

42034-08-2; (TPP)Mn(NO)⁺, 89321-11-9; (TPP)Mn(NO)⁻, 89302-22-7; (TPP)Mn(NO)²⁻, 89302-23-8; (TPP)Co(NO)⁻, 89302-24-9; (TPP)Mn(NO)(DMF), 89320-98-9; (TPP)Mn(NO)(Me₂SO), 89302-25-0; (TPP)Mn(NO)(py), 89302-26-1; [(TPP)Co(NO)-

(DMF)]⁺, 89302-27-2; [(TPP)Co(NO)(Me₂SO)]⁺, 89302-28-3; [(TPP)Co(NO)(py)]⁺, 89302-29-4; [(TPP)Cr(NO)]⁺, 89302-30-7; (TPP)Cr, 58344-06-2; [(TPP)Fe(NO)]⁺, 70622-46-7; (TPP)Fe, 16591-56-3; [(TPP)Mn]⁺, 59388-92-0; [(TPP)Cr]⁺, 63692-18-2.

Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27650

Mössbauer and Raman Spectroscopic Studies of Substituted Pyridinium Bromoantimonate(III) Compounds

SHEILA W. HEDGES and L. H. BOWEN*

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A series of substituted pyridinium bromoantimonate(III) compounds with anions SbBr₄⁻, SbBr₅²⁻, and Sb₂Br₉³⁻ have been prepared and studied by Raman and ¹²¹Sb Mössbauer spectroscopies. The Mössbauer spectra yield two main diagnostic parameters: the isomer shift and the quadrupole coupling constant. The general trend from SbBr₃ to SbBr₅²⁻ is a decrease in both these parameters as the number of bromines surrounding the antimony increases. The isomer shift (relative to InSb) ranges from -7.64 to -8.20 mm/s for the SbBr₄⁻ anion, from -8.90 to -9.01 mm/s for Sb₂Br₉³⁻, and from -8.20 to -9.33 mm/s for SbBr₅²⁻. The quadrupole coupling constant ranges from +5.9 to +8.0 mm/s for SbBr₄⁻ and from 0 to +5.2 mm/s for the Sb₂Br₉³⁻ and SbBr₅²⁻ anions. Substitution on the pyridinium ring has a significant effect on the Mössbauer parameters of a given anion, probably due to distortion of the anion geometry. Raman spectra obtained for these compounds are discussed in relation to assignments in the literature. The spectra show a surprisingly large variation in the region below 300 cm⁻¹, even between compounds with the same stoichiometry. The region between 1000 and 300 cm⁻¹ is not particularly sensitive to the stoichiometry. Two of the strongest low-frequency bands, one in the region around 150 cm⁻¹ and one in the region 60-30 cm⁻¹, exhibit distinct correlation with the changes in isomer shift as the cation is varied.

Introduction

The reaction of antimony tribromide with amine hydrobromides yields a large variety of types of compounds. Both aliphatic and aromatic amines have been used in studies of the various factors that influence the stoichiometry and structure of such compounds. For example, the various pyridinium bromoantimonates have been studied by vibrational spectroscopy,^{1,2} TGA and DTA,³ X-ray diffraction,⁴⁻⁹ NMR,¹⁰ and Mössbauer spectroscopy.¹¹⁻¹⁴ Although several metal ion, ammonium, and pyridinium bromoantimonates of various stoichiometries have been studied by Mössbauer spectroscopy, only two substituted pyridinium bromoantimonate(III) com-

pounds have been reported.^{11,12} We selected a group of substituted pyridinium bromoantimonate(III) compounds to investigate the effect of cation ring substitution on the anion using Raman and Mössbauer spectroscopies. Compounds of three different stoichiometries were examined: RSbBr₄ (R = pyH, 2-MepyH, 3-MepyH, 4-MepyH, 2,4,6-Me₃pyH, 2-Br(py)H, 2-Cl(py)H), R₂SbBr₅ (R = 3-MepyH, 4-MepyH, 2-Br(py)H, 3-COOHpyH), and R₃Sb₂Br₉ (R = 2,4-Me₂pyH, 2,4,6-Me₃pyH). The results are discussed in terms of known and likely structures of the complex Sb(III) species.

Experimental Section

The compounds RSbBr₄, R₂SbBr₅, and R₃Sb₂Br₉ were prepared by slight variations in the method described by Whealey and Yeakley¹⁵ and by Stewart et al.¹⁶ Antimony(III) bromide solution was prepared by dissolving Sb₂O₃ in hot hydrobromic acid (48% HBr). To this solution was added a stoichiometric amount of the appropriate amine dissolved in cold hydrobromic acid. The reaction mixture was then heated to dissolve any solids and set aside to cool slowly. For most of these amines, the compound obtained depends on the experimental conditions² such as concentration of reactants and particularly the solvent. When mixtures of compounds with different stoichiometries were obtained, they could usually be separated by recrystallization. Recrystallization, when necessary, was done either from hot aqueous hydrobromic acid or from acetone/HBr mixed solvent. All samples were analyzed for Sb and those that were recrystallized from acetone were also analyzed for C and H. In some cases, successive recrystallizations were needed until the material gave the appropriate elemental analysis. No sample was used for further experiments until the elemental analyses were in good agreement with theoretical values.

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Raman spectra were obtained with 90° geometry by using a Jarrell-Ash 25-300 spectrometer and a Spectra-Physics argon ion laser operated at 514.5 nm. Due to the colored nature of these compounds, minimum power levels were used to obtain the spectra. Levels of 200–300 mW were found to be satisfactory for recording spectra without any perceptible sample melting or burning. A scan speed of 10 cm⁻¹/min and slit widths of 1–2 cm⁻¹ were employed. Samples were run as powders in glass capillary tubes.

Mössbauer spectra were obtained both at liquid-helium and liquid-nitrogen temperatures. The cryostat, spectrometer, experimental procedure, velocity calibration (using laser interferometry), and data analysis have been described previously.¹⁷ The isomer shift of InSb as determined using the laser system is -1.65 ± 0.02 relative to our Ni₂Sn₂B₆ source. All samples were prepared to contain approximately 10 mg of Sb/cm² by mixing the Sb compound with powdered polyethylene.

Results and Discussion

Raman data for the pyridinium bromoantimonate(III) compounds studied in this work were recorded in the range ~ 30 –1000 cm⁻¹ and are listed in Table I. (Two compounds, (2-Br(py)H)₂SbBr₅ and (3-COOHpyH)₂SbBr₅, are highly colored and unstable to laser light; no Raman spectra could be obtained for them.) Spectra have been previously reported for four of these compounds (pyHSbBr₄, 2-MepyHSbBr₄, (3-MepyH)₂SbBr₅, (4-MepyH)₂SbBr₅) below 300 cm⁻¹ by Allen and McMeeking.¹ Our results are in good agreement with those published by these workers with the exception that we did not observe a band for 2-MepyHSbBr₄ at 218 cm⁻¹, in either the Stokes or anti-Stokes region of the spectrum. Raman data for one other compound of this type, (pyH)₂SbBr₅, have also been reported in this region by Leroy and Goetz.² As indicated in Table I, the vibrations associated with the complex anion and lattice (below 300 cm⁻¹) are considerably more intense than the bands associated with the cation (above 300 cm⁻¹).

Pyridine, the substituted pyridines, and many of the pyridinium hydrohalides have been studied extensively by using Raman spectroscopy. One excellent summary of these results is given by Dollish et al.¹⁸ Comparison of the observed frequencies for pyHSbBr₄ between 1000 and 300 cm⁻¹ to assignments for pyridine and pyridinium hydrochloride allows assignment of all the bands observed in this region (Table I) since they are shifted slightly or not at all by changing the anion (see Table II). Similarly, a number of the bands for the various substituted pyridinium compounds can be tentatively assigned by comparison with characteristic frequencies for the corresponding pyridinium hydrohalides. The strongest bands in the spectra of pyridine and the substituted pyridines are due to the ring "breathing" modes. For pyridinium tetrabromoantimonate(III) these bands are at 1012 and 1031 cm⁻¹ as compared to 993 and 1030 cm⁻¹ for pyridine and 1008 and 1027 cm⁻¹ for pyridinium hydrochloride (Table II). The substituted pyridinium bromoantimonates show similar shifts for these bands. For example, 3-methylpyridinium tetrabromoantimonate(III) has its strongest bands in this region at 1031 and 1047 cm⁻¹. Characteristic frequencies for 3-substituted pyridine are 1030–1010 cm⁻¹ and for 3-substituted pyridinium hydrochloride, 1050–1035 cm⁻¹.¹⁸ Comparing the spectra for those cations that form bromoantimonate compounds of two different stoichiometries, one sees that the bands in the region 1000–300 cm⁻¹ are essentially independent of the stoichiometry.

Of greater interest in the present studies are the Sb–Br bands, around 230–100 cm⁻¹. In this region, the spectra show a surprisingly large variation even between compounds with

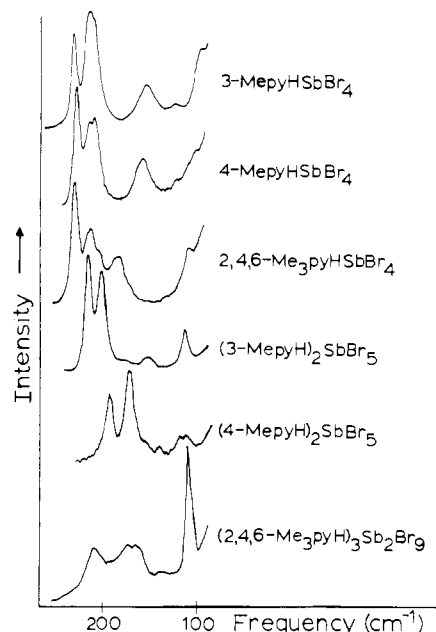


Figure 1. Comparison of the Sb–Br modes for compounds of three different stoichiometries.

the same stoichiometry. Assignments of the individual bands are not possible because of the limited structural information available for these compounds, but the strong bands at 230–200 cm⁻¹ are most probably due to terminal stretches and the less intense bands between about 200 and 100 cm⁻¹ to bridging stretches.¹ The lowest energy bands are bending, deformation, and lattice modes. The fundamental frequencies for the Sb–Br modes in the molecular solid (CH₃)₃SbBr₂ are found at 215 cm⁻¹ (asymmetric stretching, Raman inactive), 168 cm⁻¹ (symmetric stretching), and 160 cm⁻¹ (bending, Raman inactive).¹⁹ The bands in the 230–200-cm⁻¹ region, the terminal stretches, are somewhat less sensitive to changes in the cation than the lower energy bands (see Table I). However, there is a distinct shift of these bands to lower energies upon going from the SbBr₄⁻ anion to either SbBr₅²⁻ or Sb₂Br₉³⁻ as can be seen in Figure 1.

In order to discuss the Mössbauer spectral data, some structural information is helpful. A number of structures for amine bromoantimonate compounds have been determined by X-ray diffraction for trivalent, pentavalent, and mixed-valent antimony in a variety of stoichiometries. Structures of two mixed-valent compounds have been reported, both containing octahedral or near-octahedral SbBr₆³⁻ and SbBr₆⁻ anions.^{9,20} Structures of three pentavalent compounds with R₂SbBr₉ stoichiometry have been reported.^{7,8,21} Each of these has unit cells that contain one slightly distorted SbBr₆⁻ anion and a Br₃⁻ anion forming a chain sandwiched between two cations per unit cell. The structure of a pentavalent bromoantimonate compound with RSbBr₆ stoichiometry has also been reported, and it also contains slightly distorted octahedral SbBr₆⁻ anions.²² For trivalent bromoantimonate compounds, the anions formed are less symmetric. Structures of two compounds containing the Sb₂Br₉³⁻ anion have been reported.^{4,23} The Sb₂Br₉³⁻ anion has D_{3h} symmetry, with two distorted octahedra sharing a face to form the ion. Structures have been determined for only two of the compounds considered in the present

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Table I. Wavenumbers (cm^{-1}) of the Raman Bands of Substituted Pyridinium Bromoantimonates(III)^a

pyHSbBr ₄	2-MepyHSbBr ₄	3-MepyHSbBr ₄	4-MepyHSbBr ₄	2,4,6-Me ₃ pyHSbBr ₄	2-Br(py)HSbBr ₄
		28 m			
34 w, sh				34 s	31 s
	44 w, sh	43 vw, sh			46 w, sh
	52 w	51 vs	55 s	48 vw, sh	
63 s	58 m			59 vw, sh	65 s
	70 w	68 w	70 m	73 w	
	80 s	84 s	82 m		
88 m		94 m		91 w	87 m
98 w	96 w			106 vw	96 m
			115 w		115 w
		122 vw			
130 w	141 m	152 m	153 m		161 s
				183 m	180 s
	198 s				191 w, sh
	204 vs	207 vs		201 w	
212 vs		211 vs	208 vs	211 s	
219 vs	225 vs	229 vs	224 vs	228 vs	218 vs
				283 w	254 vw, sh
		344 vw	349 vvw		330 w
398 vw	360-510 w, br	398 w	399 vvw		389 vw
440 vvw		464 vvw			462 w
		536 w	521 vw	528 w	
614 w				594 w	
638 w	629 w	632 w	652 vw		621 w
682 vw		682 vvw			700 w
747 vw		781 vvw			747 vw
		791 vvw			
	808 vw	805 w	805 vw		821 vvw
875 vw		883 vw			
		924 vvw			911 vw
		989 vvw			981 vvw
1012 m	1016 w		1015 vw	1008 w	1010 m
1031 w		1031 w			
	1047 w	1047 w			1042 w
2-Cl(py)HSbBr ₄	(3-MepyH) ₂ SbBr ₅	(4-MepyH) ₂ SbBr ₅	(2,4-Me ₂ pyH) ₃ Sb ₂ Br ₉	(2,4,6-Me ₃ pyH) ₃ Sb ₂ Br ₉	
30 w	30 vs	26 w, sh			
39 m		33 w, sh			
45 w		46 s		38 m	38 vw, sh
55 m	49 vw, sh				49 m
64 w	59 w	63 m			58 w
	76 w, sh	70 w, sh			70 w
85 s			84 w		78 w
99 w	106 s	107 w	106 vs		107 vs
		116 w			
		137 w	129 w		134 vw
154 s	143 w	152 w, sh			161 s
	169 vw, sh	170 vs	176 s, br		171 s
	194 vs	190 s			
201 vs					
210 vs	208 vs		207 vs		207 s
225 vs					
			289 w		286 w
310 vw	338 vvw				
395 vvw	402 vw		409 vw		
445 w	465 vvw		438 vw		
485 vvw			523 w		519 w
522 vvw	533 w	520 vvw	550 w		530 w
625 w	630 w				594 w
	678 vw	653 vvw			
738 w			734 vw		705 vvw
767 vvw	780 vw		750 w		
	804 vw	804 vvw			
857 vvw	869 vvw				875 vvw
	918 vvw				
	979 vvw				938 vvw
1014 w		1017 vw	1013 vw		1007 w
	1032 w				1031 vw
1043 vw	1049 w				

^a w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad.

study. In pyridinium tetrabromoantimonate(III),⁵ each Sb atom has a distorted-octahedral environment with all Br-Sb-Br angles close to 90°. The Sb-Br(1) distance is 2.564 Å, and the Sb-Br(2) distance is 2.822 Å. The octahedra are completed by Br(2) from neighboring units at a distance

Sb-Br(2)' of 3.231 Å, indicating a weak, but significant, solid-state interaction. Bis(2-chloropyridinium) pentabromoantimonate(III)⁶ contains discrete SbBr₅²⁻ anions with an average Sb-Br bond distance of 2.73 Å. A sixth Br atom from a second SbBr₅²⁻ unit completes the distorted octahedron

Table II. Vibrational Spectral Assignments (cm^{-1}) of Pyridine, Pyridinium Hydrochloride, and Pyridinium Tetrabromoantimonate(III)

approx description of vib	pyridine ^a	pyHCl ^a	pyHSbBr ₄
out-of-plane ring def	375	...	398
out-of-plane ring def	405	400	440
in-plane ring def	605	607	614
in-plane ring def	652	637	638
out-of-plane C-H def	700	685	682
out-of-plane ring def	749	685	682
out-of-plane C-H def	886	756	747
out-of-plane C-H def	891	883	875
out-of-plane C-H def	942	998	
out-of-plane N-H def	...	945	
out-of-plane C-H def	986	...	
totally symm ring "breathing"	993	1008	1012
trigonal ring "breathing"	1030	1027	1031

^a Reference 18.

Table III. Mössbauer Parameters for $\text{R}_x\text{Sb}_y\text{Br}_z$ at 4 K

compd	χ^2 ^a	intens, %	Γ (± 0.05), mm/s	δ (± 0.05) ^b , mm/s	e^2qQ (± 0.5), mm/s
SbBr ₃		28 ^c	2.8 ^c	-5.9 ^c	11.6 ^c
		RSbBr ₄			
pyHSbBr ₄	462	28	2.95	-8.01	5.9
		15 ^d	3.2 ^d	-7.25 ^d	11.5 ^d
2-MepyHSbBr ₄	482	30	2.72	-8.20	7.2
				-9.6 ^e	0 ^e
3-MepyHSbBr ₄	562	31	2.70	-8.00	7.6
				-10.1 ^e	0 ^e
4-MepyHSbBr ₄	465	33	2.63	-8.08	8.0
2,4,6-Me ₃ pyHSbBr ₄	467	26	2.64	-7.64	8.1
2-Br(py)HSbBr ₄	581	30	3.09	-7.82	6.4
2-Cl(py)HSbBr ₄	504	27	2.79	-8.08	6.9
		R ₂ SbBr ₅			
(3-MepyH) ₂ SbBr ₅	517	30	2.57	-8.35	4.7
(4-MepyH) ₂ SbBr ₅	432	23	3.07	-9.33	0.0
(2-Br(py)H) ₂ SbBr ₅	508	28	2.87	-8.20	3.5
(3-COOHpyH) ₂ SbBr ₅	468	28	2.72	-8.55	4.5
		R ₃ Sb ₂ Br ₉			
(2,4-Me ₂ pyH) ₃ Sb ₂ Br ₉	633	30	2.63	-8.90	5.2
(2,4,6-Me ₃ pyH) ₃ Sb ₂ Br ₉	482	25	3.23	-9.01	0.0

^a Number of degrees of freedom = 443. ^b Relative to InSb.

^c Reference 26. ^d Reference 11. ^e Reference 12.

and forms linear chains of SbBr_5^{2-} parallel to the c axis of the unit cell. The Sb-Br distance to this sixth Br is 3.34 Å so the interaction is rather weak. Also the acidic hydrogen approaches Br at 2.3 Å, which is 0.9 Å shorter than a normal H-Br van der Waals contact and is among the shortest observed for aromatic acidic hydrogen with bromine. When piperidinium is the cation and $(\text{pip})_2\text{SbBr}_5$ is prepared, the Sb atom is again surrounded by a complex octahedron of Br atoms, but in this compound the SbBr_5^{2-} units form infinite zigzag chains.²⁴

Mössbauer spectral results at 4 K for substituted pyridinium bromoantimonate(III) compounds of three different stoichiometries are reported in Table III. We find significantly different isomer shifts (δ) and quadrupole coupling constants (e^2qQ) for SbBr_4^- than those reported for RSbBr_4 compounds by Donaldson and co-workers.^{11,12} These authors do not give a detailed description of their sample preparation but do mention that acetonitrile was used for recrystallization.¹² As pointed out above, the preparation of these compounds is rather sensitive to experimental conditions, so it is possible that their samples differed from those prepared for this study. This seems unlikely however, especially since Stewart et al.¹⁶ verified

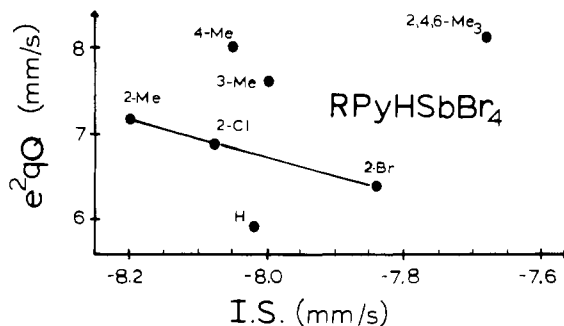


Figure 2. Quadrupole coupling constants, vs. isomer shifts for substituted pyridinium tetrabromoantimonate(III) compounds.

that pyHSbBr_4 recrystallized from hot HBr gives lattice parameters in excellent agreement with those reported by De Haven⁵ who used acetonitrile for recrystallization. Mössbauer data have also been reported for the mixed-valence pyridinium bromoantimonate $(\text{pyH})_6\text{Sb}_4\text{Br}_{24}$ ¹³ and for $(\text{pyH})_5\text{Sb}_2\text{Br}_9\text{Br}_2$ ¹⁴ but these compounds have somewhat different structures (see above) and are not directly comparable. They do, however, give isomer shift and quadrupole coupling constant values in the same general range as the stoichiometries considered here. All the literature data on these compounds have been obtained with BaSnO_3 as the source material, which necessitates the use of very large negative experimental velocities. Also velocity calibration in these cases was done indirectly using ⁵⁷Fe spectra. (Donaldson and co-workers used Fe_2O_3 ;²⁵ Ballard and co-workers used Fe foil.¹⁴) Our experimental setup should minimize both those uncertainties since our $\text{Ni}_{21}\text{Sn}_2\text{B}_6$ alloy source allows us to operate at much lower velocities and velocity calibration is done directly by using laser interferometry.

As can be seen from the series of compounds listed in Table III, the general trend on going from SbBr_3 to SbBr_4^- , $\text{Sb}_2\text{Br}_9^{3-}$, and SbBr_5^{2-} is a decrease of both the isomer shift and e^2qQ as the Sb:Br ratio decreases from 1:3 to 1:5. There is some overlap between the values for the SbBr_5^{2-} and $\text{Sb}_2\text{Br}_9^{3-}$ anions, but this is reasonable since both are expected to have nearly octahedral site symmetry around Sb. We prepared only two compounds with $\text{R}_3\text{Sb}_2\text{Br}_9$ stoichiometry. Both have large negative isomer shifts, indicating considerable s character in the lone pair and near-zero quadrupole coupling constants, consistent with the nearly octahedral site symmetry of Sb found in the $\text{Sb}_2\text{Br}_9^{3-}$ anion. The compounds with R_2SbBr_5 stoichiometry all have very small e^2qQ , suggesting that they have nearly octahedral Sb sites and are structurally similar to the 2-chloropyridinium compound described above. These compounds also have large negative isomer shifts, although slightly less negative than the $\text{R}_3\text{Sb}_2\text{Br}_9$ compounds—with the exception of bis(4-methylpyridinium) pentabromoantimonate(III). This compound has an isomer shift that is considerably more negative than the isomer shift of the other compounds. This could be the result of having the sixth Br atom considerably closer in this compound than in the others. An X-ray diffraction structure of this compound would be of interest in explaining this difference.

Figure 2 shows a plot of Mössbauer data for the RSbBr_4 compounds. Ring substitution on the pyridinium cation does indeed have a measurable effect. On this plot, the region of increasing ionicity in the Sb bond lies toward more negative isomer shifts and small quadrupole coupling constants. The unsubstituted pyridinium compound appears to have the largest ionic contribution to the Sb-Br bonds, giving a fairly negative isomer shift and a small quadrupole coupling constant. The

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Table IV. Relative Peak Areas at 77 and 4 K

compd	$A(77)/A(4)$	compd	$A(77)/A(4)$
pyHSbBr ₄	0.06	(3-MepyH) ₂ SbBr ₅	0.07
2-MepyHSbBr ₄	0.12	(4-MepyH) ₂ SbBr ₅	0.08
3-MepyHSbBr ₄	0.12	(2-Br(py)H) ₂ SbBr ₅	0.17
4-MepyHSbBr ₄	0.07	(3-COOHpyH) ₂ SbBr ₅	0.05
2,4,6-Me ₃ pyHSbBr ₄	0.04	(2,4-Me ₂ pyH) ₃ Sb ₂ Br ₉	0.07
2-Br(py)HSbBr ₄	0.10	(2,4,6-Me ₃ pyH) ₃ Sb ₂ Br ₉	0.06
2-Cl(py)HSbBr ₄	0.18		

monosubstituted pyridinium compounds are intermediate in ionicity of the Sb-Br bonds, giving slightly larger e^2qQ . Finally, the Sb-Br bonds in the collidinium compound have the most covalent character in this series, since 2,4,6-Me₃pyHSbBr₄ has a less negative isomer shift and a larger e^2qQ . However, these differences are small, and the Sb-Br bond is certainly not completely ionic or covalent in any of these compounds. It is interesting to note that the Mössbauer parameters of the 2-substituted compounds fall on a straight line in this plot, the isomer shift becoming less negative with increasing electron-withdrawing ability of the ring substituent. A plot of the pK_a values of the substituted pyridines vs. the isomer shift of the corresponding RSbBr₄ compound fails to show any correlation. Although the effect of the cation is measurable, neither the isomer shift nor the quadrupole coupling constant shows any simple trends. Additional structural information is needed in order to clarify the effect of the cation seen for these compounds. As can be seen from the structural determinations for Sb(V) compounds cited above, even small changes in the cation such as changing the location of a substituent on the ring can result in changes in the anion, particularly in chain formation.

We also obtained Mössbauer spectra for all the substituted pyridinium bromoantimonate(III) compounds listed in Table III at liquid-nitrogen temperature. The results are quite similar except that the peak intensities are much lower. Table IV shows the relative peak areas at 77 and 4 K. Solids with high lattice temperatures should have large ratios, and ionic solids should have high lattice temperatures. Interestingly, 2,4,6-Me₃pyHSbBr₄ has the smallest ratio of any compound investigated, again indicating a more covalent character in this compound. However, 2-Cl(py)HSbBr₄, which has the largest area ratio, has an isomer shift and a quadrupole coupling constant that are intermediate for the RSbBr₄ compounds. Thus, ionicity in the Sb-Br bonds is not the only influence on the lattice temperature, which depends on other crystal parameters such as the nature of the lattice vibrations.

It has been pointed out by Shenoy and co-workers²⁷⁻²⁹ that there are dangers in using the "thin" approximation for analysis of partially resolved spectra such as those obtained for quadrupole splitting in ¹²¹Sb. They point out that effects due to saturation by a thick absorber cause inaccuracies resulting from use of this simplifying approximation, particularly for large quadrupole coupling constants. Using the awareness diagram given by these authors,²⁹ we estimate errors of about 10-15% in the quadrupole coupling constants determined for the compounds in the present study, using the "thin" approximation. Using the transmission integral, which is a much more elaborate computation, would account for absorber thickness effects and improve the calculated values for the hyperfine parameters. However, this improvement would be small in the present case because of the inherent difficulty in fitting small values of e^2qQ for ¹²¹Sb. Also, the errors asso-

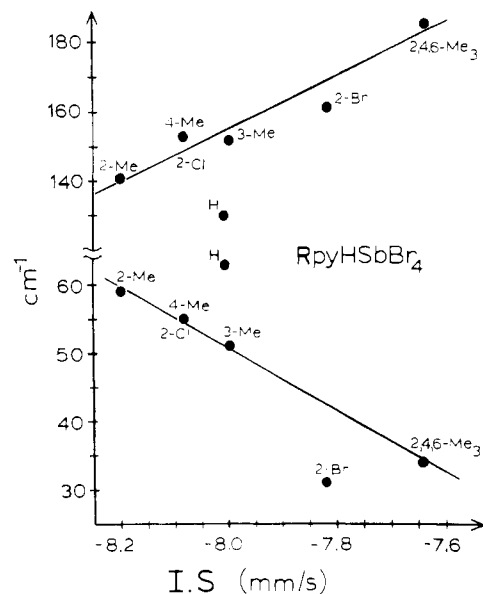


Figure 3. Wavenumbers of the strongest band in the bridge stretching region and in the low-energy region of the spectra of the RSbBr₄ compounds vs. isomer shifts.

ciated with the "thin" approximation should not affect the trends seen for this series of compounds, since the samples all have roughly the same effective thickness.

Figure 3 shows a plot of band frequency vs. isomer shift for the strongest band in each of two regions in the Raman spectra of the RSbBr₄ compounds. The strongest band in the region around 150 cm⁻¹, which is assigned to bridging Br stretching modes by Allen and McMeeking,¹ shows an interesting correlation with the isomer shift. The collidinium compound, whose less negative isomer shift value indicates more covalent character in the Sb-Br bonds, also has the highest frequency band. This larger frequency probably does not result from a larger "force constant" for this vibration in the collidinium compound but from a change in the solid-state geometry. One possibility is that the collidinium cation is sufficiently larger than the other cations to cause considerable distortion in the SbBr₄⁻ anion in this compound relative to that of the other RSbBr₄ compounds. This solid-state distortion has the effect of decreasing the s electron density in the Sb lone pair (as indicated by the less negative isomer shift) and increasing the frequency of this bridge stretching mode. The strongest low-frequency band, presumably a lattice mode, shows a similar sort of correlation except in this case the collidinium compound has the lowest frequency. Interpretation of these trends is hindered by the very limited amount of structural information available. The structural information that is available shows a great variability in the extent and configuration of the anion chains in bromoantimonate compounds. These are the distortions most likely to affect the bridge stretching modes and lattice modes. The correlation observed with isomer shift indicates that these distortions also affect the electronic hybridization and thus the s electron density at the Sb site. None of the bands in the 230-210-cm⁻¹ region, the Sb-Br terminal stretching modes, show any correlation with isomer shift. However, the frequencies of these bands do not vary nearly as much with substitution on the cation. The two low-frequency bands discussed above, which do vary significantly with substitution, do so in a way that relates to the bond hybridization of the antimony. This very small effect is seen only because of the sensitivity of the isomer shift to the nature of the lone-pair electrons in Sb(III).

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for performing the elemental analyses for antimony. They are thankful to H. W. Patrick for his skillful technical assistance.

Registry No. pyHSbBr₄, 52279-30-8; 2-MepyHSbBr₄, 50284-20-3; 3-MepyHSbBr₄, 52279-31-9; 4-MepyHSbBr₄, 89438-19-7; 2,4,6-

Me₃pyHSbBr₄, 89438-20-0; 2-Br(py)HSbBr₄, 89438-21-1; 2-Cl(py)HSbBr₄, 89438-22-2; (3-MepyH)₂SbBr₅, 89438-23-3; (4-MepyH)₂SbBr₅, 89438-24-4; (2,4-Me₂pyH)₃Sb₂Br₉, 89486-22-6; (2,4,6-Me₃pyH)₃Sb₂Br₉, 89438-25-5; (2-Br(py)H)₂SbBr₅, 89438-26-6; (3-COOHpyH)₂SbBr₅, 89438-27-7.

Contribution from the Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019, and Division of Biochemistry, Department of Basic and Clinical Research, Scripps Clinic and Research Foundation, La Jolla, California 92037

Acid-Base Properties of α -Ribazole and the Thermodynamics of Dimethylbenzimidazole Association in Alkylcobalamins

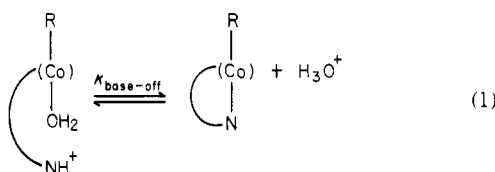
KENNETH L. BROWN,*† JANETTE M. HAKIMI,† DEBRA M. NUSS,† YOLANDA D. MONTEJANO,† and DONALD W. JACOBSEN†

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1- α -D-Ribofuranosyl-5,6-dimethylbenzimidazole (α -ribazole) has been prepared by cerous hydroxide catalyzed hydrolysis of cyanocobalamin, purified, and characterized by elemental analysis and ¹H and ¹³C NMR and UV-visible spectroscopy. Values of the pK_a of N-3-protonated α -ribazole have been determined at several temperatures (ionic strength 1.0 M) and the pK_a of N-1-protonated α -ribazole has been estimated to be -7.2 from UV-visible spectral changes in sulfuric acid-water mixtures. Seven alkylcobalamins have been synthesized by standard reductive alkylation procedures and purified chromatographically. It has been found that reductive alkylation with CF₃Br produces mixtures of (trifluoromethyl)cobalamin and (difluoromethyl)cobalamin because the former is reductively converted to the latter by reducing agents commonly employed for reduction of cobalt(III) cobalamins to cob(I)alamin. The pK_a's for the base-on-base-off transition of these seven alkylcobalamins and methylcobalamin have been determined at the same temperatures as the α -ribazole pK_a's. From these values the apparent binding constants for ligation of the free-base benzimidazole nucleotide and the enthalpy and entropy changes for this ligand substitution have been calculated. The enthalpy change has been found to be quite insensitive to the nature of the organic ligand while the entropy change is quite sensitive. These results are discussed in terms of the probable importance of steric effects of the organic ligands on the base-on-base-off pK_a's of alkylcobalamins.

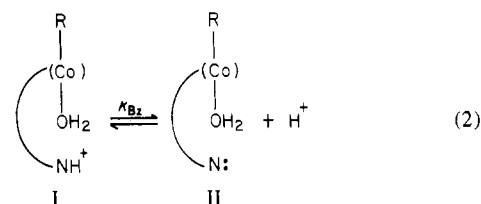
Introduction

One of the most characteristic and perhaps one of the most thoroughly studied chemical properties of cobalamins is the so-called base-on-base-off reaction in which the axially coordinated dimethylbenzimidazole nucleotide is displaced by water and protonated (i.e., the reverse of eq 1). This reaction

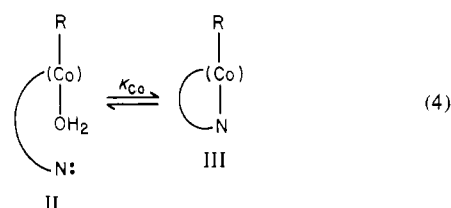


is sometimes referred to as the red-yellow shift due to the large changes in electronic spectrum attendant upon conversion of the base-on to the base-off form.¹ Values of pK_{base-off} (eq 1) have been reported for a large number of cobalamins² and range from about 4.0 (*n*-heptyl(Cbl))³ to -2.4 (H₂O(Cbl))⁴. Hogenkamp et al.⁵ have shown that the values of pK_{base-off} for most (but not all) of a series of alkylcobalamins can be successfully correlated with the Hammett σ_m substituent constant of the cobalt-bound alkyl group but that the values fall on two lines of approximately equal slope but different intercepts, one for substituted methylcobalamins and one for substituted ethylcobalamins. This observation has never been satisfactorily explained.

It is often pointed out that the base-on-base-off reaction of cobalamins (eq 1) may be viewed as the sum of two consecutive equilibria, i.e., the deprotonation of the benzimidazole-protonated base-off species (eq 2 and 3), and the substitution of free-base benzimidazole for water in the resulting deprotonated, base-off species (eq 4 and 5). Equation



$$K_{\text{Bz}} = [\text{II}][\text{H}^+]/[\text{I}] \quad (3)$$



$$K_{\text{Co}} = [\text{III}]/[\text{II}] \quad (5)$$

6 may then be derived (from consideration of the law of mass

$$K_{\text{base-off}} = (1 + K_{\text{Co}})K_{\text{Bz}} \quad (6)$$

action), which relates $K_{\text{base-off}}$ to K_{Co} (eq 4 and 5) and K_{Bz} (eq 2 and 3) and allows calculation of K_{Co} from $K_{\text{base-off}}$ provided that a value of K_{Bz} is available. It is then often assumed that K_{Bz} for deprotonation of the base-off benzimidazolium species (I, eq 2) is approximately equivalent to that of the detached benzimidazole ribonucleoside, i.e., the conjugate acid of 1- α -D-ribofuranosyl-5,6-dimethylbenzimidazole (or α -ribazole).

* The University of Texas at Arlington.

† Scripps Clinic and Research Foundation.

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