $F_O < 3\sigma(F_O)$, all but 1058[23] independent reflections were rejected as being statistically insignificant.

Solution and Refinement of the Structure. The structure was solved by standard heavy-atom techniques. A three-dimensional Patterson function yielded a consistent set of trial coordinates for

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(17) S. L. Lawton, E. R. McAfee, J. E. Benson, and R. A. Jacobson, Mobil Research and Development Corp. and Iowa State University, to be submitted for publication.

(18) D. E. Williams, "LCR-2, a Fortran Lattice Constant Refinement Program," Report IS-1052, Ames Laboratory, Iowa State University, Ames, Iowa, 1964.

(19) In the region examined, $2\theta < 11°$, the 2θ-scan and ω-scan techniques yield comparable results: T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

(20) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 122, 24 (1965).

(21) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(22) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

(23) Two of these, *viz.*, 001 and 200, occurred at $2\theta < 5°$ and could not be accurately measured; they were subsequently excluded from the refinement.

antimony and the bromine atoms.[24] A Fourier synthesis phased by these atoms revealed the location of the cation.

The structure was refined by using a full-matrix least-squares procedure. The function minimized was $\Sigma w(\Delta F)^2$, where $\Delta F = |F_o| - |F_c|$, 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.*,[25] were used. Real and imaginary dispersion corrections of Templeton[26] for Sb and Br were applied to the calculated structure factors.[27] The pyridinium ring, including hydrogen atoms, was geometrically constrained as a rigid body to C_{2v} symmetry,[28] using the least-squares group refinement procedure described by Ibers, *et al.*[30] The variable parameters for the ring included an individual isotropic thermal parameter for each nonhydrogen atom, the coordinates of the group center, and three orientation angles. The positional coordinates of the methyl carbon C(7) were allowed to refine independently of the ring because of the anticipated foreshortening of the C(4)–C(7) bond resulting from the C(7) anisotropy of thermal motion. In the absence of evidence supporting ordered methyl hydrogen atoms, these hydrogens were treated as disordered half-atoms. The isotropic temperature factors for all hydrogen atoms were fixed throughout the refinement at B = 4.0 Å^2.

Six cycles of least-squares refinement resulted in reliability values of $R_1 = \Sigma|\Delta F|/|F_o| = 0.072$ and $R_2 = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2} = 0.073$. Six additional cycles with anisotropic thermal parameters assigned to antimony, bromine, and the methyl carbon reduced R_1 and R_2 to 0.051 and 0.035, respectively.

Examination of the data revealed that some of the strong low-angle data were too weak, indicating that they might be suffering from secondary extinction. An isotropic correction of the form described by Zachariasen[31] was therefore applied. The least-squares refinement proceeded smoothly and after several cycles the parameter shifts reduced to 50% of their standard deviations.

Maximum accuracy is obtained by the least-squares method only when the weights assigned to the observations are valid. The requirement is that $w(\Delta F)^2$ should be a constant function of $|F_o|$ and of $(\sin\theta)/\lambda$.[32] Accordingly, analyses of these weighting schemes indicated that the strong reflections were somewhat overweighted, so the weights were modified by an appropriate expression to remove this dependency. Also, three reflections (600, $\bar{1}11$, $\bar{8}22$) satisfying the condition $|\Delta F| > 3\sigma(F_o)$ were given zero weight. After four additional interations of refinement, parameter shifts reduced to 1.2% of their standard deviations, indicating the refinement had converged. The final values of R_1 and R_2 were 0.050 and 0.031, respectively, and the final value of the extinction coefficient was 3.50 (13) × 10^{-7}. The final error of fit based on the 46 variables was 1.22. A final difference Fourier synthesis was featureless, indicating that all scattering matter had been correctly accommodated.

The final positional, thermal, and group parameters derived from the last cycle of least-squares refinement are presented in Table II, along with the associated standard deviations in these parameters as estimated from the inverse matrix.[33] Root-mean-

Table II. Final Positional, Thermal, and Group Parameters for $(4\text{-}C_6H_7NH)_2SbBr_9$[a]

Positional Parameters

Atom	x	y	z	Iso equiv B,[c] Å^2
Sb	0*[b]	0*	0*	2.57
Br(1)	0.14895 (6)	0*	0.15622 (15)	3.70
Br(2)	0.02051 (5)	0.24295 (15)	−0.16475 (10)	3.66
Br(3)	0.5*	0*	0.5*	3.41
Br(4)	0.35298 (7)	0*	0.33413 (17)	4.64
C(7)	0.1052 (7)	0*	0.5589 (16)	5.3

Thermal Parameters

Atom	β_{11}[d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	201 (4)	1198 (27)	744 (16)	0*	94 (6)	0*
Br(1)	218 (4)	1967 (36)	1078 (20)	0*	65 (8)	0*
Br(2)	342 (3)	1543 (20)	1103 (12)	−24 (8)	234 (5)	262 (16)
Br(3)	335 (7)	1564 (45)	924 (26)	0*	237 (11)	0*
Br(4)	301 (5)	2602 (43)	1314 (23)	0*	177 (9)	0*
C(7)	24 (5)	336 (48)	137 (23)	0*	3 (8)	0*

Group Parameters for the Cation

x_c[e]	y_c	z_c	δ	ϵ	η
0.2715 (4)	0*	0.7530 (7)	90*	165.2 (3)	90*

Positional and Thermal Parameters for Group Atoms

Atom	x[f]	y	z	B, Å^2
N(1)	0.3514 (7)	0*	0.8479 (16)	4.8 (3)
C(2)	0.2941 (8)	0*	0.8999 (18)	4.4 (3)
C(3)	0.2136 (9)	0*	0.8101 (19)	6.0 (4)
C(4)	0.1910 (8)	0*	0.6573 (17)	3.8 (3)
C(5)	0.2498 (8)	0*	0.6013 (17)	5.1 (3)
C(6)	0.3286 (9)	0*	0.7007 (19)	4.6 (3)
H(1)	0.4051	0*	0.9117	
H(2)	0.3096	0*	1.0073	
H(3)	0.1739	0*	0.8534	
H(5)	0.2361	0*	0.4944	
H(6)	0.3697	0*	0.6607	
H(7a)	0.0864	−0.1242	0.5374	
H(7b)	0.0975	0.0620	0.4664	
H(7c)	0.0754	0.0620	0.6084	
H(7a′)	0.0864	0.1242	0.5374	
H(7b′)	0.0975	−0.0620	0.4664	
H(7c′)	0.0754	−0.0620	0.6084	

[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] An asterisk denotes a parameter fixed by symmetry. [c] B's are isotropic thermal parameters equivalent to the anisotropic tensors: W. C. Hamilton, *Acta Crystallogr.*, 12, 609 (1959). [d] β's × 10^5 for Sb and Br; β's × 10^4 for C. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [e] x_c, y_c, z_c are the fractional coordinates of the ring center, taken as the midpoint of C(2), C(3), C(5), and C(6). The angles δ, ϵ, η (in degrees) are those described in ref 30. The origin of the internal system was taken at the group center with a_3' normal to the plane and a_2' bisecting the C–N–C angle. [f] The positional coordinates and their estimated standard deviations for the ring atoms N(1) through C(6) were derived from the six group coordinates.

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(24) In addition to various local programs for the CDC 1604B and IBM 360/67 computers, local modifications of the following programs were used in the solution and refinement of the structure: 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.

(25) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(26) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol III, Kynoch Press, Birmingham, England, 1962, pp 215, 216.

(27) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(28) The ring was assigned the following dimensions (based in part on those of Bak, *et al.*, for pyridine[29]): C–N, 1.340 Å; C–C, 1.394 Å; N–H, 0.94 Å; C–H, 0.98 Å; C(6)–N(1)–C(2), 117°; N(1)–C(2)–C(3), 123° 47′; C(2)–C(3)–C(4), 118° 28′; C(3)–C(4)–C(5), 118° 30′. The pyridinium ring was constrained as a rigid group owing primarily to the small scattering power of each constituent atom (only 1.3%) relative to the total electron density. This electronic contribution was considered to be too small to justify refinement of the three positional coordinates of each atom, particularly in the presence of the heavy scatterers Sb and Br. Furthermore, since the cation · · · anion contacts were not found to be appreciably less than normal van der Waals distances, there was no reason to expect induced perturbations of the ring geometry and bond lengths to occur from those found in normal pyridine.

(29) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, 2, 361 (1958).

(30) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

(31) W. H. Zachariasen, *Acta Crystallogr.*, 16, 1139 (1963); 23, 558 (1967); *Acta Crystallogr., Sect. A*, 24, 212 (1968).

(32) D. W. J. Cruickshank and D. E. Pilling in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Roberts, and J. C. Speakman, Eds., Pergamon Press, New York, N. Y., 1961.

(33) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, 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-73-277.

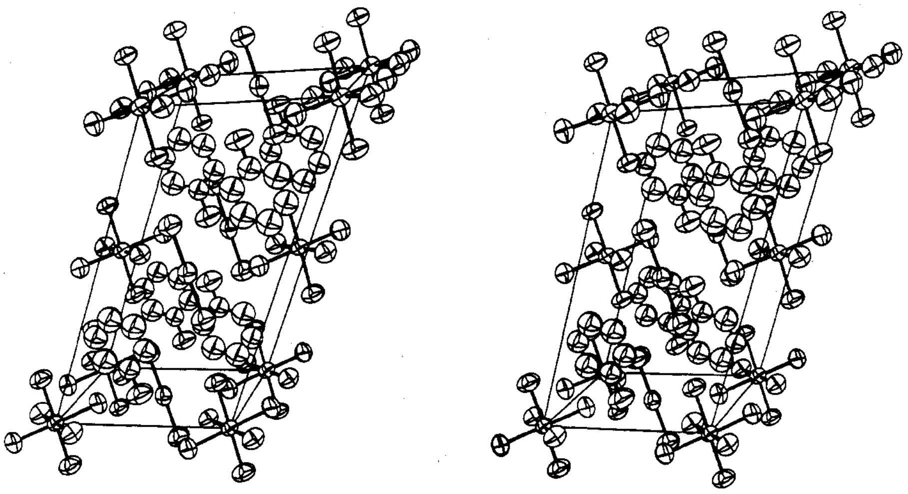

Figure 1. A stereographic view of the packing of ions in crystals of $(4\text{-}C_6H_7NH)_2SbBr_9$. View depicts the contents of one unit cell, with the origin in the front lower right with *a* vertical and *c* horizontal. For clarity, hydrogen atoms are not shown. Ellipsoidal boundaries of all atoms are at the 90% probability level.

Table III. Final Root-Mean-Square Thermal Amplitudes of Vibration (Å) of Atoms in $(4\text{-}C_6H_7NH)_2SbBr_9$

Atom	Min	Med	Max
Sb	0.163 (2)	0.183 (1)	0.194 (2)
Br(1)	0.170 (2)	0.235 (3)	0.238 (2)
Br(2)	0.185 (2)	0.221 (1)	0.236 (2)
Br(3)	0.192 (3)	0.209 (3)	0.220 (2)
Br(4)	0.207 (2)	0.246 (2)	0.270 (2)
C(7)	0.18 (2)	0.27 (2)	0.31 (2)

Table IV. Dimensions of the Ions in $(4\text{-}C_6H_7NH)_2SbBr_9$[a,b]

Atoms	Dist, Å	Bond notation in Fig 2	Atoms	Angle, deg
Sb-Br(1)	2.561 (2)	*a*	Br(1)-Sb-Br(2)	89.49 (6)
Sb-Br(2)	2.553 (2)	*b, c*	Br(2)-Sb-Br(2a)[c]	90.15 (8)
Br(3)-Br(4)	2.551 (2)	*d*	C(7)-C(4)-C(3)	119.4 (14)
C(4)-C(7)	1.49 (3)		C(7)-C(4)-C(5)	122.1 (13)

[a] Uncorrected for thermal or librational effects. [b] Dimensions of the pyridinium ring appear in footnote 28. [c] Br(2a) occurs at $x, \bar{y}, z$.

Table V. Comparison of Selected Distances (Å) and Angles (deg) in 2-MPNA and 4-MPNA[a]

Identification[b] (Fig 2)	2-MPNA	4-MPNA
a[c]	2.565 (3)	2.568 (3)
b[c]	2.547 (3)	2.561 (2)
c[c]	2.548 (3)	2.561 (2)
d	2.554 (3)	2.561 (4)
e	3.473 (3)	3.444 (4)
f	0.770 (3)	0.343 (4)
g	3.749 (3)	3.695 (4)
h	3.709 (3)	3.695 (4)
i	3.717 (3)	3.857 (4)
j	3.819 (3)	3.857 (4)
k	4.069 (3)	3.814 (4)
ae	166.77 (8)	174.16 (9)
ed	164.88 (11)	171.63 (10)
ad[d]	4.44 (6)	2.53 (8)
Av Sb-Br[e]	2.553 (9)	2.563 (4)

[a] Distances and angles include a correction for libration ($SbBr_6^-$) and thermal motion (Br_3^-) (see text). The estimated standard deviations include an arbitrary uncertainty factor of 1.4 for this correction. [b] One letter designates a bond shown in Figure 2; two letters designate an angle between the indicated bonds. [c] The atom *types* in the $SbBr_6^-$ ion are as follows (given in order of 2-MPNA and 4-MPNA for each bond): bond *a* is Sb with Br(1) and Br(1), respectively; bond *b* is Sb with Br(2) and Br(2), respectively; bond *c* is Sb with Br(3) and Br(2), respectively. For example, bond *a* in 2-MPNA is of the type Sb-Br(1). Bonds *b* and *c* in 4-MPNA are related by $x, \bar{y}, z$. [d] *ad* designates the angle of inclination between the *axial* Sb-Br bond in the $SbBr_6^-$ ion and the Br_3^- axis, as discussed in the text. [e] 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 (see Table VI, footnote *a*, of ref 7).

square thermal displacements along the directions of the principal axes for those atoms refined anisotropically are given in Table III.

Description of the Structure

Crystals of 4-MPNA consist of monovalent 4-methylpyridinium cations, slightly distorted $Sb^VBr_6^-$ anions, and centrosymmetric Br_3^- anions, arranged as shown in Figure 1. The ionic packing is very similar to that in 2-MPNA in which alternating layers of parallel $\cdots SbBr_6^- \cdots Br_3^- \cdots$ chains and cations coexist.[8]

Dimensions of the ions and associated standard deviations are documented in Table IV. The standard deviations were based on the final variance-covariance matrix containing the estimated uncertainties in lattice parameters. Analysis of the thermal motion[34] of the atoms in the $SbBr_6^-$ anion indicates that their motion can well be approximated to that of a rigid body. This motion has a significant effect on the bond lengths and the corrected values are given in Table V. In making this correction, the breadth parameter, q^2, was assigned a value of 0.12 Å^2. The fit of the rigid-body model to the thermal parameters can be gauged from the rms ΔU_{ij} of 0.0003 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 one individual ΔU_{ij}'s were less than 1.5 times their estimated standard deviation, so the rigid-body approximation appears to be within the precision of the data. The average Sb-Br bond length for the ion, 2.563 (4) Å (Table V), is in good agreement with the average length, 2.55 (2) Å, reported in other structures.[4-8] 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, 2.561 (4) Å in length (Table V), is comparable with the average, 2.54 Å, reported for centrosymmetric ions in other structures.[8,14,15] These

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(34) D. W. J. Cruickshank, *Acta Crystallogr.*, 9, 754, 757 (1956); 14, 896 (1961); C. L. Coulter, P. K. Gantzel, and K. N. Trueblood, ACA Computer Program 232 (UCLAT01), Department of Chemistry, University of California, Los Angeles, Calif., 1961.

Table VI. Summary of Short Bromine · · · Bromine Contacts (<3.7 Å) between Ions and Molecules in Known Structures

Compd	Interacting species[a]	Br · · · Br contact, Å	Ref
	Ionic · · · Ionic		
PBr_5	$PBr_4^+ \cdots Br^-$	3.06 (2), 3.12 (2), 3.19 (2)	*c*
PBr_7	$PBr_4^+ \cdots Br_3^-$	3.14, 3.26, 3.36	*d*
$SrBr_2$	$Br^- \cdots Br^-$	3.573 (2), 3.624 (5), 3.678 (6)	*e*
$(2\text{-}C_6H_7NH)_2SbBr_9$	$Sb^VBr_6^- \cdots Br_3^-$	3.473 (3)[b]	*f*
$(4\text{-}C_6H_7NH)_2SbBr_9$	$Sb^VBr_6^- \cdots Br_3^-$	3.444 (4)[b]	*g*
$(C_5H_5NH)_6Sb_4Br_{24}$	$Sb^VBr_6^- \cdots Sb^VBr_6^-$	3.220 (10)[b]	*h*
	$Sb^VBr_6^- \cdots Sb^{III}Br_6^{3-}$	3.473 (10)[b]	*h*
$(C_2H_5)_4NSbBr_6$	$Sb^VBr_6^- \cdots Sb^VBr_6^-$	3.584 (5)	*i*
$Cs_2Re_2Br_8$	$Re_2Br_8^{2-} \cdots Re_2Br_8^{2-}$	3.66 (1)	*j*
$Cs_2Re_3Br_{11}$	$Re_3Br_{11}^{2-} \cdots Re_3Br_{11}^{2-}$	3.46, 3.52	*k*
	Ionic · · · Molecular		
$(C_7H_{13}NH)_4Sb_2Br_{16}$	$Sb^{III,V}Br_6 \cdots Br_2$	3.11 (2)	*l*
$[(CH_3)_4N]_3Sb_2Br_{11}$	$Sb^{III}{}_2Br_9^{3-} \cdots Br_2$	2.89 (1)	*m*
	Molecular · · · Molecular		
Br_2		3.30, 3.30	*n*
$C_4H_6S_2Br_2$		3.49	*o*
$C_7H_3Br_5$		3.62, 3.64	*p*
$C_{10}H_5NBr_2$		3.59	*q*
$C_{10}H_{16}OBr_2$		3.52 (1)	*r*
$C_{14}H_6O_2Br_2$		3.68	*s*
$C_{14}H_7O_2Br$		3.66	*t*
$C_{14}H_{14}SeBr_2$		3.58 (4)	*u*
$C_{18}H_{22}O_2Br_2$		3.62	*v*
$C_{19}H_{12}N_2Br_2$		3.66	*w*
$C_{19}H_{15}Br$		3.35	*x*

[a] Indicated only for contacts involving ionic species. [b] Distances reflect a correction in the bond lengths of the ions for thermal or librational effects. [c] W. Gabes and K. Olie, *Acta Crystallogr., Sect. B*, **26**, 443 (1970). [d] G. L. Breneman and R. D. Willett, *Acta Crystallogr.*, **23**, 467 (1967). [e] J. G. Smeggil and H. A. Eick, *Inorg. Chem.*, **10**, 1458 (1971). [f] See ref 8. [g] This study. [h] See ref 7. [i] See ref 6. [j] F. A. Cotton, B. G. DeBoer, and M. Jeremic, *Inorg. Chem.*, 9, 2143 (1970). [k] M. Elder and B. R. Penfold, *ibid.*, **5**, 1763 (1966). [l] See ref 9. [m] C. R. Hubbard and R. A. Jacobson, *Inorg. Chem.*, **11**, 2247 (1972). [n] B. Vonnegut and B. E. Warren, *J. Amer. Chem. Soc.*, **58**, 2459 (1936). [o] H. T. Kalff and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **85**, 198 (1966). [p] W. R. Krigbaum and G. C. Wildman, *Acta Crystallogr., Sect. B*, **27**, 2353 (1971). [q] A. W. Hanson, *Acta Crystallogr.*, **14**, 124 (1961). [r] J. A. Wunderlich and W. N. Lipscomb, *Tetrahedron*, **11**, 219 (1960). [s] L. A. Chetkina and G. A. Gol'der, *Sov. Phys.–Crystallogr.*, **12**, 349 (1967). [t] N. L. Klimasenko, G. A. Gol'der, and G. S. Zhdanov, *ibid.*, **14**, 207 (1969). [u] J. D. McCullough and R. E. Marsh, *Acta Crystallogr.*, 3, 41 (1950). [v] V. Cody, F. DeJarnette, W. Daux, and D. A. Norton, *Acta Crystallogr., Sect. B*, **27**, (1971). [w] J. Van Thuijl and C. Romers, *Acta Crystallogr.*, **20**, 899 (1966). [x] C. Stora, *Bull. Soc. Chim. Fr.*, 1059 (1953).

corrected values will be used throughout the discussion which follows.

A structural feature characteristic of a number of the $R_xSb_yBr_z$ salts investigated so far is the presence of nearly linear chains of hexabromoantimonate ions displaying bromine · · · bromine contacts which are shorter than the sum of the van der Waals radii of the bromine atoms. A summary of these distances is presented in Table VI. They range from 3.220 (10) Å in the pyridinium compound $(C_5H_5NH)_6Sb_4Br_{24}$ to 3.584 (5) Å in the tetraethylammonium compound $(C_2H_5)_4NSbBr_6$. These values are appreciably shorter than the expected van der Waals contact of 3.90 Å using Pauling's radius of 1.95 Å from bromine.[35] However, they are only slightly shorter than the van der Waals sum of 3.70 Å using Bondi's corrected radius of 1.85 Å for bromine.[36] As is shown by Table VI, short Br · · · Br contacts are not unique among the antimony bromides since they are also observed in a variety of other compounds.

In the MPNA series $\cdots Sb^VBr_6^- \cdots Br_3^- \cdots$ chains are sandwiched between planar cations. Bromine · · · bromine contacts within these chains are 3.473 (3) Å in 2-MPNA and 3.444 (4) Å in 4-MPNA (Table V). Comparatively speaking, this chain is more linear in 4-MPNA than in 2-MPNA with lateral displacements of the anions being only 0.34 Å in the former compared with 0.77 Å[37] in the latter. This displacement is illustrated in Figures 2a and 3. The Br–Sb–Br and Br–Br–Br bond arrays along the chain are also more nearly parallel in 4-MPNA, displaying a relative twist of 2.53° compared with 4.44° in 2-MPNA.

The anionic environment of the tribromide ion is illustrated in Figure 2b. These ions make contact with six surrounding $SbBr_6^-$ ions, two along the axis at the short distances of *ca.* 3.5 Å and four approximately perpendicular to the axis at longer distances of 3.7–3.9 Å. In like manner, each $SbBr_6^-$ ion is also surrounded by six Br_3^- ions. Those (bond *a*) making the short contact (*e*) may be considered as "axial bonds" in the sixfold coordination of bromine around antimony(V); those (bonds *b* and *c*) making the longer contacts (*g*–*j*) perpendicular to the Br_3^- ions may be considered as the "equatorial bonds." Inspection of the packing diagrams (Figures 1 and 2b) reveals that the four equatorial Sb–Br bonds are directed more or less toward the centers of the Br–Br bonds rather than toward the center of the ion itself.

Curiously, the axial Sb–Br bonds in both 2-MPNA and 4-

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

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

(37) The value 0.77 Å is the distance between antimony in $SbBr_6^-$ and the vertex bromine atom in Br_3^- *within* the least-squares plane constructed through the $SbBr_6^-$ *equatorial* bromine atoms, as shown in Figure 3. Alternately, the vertex bromine atom in Br_3^- may be projected onto a least-squares plane defined by *axial* bromine atoms of $SbBr_6^-$ (specifically Br(4) projected onto the plane defined by atoms Br(1a), Br(1b), Br(1c), and Br(1d), using the atom identification given in Figure 4 of ref 8); the length of this projection is 1.00 Å, the value cited in Figure 4 of ref 7.

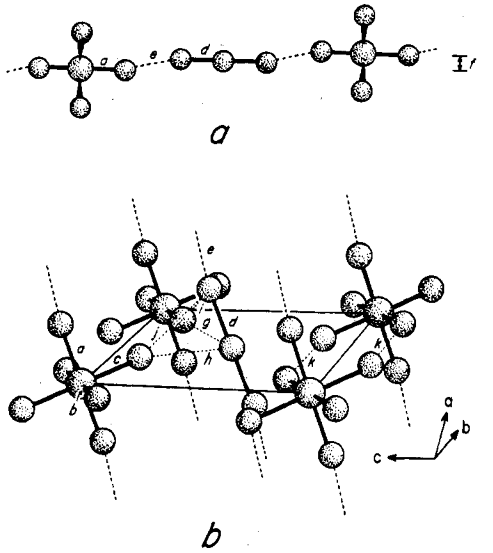

Figure 2. Anion · · · anion van der Waals contacts in crystals of 2-MPNA and 4-MPNA: (a) view of the nearly linear · · · $Sb^VBr_6^-$ · · · Br_3^- · · · chain in the [010] crystal plane of the C-centered cells; (b) view of the environment of a Br_3^- ion in the [100] crystal plane of the C-centered cells. Values for the distances and angles, denoted by letters, are given in Table V. The distance *f* corresponds to the perpendicular displacement of the anionic centers from strict linearity.

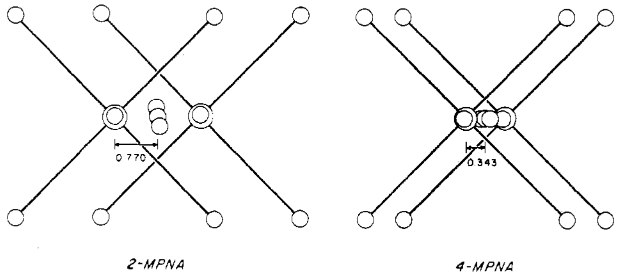

Figure 3. View down the · · · $SbBr_6^-$ · · · Br_3^- · · · chain in 2-MPNA and 4-MPNA projected onto a plane defined by the four "equatorial" bonds of the $SbBr_6^-$ ion. Lateral displacements of the anionic centers from strict linearity are denoted by the distances (Å) shown (also denoted by *f* in Figure 2).

MPNA are longer, by 0.018 (3) and 0.007 (3) Å, respectively, than the equatorial bonds. While a weakening of these bonds along the · · · $SbBr_6^-$ · · · Br_3^- · · · chains displaying the short Br · · · Br contacts appears attractive in accounting for possible donor-acceptor interactions between the ions (of the type proposed for solid Br_2 [38]), *no such weakening* is evident in the nearly linear chains · · · $Sb^VBr_6^-$ · · · $Sb^VBr_6^-$ · · · (displaying a Br · · · Br separation of 3.22 Å) and · · · $Sb^VBr_6^-$ · · · $Sb^{III}Br_6^{3-}$ · · · (displaying a Br · · · Br separation of 3.47 Å) found in $(C_5H_5NH)_6Sb_4Br_{24}$.[7] In fact, the axial Sb-Br bonds along these two chains are among the *shortest* in the three independent anions. It is evident that, in the absence of suitable spectroscopic data, none of these structural parameters—namely, short bromine · · · bromine contacts and lengthening of Sb-Br bonds—can be considered *sufficient* evidence for the unequivocal existence of weak donor-acceptor bonds.

There is also no structural evidence that the π electrons of the pyridinium ring participate in any donor-acceptor interactions of the type found in crystals of benzene with bromine[39] and *p*-xylene with carbon tetrabromide.[40] Figure 4 shows how the $SbBr_6^-$ · · · Br_3^- chains are sandwiched between the planar cations. The perpendicular distance between the cation and the chain is 3.72 Å. The closest nonbonded contact between a ring atom and a bromine atom is nitrogen with Br(1), also 3.72 Å. This distance is slightly longer 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.[36]

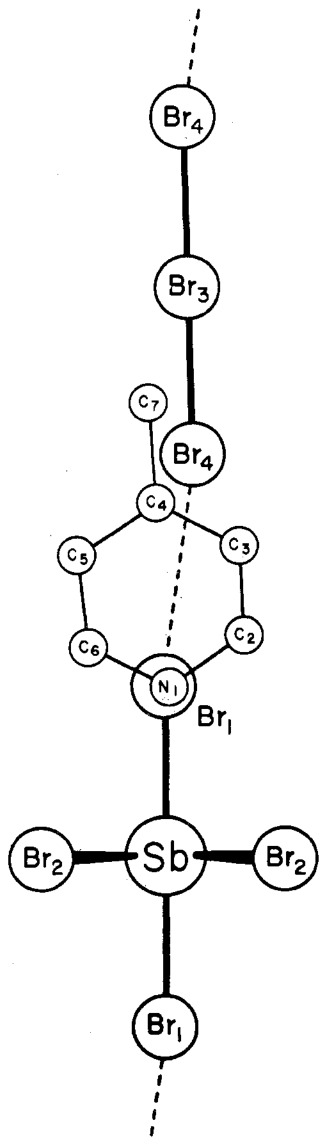

Figure 4. Projection of the cation onto the · · · $SbBr_6^-$ · · · Br_3^- · · · chain in 4-MPNA. The cation · · · chain separation, equivalent to *b*/2, is 3.72 Å. Other distances are as follows: N(1) · · · Br(1), 3.72 (3) Å; C(4) · · · Br(4), 3.81 (3) Å, C(7) · · · Br(4), 3.86 (3) Å. This figure may be compared directly with Figure 6 of ref 8 for 2-MPNA.

In both 2-MPNA and 4-MPNA the shortest H · · · Br distances involve the *N*-H proton of the cation. In 4-MPNA this proton is directed toward the center of a rectangle of four bromine atoms formed by two adjacent $SbBr_6^-$ anions arranged edge-to-edge parallel with the unit cell *b* axis and separated by a Br · · · Br distance of 3.814 (4) Å (distance *k* in Figure 2). Two of the H · · · Br separations are 2.9 (1) Å;[41] the other two are longer, occurring at 3.1 (1) Å. The N-H · · · Br angle involving the shorter distance is 123 (4)°.

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(38) H. A. Bent, *Chem. Rev.*, **68**, 587 (1968).

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

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

In 2-MPNA the *N*-H proton is directed toward the center of a face of the $SbBr_6^-$ octahedron. Of the three possible H · · · Br contacts, the shortest, 2.9 (1) Å, also involves an equatorial bromine atom; this N-H · · · Br angle is 154 (4)°. A slightly shorter distance, 2.8 (1) Å, is also observed in 2-MPNA and involves a ring *C*-H with a terminal bromine atom of the tribromide ion; the C-H · · · Br angle is 134 (4)°. These H · · · Br contacts are marginally shorter than the sum of the appropriate van der Waals radii (3.15 Å[35] or 3.05 Å[36]), indicative of very weak interactions. By contrast, certain pyridinium complexes[7,42,43] exhibit relatively strong N^+-H · · · Br-(M) hydrogen bonds with H · · · Br separations ranging from 2.3 to 2.6 Å.

In conclusion, the following remarks may be made with regard to differences in bonded and nonbonded interactions in the two MPNA analogs. (1) The $SbBr_6^-$ ion in both structures exhibits tetragonal deformation from octahedral symmetry by a *lengthening* of two bonds. The difference between the lengths of the axial and equatorial bonds is smaller in 4-MPNA (Δ = 0.007 (3) Å) than in 2-MPNA (Δ = 0.018 (3) Å). (2) The average length of the bond in the $SbBr_6^-$ ion is 0.010 (3) Å longer in 4-MPNA than in 2-MPNA. (3) The bond in the tribromide ion is also longer in 4-MPNA, by 0.007 (4) Å. (4) Bromine · · · bromine separations along the · · · $SbBr_6^-$ · · · Br_3^- · · · chains are 0.029 (4) Å shorter in 4-MPNA. And (5) the axes of the anions along the · · · $SbBr_6^-$ · · · Br_3^- · · · chains are more nearly collinear in 4-MPNA than in 2-MPNA. Clearly, differences between the two structures are small. It would appear, in fact, that these differences are much too small to account for the change in absorption by the compound relative to others in the series. Subsequently, examination of the quinolinium analog should prove enlightening in view of the anticipated structural change necessary to accommodate the larger cation.

Registry No. $(RH)_2Sb^VBr_9$, RH = 2-methylpyridinium, 12798-43-5; $(RH)_2Sb^VBr_9$, RH = 3-methylpyridinium, 12798-44-6; $(RH)_2Sb^VBr_9$, RH = 2-bromopyridinium, 12798-41-3; $(RH)_2Sb^VBr_9$, RH = 2-chloropyridinium, 12798-42-4; $(RH)_2Sb^VBr_9$, RH = 2,4-dimethylpyridinium, 12798-47-9; $(RH)_2Sb^VBr_9$, RH = quinolinium, 12798-48-0; $(C_6H_7NH)_2Sb^VBr_9$, 12798-45-7.

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(41) This and the other H · · · Br distances discussed here are based on Sb-Br and Br-Br bond lengths corrected for librational and "riding" motions, respectively. The N-H and C-H bonds were assigned lengths of 1.05 and 1.10 Å, respectively. Standard deviations in the H · · · Br distances were estimated to be 5 times those for C · · · Br distances.

(42) M. L. Hackert and R. A. Jacobson, *Acta Crystallogr., Sect. B*, 27, 1658 (1971).

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Bonding Trends in M(III) Transition Metal Hexacyanides. Crystal Structures of $Cs_2LiM(CN)_6$ (M = Mn, Fe, Co)[1]

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The hexacyano complexes $Cs_2LiM(CN)_6$ (M = Mn, Fe) have been prepared and their crystal structures determined. The structure of $Cs_2LiCo(CN)_6$ has been redetermined. Least-squares refinement of three-dimensional X-ray data led to conventional *R* factors of 2.02, 1.58, and 1.74 and weighted *R* factors of 2.05, 1.69, and 1.60% (142, 149, and 149 observed reflections) for Mn, Fe, and Co, respectively. The $Cs_2LiM(CN)_6$ salts crystallize in the space group $Fm3m$ (four molecules per unit cell) with unit cell dimensions of a = 10.667 (3), 10.571 (1), and 10.495 (1) Å for Mn, Fe, and Co, respectively. The M-C bond lengths decrease significantly proceeding from Mn through Co [r_{MC} = 1.976 (4), 1.926 (3), and 1.886 (3) Å]. The C-N bond lengths do not change significantly in the series. These results are discussed in terms of changes in the M-CN σ and π bonding.

Introduction

The structures of hexacyano complexes of Mn(III), Fe(III), and Co(III) have been studied extensively. The tripotassium salts $K_3M(CN)_6$ are known to be isomorphous.[3,4] Unfortunately, polytypism[4,5] and the low site symmetries for the $M(CN)_6^{3-}$ moieties have prevented the determination of significant trends in the M-C and C-N bond lengths in this series of complexes.[6] Early structural studies of the Prussian Blue analogs ($M_3[M'(CN)_6]_2 \cdot xH_2O$, where M = Fe(II), Co(II), etc. and M′ = Fe(III), Co(III), etc.) were limited to powder methods as single crystals could not be obtained.[7] Recently,[8] single crystal studies have been made of Prussian Blue

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(2) To whom correspondence should be addressed.

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