CHEMISTRY LETTERS, pp. 209-212, 1981. © The Chemical Society of Japan 1981

^{81}Br NQR STUDY ON THE MIXED-VALENCE COMPOUNDS $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ AND $Rb_4Sb^{III}Sb^{V}Br_{12}$

Hiromitsu TERAO*, Tsutomu OKUDA, and Hisao NEGITA
*Department of Chemistry, Faculty of Education, Tokushima University,
Tokushima 770
Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima 730

^{81}Br NQR spectra were observed on the mixed-valence compounds $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ and $Rb_4Sb^{III}Sb^{V}Br_{12}$ between 77 K and room temperature. Their temperature dependences exhibit some interesting features. The $Sb^{III}Br_6{}^{3-}$ in the NH_4 salt is slightly distorted to the D_{2d} symmetry. The Townes-Dailey analysis reveals that the net charges on both Sb^{III} and Sb^{V} are almost the same.

The existence of the different oxidation states of the antimony atom, Sb(III) and Sb(V), in the crystals of the hexahalogenoantimonates has been confirmed by various methods,[1,2] especially X-ray single crystal analyses[3,4] and ^{121}Sb Mössbauer effects.[5-8] The present paper provides further evidence of the existence of the mixed oxidation states in $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ and $Rb_4Sb^{III}Sb^{V}Br_{12}$ crystals by means of the bromine nuclear quadrupole resonance. And it has been intended to obtain the information regarding the mixed-oxidation states in these compounds through NQR frequencies and their temperature dependences.

The samples were prepared according to the method described by Lawton and Jacobson.[3] The NQR spectra were obtained with a self-quenching superregenerative oscillator described by Herlach,[9] which was used with frequency modulation. Signals were observed on a recorder.

Resonance spectra were searched for in the frequency region between 50 and 190 MHz. Table 1 shows the ^{81}Br resonance frequencies obtained at liquid nitrogen and room temperatures. ^{79}Br resonances were also detected and the frequency ratio $\nu(^{79}Br)/\nu(^{81}Br)$ was in agreement with the known quadrupole moment ratio $Q(^{79}Br)/Q(^{81}Br) = 1.1971$ within experimental errors.

Both the crystals of $(NH_4)_4Sb_2Br_{12}$[3] and $Rb_4Sb_2Br_{12}$[4] take the tetragonally distorted K_2PtCl_6 structures ($I4_1/amd$) in which the component ions are arranged in an ordered array with repeating the ions of the same oxidation state of antimony along the a and b directions in the unit cell but alternating the ions of the different states along the c direction.

Two sets of widely spaced resonance frequencies observed in both compounds are assigned unambiguously to $Sb^{III}Br_6{}^{3-}$ and $Sb^{V}Br_6{}^{-}$, as listed in Table 1. The existence of the two resonance lines ascribed to $Sb^{III}Br_6{}^{3-}$ in the NH_4 salt shows that these anions are also slightly distorted to the D_{2d} symmetry in the same manner as

Table 1. ^{81}Br NQR frequencies in MHz for $(NH_4)_4Sb_2Br_{12}$ and $Rb_4Sb_2Br_{12}$.

Compound	Frequency[a)]		$(\frac{d\nu}{dT})_{300K}$ [c)]	Assignment[d)]	
	77 K	298 K			
$(NH_4)_4Sb_2Br_{12}$	57.79 (18)[b)]	58.22 (17)	0.50	a	$Sb^{III}Br_6^{3-}$
	62.07 (24)	61.85 (26)	0.00	e	
	155.91 (10)	152.05 (14)	-12.3	a	$Sb^{V}Br_6^{-}$
	160.63 (29)	153.93 (36)	-12.0	e	
$Rb_4Sb_2Br_{12}$	60.98 (15)	61.12 (8)	0.80	a	$Sb^{III}Br_6^{3-}$
	65.36 (38)	64.88 (18)	-2.00	e	
	155.30 (10)	152.88 (8)	-10.8	a	$Sb^{V}Br_6^{-}$
	157.11 (27)	154.93 (18)	-10.0	e	

a) The estimated accuracy is within ±0.01 MHz. b) Parenthetical numbers are signal-to-noise ratios. c) Temperature coefficient in KHz/K at 300 K. d) a: axial; e: equatorial.

the $Sb^{V}Br_6^{-}$ in the NH_4 salt and both anions in the Rb salt, though the X-ray analysis[3)] and the ^{121}Sb Mössbauer effect[7)] have not detected the distortion. (The $Sb^{III}Br_6^{3-}$ in the NH_4 salt lie on the D_{2d} positions from X-ray.[3)]) Further, the lower and higher resonance lines in each set were assigned to the axial (parallel to c axis) and the equatorial (approximately parallel to a or b axis) bromine atoms as shown in Table 1, referring to the signal to noise ratios.

The abnormally dark colors of the hexahalogenoantimonates have been attributed to the intermolecular charge-transfer transitions.[1)] The charge-transfer from $Sb^{III}Br_6^{3-}$ to $Sb^{V}Br_6^{-}$ will affect their NQR frequencies to approach each other. Atkinson and Day, however, have observed the electronic spectra of the series of hexachloroantimonates, and estimated the delocalization of 5s electrons of $Sb^{III}Cl_6^{3-}$ on to the neighboring $Sb^{V}Cl_6^{-}$ to be less than 0.1 % in the ground state.[10)] Therefore, the effect of the charge-transfer on NQR frequencies may be negligible in the present compounds.

The temperature dependences of the resonance lines observed between 77 K and room temperature are shown in Figs. 1 and 2 for the two compounds. From these figures one may notice three interesting features as described below. First, the curves of frequency vs. temperature in the NH_4 salt have discontinuous points on their temperature gradients at 214 K. Therefore, it is thought that the crystals may undergo phase transition at this temperature. In order to investigate the motion of NH_4^+ ions in both phases we have measured the broad-line ^{1}H NMR spectrum of the powder sample of the NH_4 salt at various temperatures. However, the linewidth was almost constant between 128 K and room temperature, the maximum-slope width being about 2.4×10^{-4} T. The narrow linewidth indicates the presence of tunneling of protons in crystals.[11)] Second, the absolute values of dν/dT of the resonance lines of $Sb^{V}Br_6^{-}$ are larger than those of $Sb^{III}Br_6^{3-}$ in both salts and other hexahalogenometallate ions.[12)] This finding may be ascribed to the large coupled librational motion of the $Sb^{V}Br_6^{-}$, in which the distances between bromine atoms are much shorter than those in the $Sb^{III}Br_6^{3-}$, as observed by X-ray analyses.[3,4)] (The mean lengths of the Sb^{III}-Br bonds are 2.795 and 2.762 Å respectively

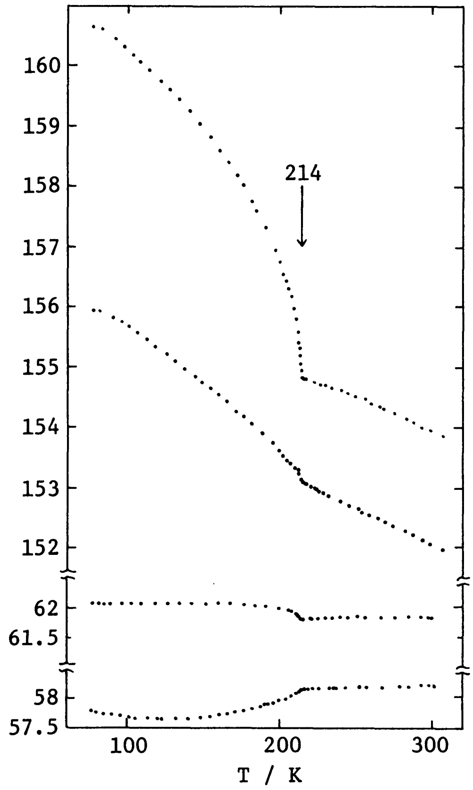

Fig. 1. Temperature dependence of the ^{81}Br NQR frequencies in $(NH_4)_4Sb_2Br_{12}$.

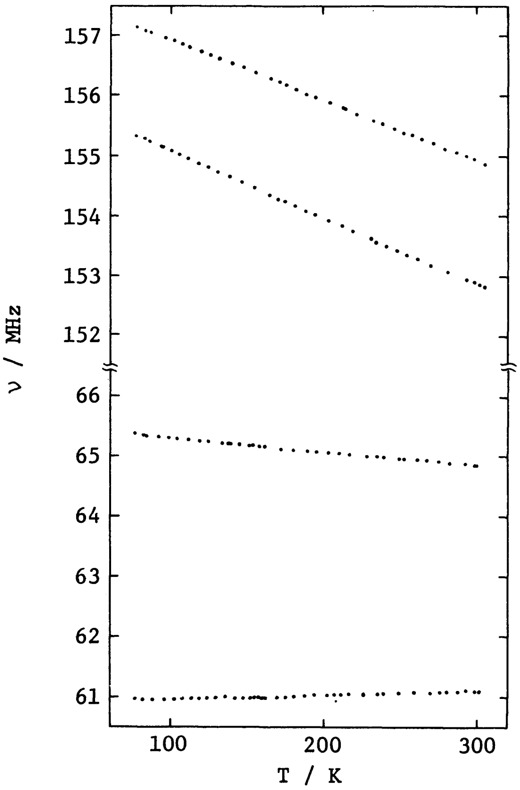

Fig. 2. Temperature dependence of the ^{81}Br NQR frequencies in $Rb_4Sb_2Br_{12}$.

for the NH_4 and Rb salts, whereas those of the Sb^V-Br bonds are 2.564 and 2.582 Å.) Third, the lowest lines of both salts have positive temperature coefficients contrary to the normal case.[13)] These unusual positive temperature coefficients may be interpreted by the mechanism proposed in TlI_3 by Nakamura and Kubo.[14)] In the present crystals each bromine atom has four neighboring cations in directions almost perpendicular to the Sb-Br bond. When the lone pair electrons of the bromine atom are exposed under the strong electrostatic field of the cations at close distances, the contributions for the q_{zz} (the main component of the electric field gradients) of the lone pairs will be decreased.[14)] Accordingly q_{zz} (or resonance frequency) decreases. The relatively close distances are observed for both the axial bromine atoms (Br_a) and the equatorial bromine atoms (Br_e) in $Sb^{III}Br_6{}^{3-}$. The cations, however, surround more symmetrically Br_a than Br_e, and in addition, the Sb-Br_e bond deviates slightly above or below from the a-b plane. The effect of the cations may be thereby smaller for Br_e of $Sb^{III}Br_6{}^{3-}$ as well as Br_a and Br_e in $Sb^VBr_6{}^-$ than for Br_a of $Sb^{III}Br_6{}^{3-}$. In fact, the frequency lowering of the lower line from the upper line in each anion is considerably larger in $Sb^{III}Br_6{}^{3-}$ than in $Sb^VBr_6{}^-$ in both compounds. This fact may suggest that the axial bromine atoms in $Sb^{III}Br_6{}^{3-}$ are strongly affected by the neighboring cations. It is, thus, considered that the lower line of $Sb^{III}Br_6{}^{3-}$ has the positive coefficient, because the thermal vibrations partially suppress the above effect of cations and hence the resulting increase in q_{zz} overcomes the usual Beyer effect. In the NH_4 salt the motion of $NH_4{}^+$ ions may have some effects on the temperature curves.

Table 2. The ionic character, i, of Sb-Br bonds and the net charge, ρ, on the Sb atoms

Compound	Anion	i	ρ
$(NH_4)_4Sb_2Br_{12}$	$Sb^{III}Br_6^{3-}$	0.78	1.66
	$Sb^{V}Br_6^{-}$	0.44	1.63
$Rb_4Sb_2Br_{12}$	$Sb^{III}Br_6^{3-}$	0.77	1.60
	$Sb^{V}Br_6^{-}$	0.44	1.61

One may estimate the ionic character of the Sb-Br bonds, i, and the net charge on the Sb atoms, ρ, using a simple Townes-Dailey method according to the following equations:[15)]

$$|e^2Qq_{zz}/h|_{obs}/|e^2Qq_{zz}/h|_{atom} = (1-s)(1-i), \tag{1}$$

and

$$\rho = F - 6(1-i), \tag{2}$$

where $|e^2Qq_{zz}/h|_{obs}$ is a quadrupole coupling constant, which is obtained by assuming $\eta = 0$; $|e^2Qq_{zz}/h|_{atom}$ is an atomic quadrupole coupling constant which is 643.03 MHz for ^{81}Br; s electron character, s, is taken as 0.15; F denotes the formal charge on antimony atoms. ($F = 3$ for $Sb^{III}Br_6^{3-}$, $F = 5$ for $Sb^{V}Br_6^{-}$, respectively); and the figure 6 in Eq. 2 denotes the coordination number of antimony atoms. The calculated values of i and ρ are listed in Table 2, where the frequencies at 298 K was used. It is interesting that the ionicity of Sb-Br bond in $Sb^{III}Br_6^{3-}$ is quite large compared to that in $Sb^{V}Br_6^{-}$, so that the net charges on both Sb atoms are almost the same in spite of different formal charge, and also almost equal to the net charges, 1.60, on Sn atoms in $Sn^{IV}Br_6^{2-}$.[15)]

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 474204).

References

1) M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem., 10, 247 (1967).

2) T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, J. Chem. Soc. (A), 1967, 1810.

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

4) C. R. Hubbard and R. A. Jacobson, Proc. Iowa Acad. Sci., 75, 85 (1968).

5) T. Birchall, B. D. Valle, E. Martineau, and J. B. Mline, J. Chem. Soc. (A), 1971, 1855.

6) A. Yu. Aleksandrov, S. P. Ionov, A. M. Pritchard, and V. I. Gol'danskii, JETP Letters, 13, 8 (1971).

7) J. D. Donaldson, M. J. Tricker and B. W. Dale, J. Chem. Soc., Dalton, 1972, 893.

8) G. Longworth and P. Day, Inorg. Nucl. Chem. Lett., 12, 451 (1976).

9) F. Herlach, Helv. Phys. Acta, 34, 305 (1961).

10) L. Atkinson and P. Day, J. Chem. Soc. (A), 1969, 2423.

11) A. Watton, A. R. Sharp, H. E. Petch, and M. M. Pintar, Phys. Rev. B, 5, 4281 (1972).

12) See e.g. T. L. Brown and L. G. Kent, J. Phys. Chem., 74, 3572 (1970).

13) H. Bayer, Z. Physik., 130, 227 (1951).

14) D. Nakamura and M. Kubo, "Advances in Nuclear Quadrupole Resonance," ed by J. A. S. Smith, Heyden, London (1975), vol. 2, p. 117.

15) M. Kubo and D. Nakamura, Advan. Inorg. Chem. Radiochem., 8, 257 (1966).

(Received October 23, 1980)