# $^{121}$Sb NMR and SCF-MS-Xα Studies of Quadrupole Interaction and The Electronic Structure of Mixed-Valence Compound, $Cs_2SbCl_6$ *

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$Cs_2SbCl_6$ is known as a typical mixed-valence compound. It crystallizes into a tetragonal space group $I4_1/amd$ and contains two different complex anions, $Sb(III)Cl_6^{3-}$ and $Sb(V)Cl_6^-$. The dark blue color of this compound has been considered to originate from a charge transfer between the above two anions. In order to study the electronic structure of these complex anions and the existence of charge transfer between them we measured the $^{121}$Sb NMR spectrum and carried out molecular orbital calculations on the electronic states of these anions. The $^{121}$Sb NMR spectrum consists of two peaks at 0 and 30 kHz which can be assigned to the central transition of $^{121}$Sb in $Sb(V)Cl_6^-$ and $Sb(III)Cl_6^{3-}$, respectively. The line shape analyses of the spectra led to nuclear quadrupole coupling constants of nearly zero for $Sb(V)Cl_6^-$ and $4.9 \pm 0.5$ MHz for $Sb(III)Cl_6^{3-}$ at room temperature. The quadrupole coupling constant of $^{121}$Sb(III) decreases steadily on heating. The calculations of the electronic ground state energies of both anions were calculated by the MS-Xα molecular orbital method. The calculated charge-transfer band from the $A_{1g}$ state of $Sb(III)Cl_6^{3-}$ to the $A_{1g}$ state of $Sb(V)Cl_6^-$ appears at 610 nm and can account for the experimental electronic spectrum, the calculated quadrupole coupling constant in $Sb(III)Cl_6^{3-}$ however is far larger than the experimental one. The contribution of the charge-transferred state to the ground state is negligible and so the temperature dependence of the quadrupole coupling constant of $^{121}$Sb(III) is attributed to an anisotropic thermal expansion of the compound.

*Key words:* NMR, Quadrupole interaction, Molecular orbital, Mixed valence.

## Introduction

Cesium hexachloroantimonate(III, V), $Cs_2SbCl_6$, is a classical Robin-Day class II mixed-valency compound [1] in which the valence mixing between the two oxidation states of antimony, i.e., Sb(III) and Sb(V) may cause the deep color of the compound.

Its crystal structure has been determined by a powder Neutron diffraction experiment [2]. The $Cs_2SbCl_6$ crystal has a tetragonal lattice, space group of which is $I4_1/amd$ with $a = 1.03092$ nm, $c = 2.07288$ nm, and the unit cell is doubled along one axis due to a superlattice ordering of Sb(III) and Sb(V) at low temperatures. Each $Sb(III)Cl_6^{3-}$ is surrounded by eight $Sb(V)Cl_6^-$ and four $Sb(III)Cl_6^{3-}$, the latter at the corners of a tetrahedron. The eight cesium ions sit at the corners of a cube centered on the $Sb(III)Cl_6^{3-}$. They show less than 0.5° angular distortion of the $SbCl_6^-$ but a small (2.5°) $D_{2d}$ distortion of $SbCl_6^{3-}$ in contrast to $(NH_4)_2SbCl_6$ [3]. The bond lengths between Sb and Cl are 0.2646 nm and 0.2384 nm for Sb(III) and Sb(V), respectively.

The most interesting question is whether electron transfer between Sb(III) and Sb(V), in other words, mixing of the valence states occurs or not. Regarding to this point, much theoretical [4], and experimental works such as Mössbauer [5], far infrared [6], Raman [7], visible [8, 9], photoelectron spectra [10] and D. C. conductivity [11] have been performed. Among these, UV absorption spectra, Mössbauer, photoelectron spectroscopy and conductivity measurements have confirmed the existence of distinguishable $Sb(III)Cl_6^{3-}$ and $Sb(V)Cl_6^-$ anions. Atkinson and Day estimated from optical absorption measurements that the mixing of valence states is smaller than 0.1% at room temperature. Recent measurements of far infrared and Raman spectra suggested that the degree of delocal-

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ization of the Sb oxidation states decreases on cooling [6]. Possible mechanisms for the valence mixing have been investigated.

The chemical exchange in solids can be detected by NMR [12]. In particular, the quadrupole interaction is rather sensitive to fluctuations of the electric field gradient (EFG) and has extensively been used to study the molecular and lattice dynamics in solid [13].

In this work we perform $^{121}$Sb (spin 5/2) solid state NMR measurements at various temperatures to study the possible valence mixing, that is to check the existence of the Sb(IV) oxidation state. In addition we calculate the energies of the electronic state in Sb(III)$Cl_6^{3-}$, Sb(V)$Cl_6^-$, Sb(III)$Cl_6^{2-}$ and Sb(V)$Cl_6^{2-}$ to estimate the transition energy and degree of mixing of the valence states.

## Experimental

### *Sample Preparation*

The compound $Cs_2SbCl_6$ was prepared by the method described by Atkinson and Day [9]. Stock solutions of $Sb_2O_3$, $Sb_2O_5$ in 12M-HCl were mixed and the mixture was warmed, then the CsCl HCl solution was added to it. The deep purple precipitates of $Cs_2SbCl_6$ immediately collected and filtered. The sample was dried by storing over $P_2O_5$ in a vacuum desiccator.

### *$^{121}$Sb NMR Spectra Measurements*

NMR measurements were carried out with a Bruker Model MSL-200 spectrometer operating at a Larmor frequency of 48 MHz for $^{121}$Sb. The central transitions $(-1/2 \leftrightarrow 1/2)$ of $^{121}$Sb NMR were measured with solid echo pulse sequence [14]. The $\pi/2$ pulse width for central transition was 7 μsec. Temperature control was achieved by the Bruker variable temperature unit VT-1000 within ±1 K.

### *Molecular Orbital Energy Calculation*

We carried out SCF-MS-X$\alpha$ molecular orbital calculations on $SbCl_6$ anions in order to study the possibilities of valence mixing in the $Cs_2SbCl_6$ crystal. This method has been used successfully be several authors to study the electronic state and the quadrupole interaction in various molecules containing very heavy elements [15]. All calculations were carried out using the SCF-MS-X$\alpha$ program XASW obtained from QCPE [16]. The $\alpha$ values proposed by Schwartz for free atoms were used for atomic regions while the innersphere and outersphere values were taken as the valence-electron number-averages of the atomic values. The Normal reduction factor was chosen to be 0.80 [17]. The parameters used for the calculations are listed in Table 1. The experimental geometries of the anions were taken from [2]. The point group of all anions is $D_{4h}$; 5 s, 5 p, and 4 d orbitals of Sb, and 3 s and 3 p orbitals of Cl were taken as the valence orbitals and the other inner orbitals were treated as part of the core. The tangent Watson spheres [18] with the appropriate positive charges were used to account for the negative charges of the complex anions (see in Table 1). The spin restricted Hartree-Fock-Slater calculations were carried out, and the iterative SCF procedure was stopped when the maximum relative change in the potential was $<10^{-4}$.

Table 1. Parameters used in the X$\alpha$ calculations.

| Anion | $\alpha_{out}$ | Sphere radii (a.u.) | | | | |
|---|---|---|---|---|---|---|
| | | $R_{out}$ | $R$(Sb) | $R(Cl_{ax})^a$ | $R(Cl_{eq})^b$ | $R_{Watson}{}^c$ |
| Sb(III)$Cl_6^{3-}$ | 0.71871 | 7.3582 | 3.1574 | 2.5592 | 2.5593 | 7.70718 |
| Sb(V)$Cl_6^-$ | 0.71934 | 6.8373 | 3.0058 | 2.5235 | 2.5217 | 7.18146 |
| Sb(III)$Cl_6^{2-}$ [d] | 0.71902 | 7.3798 | 3.2893 | 2.5808 | 2.5809 | 7.73171 |
| Sb(V)$C_6^{2-}$ [e] | 0.71902 | 6.8284 | 2.8961 | 2.5146 | 2.5126 | 7.17131 |

[a] Axial chlorine; Equatorial chlorine; [c] Watson sphere radius; [d] Charge-tranfered anion with the Sb(III)$Cl_6^{3-}$ structure; [e] Charge-transfered anion with the Sb(V)$Cl_6^-$ structure.

## Results and Discussion

### *$^{121}$Sb NMR for $Cs_2SbCl_6$*

Figure 1 (a) shows the $^{121}$Sb NMR spectrum of cesium hexachloroantimonate(III, V) observed at room temperature. The spectrum consists of two peaks at nearly zero and 30 kHz from an external reference signal of $^{121}$Sb in $Sb_2O_5$ in conc. HCl solution. The high field line is strong and sharp without any structure. The low field signal is weak and broad with a significant structure, indicating that this signal represents the central transition in the presence of second order quadrupole interaction. We compared the spectrum of $Cs_2SbCl_6$ with those of $Sb_2O_5$ (Fig. 1 (b)) and $Sb_2O_3$ (Fig. 1 (c)) in concentrated HCl solutions and assigned the high field line to $^{121}$Sb in Sb(V)$Cl_6^-$ and

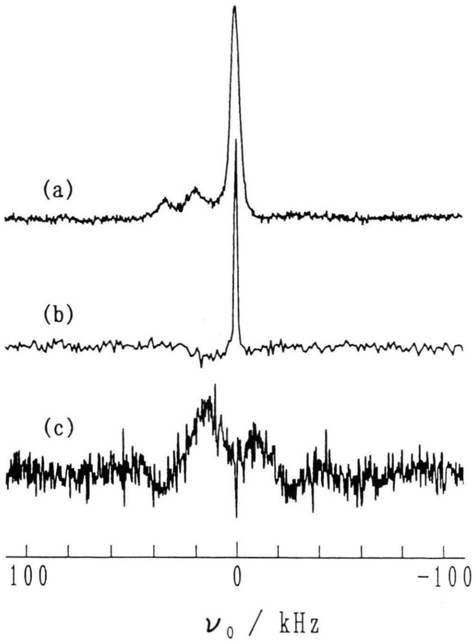

Fig. 1. The $^{121}$Sb NMR spectra observed at room temperature of $Cs_2SbCl_6$ (a), $Sb_2O_5$ in conc. HCl solution (b) and $Sb_2O_3$ in conc. HCl solution (c). The chemical shift scale is measured from $^{121}$Sb in an external reference sample of $Sb_2O_5$ in conc. HCl solution.

the low field one to $^{121}$Sb in Sb(III)$Cl_6^{3-}$. The spectrum of $Sb_2O_5$ is sharp and could be measured with a good S/N ratio and so we used its spectrum as the external reference for the antimony chemical shift. The spectrum of $Sb_2O_3$ is very broad due probably to unfavorable relaxation process of the spin state of Sb(III).

The observed sharp and structureless peak of $^{121}$Sb(V) suggests that the quadrupole interaction of Sb(V) in Sb(V)$Cl_6^-$ anion is zero. On the other hand the quadrupole interaction for Sb(III) is finite; we estimated its quadrupole coupling constant from the splitting of the spectrum to be 4.9 ± 0.5 MHz at 285 K. The asymmetry parameter of the EFG-tensor, $\eta$, is zero because the Sb(III) anion locates on the four-fold symmetry axis of the crystal. These results are consistent with the results of $^{121}$Sb Mössbauer effect experiments of this compound by Donaldson and coworkers. They postulated that the $e^2Qq/h$ is zero for Sb(V) but finite for Sb(III), though they did not determine its value [5]. The finite quadrupole coupling constant for Sb(III) is also supported by the neutron diffraction study of this compound [2].

### *Temperature Dependence of the Quadrupole Interaction in $Cs_2SbCl_6$*

Possible electron transfer between Sb(III)$Cl_6^{3-}$ and Sb(V)$Cl_6^-$ have been discussed by number of workers as we stated in Introduction. If this process can happen to occur and the resultant charge-transferred state has a finite lifetime, the process can be regarded as a thermally activated process or a photo-excited electronic process. The population of the charge-transferred mixed-valence state, Sb(III)$Cl_6^{2-}$ + Sb(V)$Cl_6^{2-}$, $n_{mv}$ is then given by

$$\frac{n_{mv}}{n_g} = \exp\left(\frac{-\Delta E}{RT}\right), \qquad (1)$$

where $n_g$ is the population of the original ground state and $\Delta E$ denotes the excitation energy to the mixed-valence state. Since the quadrupole coupling depends sensitively on the electronic state of the anions, it depends on temperature as a result of thermal activation of the valence-mixed state. We measured the temperature dependence of the $^{121}$Sb NMR spectrum as shown in Figure 2. No significant change was ob-

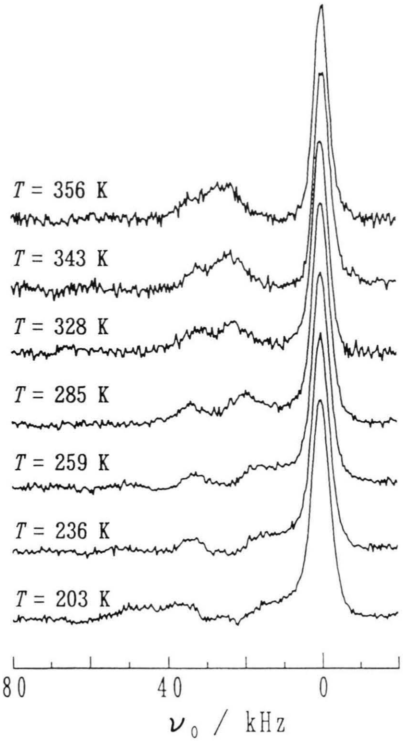

Fig. 2. The temperature dependence of the $^{121}$Sb NMR spectrum in $Cs_2SbCl_6$.

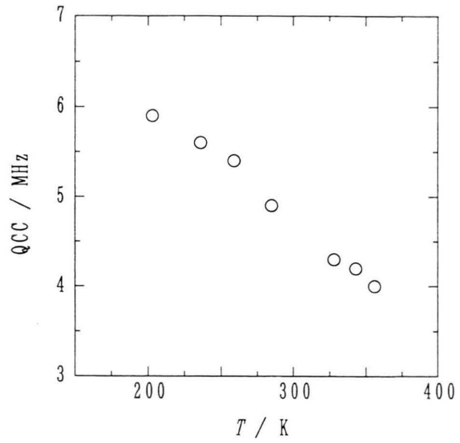

Fig. 3. The temperature dependence of the quadrupole coupling constant (QCC) for Sb(III) nucleus.

served in the Sb(V) peak except that its linewidth is reduced by only 1 kHz on heating from 203 K to 356 K. On the other hand the line shape of the Sb(III) signal varied drastically with temperature. The quadrupole coupling constant (QCC) estimated from the line shape is plotted against temperature in Figure 3. The QCC decreases almost linearly with temperature from 6 MHz at 203 K to 4 MHz at 356 K. The temperature coefficient of the quadrupole coupling constant is obviously too large to be accounted for by the usual Bayer effect [19]. Such a large temperature coefficient of the quadrupole resonance frequency of the central antimony nucleus of $Sb(III)Cl_6^{3-}$ may be attributed to the valence mixing as was mentioned above. However, there may be other reasons for the drastic temperature dependence of the quadrupole interaction in the complex anions. One is an anisotropic thermal expansion of the crystal lattice, i.e., a decrease in the ratio $c/a$ on heating, which can cause changes in the shape of the anions and therefore in the quadrupole interaction of the central antimony nucleus in $Sb(III)Cl_6^{3-}$. It can not be ruled out that the anisotropic change in the geometrical shape of the anion is triggered by the valence mixing.

## *Electronic Structure of $SbCl_6$ Anions*

The 33 valence orbitals in the octahedral complex anions which have $D_{4h}$ symmetry fall into eight groups according to orbital composition $6A_{1g}+A_{2g}+3B_{1g}+2B_{2g}+4A_{2u}+B_{2u}+3E_g+5E_u$. We calculated the orbital energies, the total electronic energies, and the EFG-tensor values for $Sb(III)Cl_6^{3-}$, $Sb(V)Cl_6^-$, $Sb(III)Cl_6^{2-}$, and $Sb(V)Cl_6^{2-}$. The calculated total energies of the ionic species, the virial ratios and the strength of the EFG's at the antimony sites are listed in Table 2. The calculated values of the prinicpal components of the EFG in all ionic species indicate that the asymmetry parameter, $\eta$, is zero in all ionic species, being consistent with the tetragonal point group of these ions in the crystal. The EFG at the antimony site in $Sb(V)Cl_6^-$ is negligibly small but finite at the central antimony site in $Sb(III)Cl_6^{3-}$. Thus the MS-Xα calculation can interpret the experimental QCC in both complex ions in a qualitative manner. However, the values of the principal components of the EFG obtained in the present calculation are too large compared with those for the antimony nucleus in $SbCl_3$ molecule [20] obtained by the use of the same MS-Xα program, as can be seen in Table 2.

Day and his collaborators studied the electronic spectra and other properties of $Cs_2SbCl_6$ and its analogous series materials experimentally and theoretically and proposed the charge-transfer mechanism for these mixed valence compounds [8, 9]: They stated that among the large number of valence orbitals mentioned above the valence mixing can be realized between an occupied $A_{1g}$ orbital of Sb(III) in $Sb(III)Cl_6^{3-}$ and an unoccupied $A_{1g}$ orbital of Sb(V) in $Sb(V)Cl_6^-$ as [9]

$$(5\,s_A^2,\ ^1A_{1g})(5\,s_B^0,\ ^1A_{1g})^1\Sigma^+ \\ \rightarrow (5\,s_A^1,\ ^2A_{1g})\,5\,s_B^1,\ ^2A_{1g})^1\Sigma^-,$$

where the A-site ion is $Sb(III)Cl_6^{3-}$ and the B-site one is $Sb(V)Cl_6^-$ in the ground state. We found in our calculations that the corresponding $A_{1g}$ orbitals are

Table 2. Total energies, virial ratios, and principal EFG values at Sb sites in complex anions.

| Anion | Total energy ($10^4$ Ry) | Virial ratio | EFG/a.u.[a] | |
|---|---|---|---|---|
| | | | $V_{xx}$, $V_{yy}$ | $V_{zz}$ |
| $Sb(III)Cl_6^{3-}$ | −1.8139871 | 1.999587 | −3.7570 | 7.5140 |
| $Sb(V)Cl_6^-$ | −1.8143087 | 2.000139 | 0.0037 | −0.0074 |
| $Sb(III)Cl_6^{2-}$ [b] | −1.8138040 | 1.999661 | −7.9695 | 15.9390 |
| $Sb(V)Cl_6^{2-}$ [c] | −1.8142453 | 1.999865 | | |
| $SbCl_3$ [d] | −1.5379329 | 1.999631 | −0.3510 | 0.7020 |

[a] The $z$-axis denotes the four-fold symmetry axis of the crystal; [b] Charge-transfered anion with the $Sb(III)Cl_6^{3-}$ structure; [c] Charge-transfered anion with the $Sb(V)Cl_6^-$ structure; [d] The EFG at the antimony site. The $z$-axis is the three-fold symmetry axis of the molecule. $e^2Qq/h$ ($^{121}$Sb) = 489.21 MHz for $SbCl_3$.

located at $-0.3592752$ Ry and $-0.2126121$ Ry in Sb(III)$Cl_6^{3-}$ and Sb(V)$Cl_6^-$, respectively. The wave length of the electronic transition between these orbitals is 621 nm; the charge-transfer absorption gives rise to a greenish blue colour, being consistent with the dark blue colour of the substance.

In order to discuss the possible influence of the valence mixing on the antimony quadrupole coupling and other physical properties of the $Cs_2SbCl_6$ crystal at ambient temperature it is necessary to evaluate the number of excited mixed valence state, $n_{mv}$, given in (1). We assume that $-\Delta E$ in (1) can roughly be regarded as the difference between the total electronic energies of the excited and the ground states of the anions. This energy difference is calculated to be 2.465 Ry (see Table 2), indicating that any trace of the excited mixed valence state can not exist at ambient temperature. Hence the drastic temperature dependence of the antimony quadrupole coupling constant in Sb(III)$Cl_6^{3-}$ is attributed to the anisotropic thermal expansion of the crystal which would bring about a decrease of the $c/a$ ratio in the unit cell on heating.

## Conclusion

The central transitions of the $^{121}$Sb NMR spectrum were observed in $Cs_2SbCl_6$ crystal and the quadrupole coupling constant was estimated to be $4.9 \pm 0.5$ MHz for Sb(III)$Cl_6^{3-}$ and zero for Sb(V)$Cl_6^-$ at room temperature. A very large temperature coefficient of the quadrupole coupling constant was observed and examined from the view points of valence mixing and lattice distortion. A molecular orbital energy calculation by the MS-Xα method can interpret the colour of the compound but predicts that there is little possibility for the existence of the excited mixed valence state at ambient temperature. The temperature dependence of the quadrupole interaction was attributed to an anisotropic thermal expansion of the crystal lattice.

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