A $^{35}$Cl NQR Study on Cs$_2$[Au$^I$Cl$_2$][Au$^{III}$Cl$_4$]*

A. Ishikawa, M. Kurasawa, S. Kitahara, A. Sasane, N. Kojima$^a$, and R. Ikeda$^b$

Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390, Japan

$^a$ Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Tokyo 153, Japan

$^b$ Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan

Z. Naturforsch. 53a, 590–594 (1998); received December 31, 1997

A pair of $^{35}$Cl NQR spin echo signals has been observed for the mixed valence complex Cs$_2$[Au$^I$Cl$_2$][Au$^{III}$Cl$_4$] between 77 and 243 K. At 77 K, two resonance lines with the half widths $\Delta v_0$ = 50 kHz were located at $v_0$ = 17.28 MHz for the Au$^I$-Cl chlorine and at $v_0$ = 27.10 MHz for the Au$^{III}$-Cl chlorine in accordance with the crystal structure. The chloronic chlorine characters of the Au$^I$-Cl and Au$^{III}$-Cl bonds are estimated as 0.63 and 0.42, respectively. The central gold atom carries a fractional protonic charge of 0.26 in [Au$^I$Cl$_2$]$^-$ and 0.68 in [Au$^{III}$Cl$_4$]$^2-$. The charge distributions in the complex anions differ significantly from those in the isolated [AuCl$_2$]$^-$ and [AuCl$_4$]$^2-$ for ordinary complexes, indicating that the charge transfer interactions between the anions are weak in the mixed valence complex. The observed linear temperature dependencies of $V_g$ and log $T_Q$ are well explained by the lattice vibration. When the temperature was increased from 77 K, the resonance lines became gradually weak without changing $\Delta v_Q$ and immeasurable above 215 K. ESR spectra taken at various temperatures revealed the presence of paramagnetic sites of ca. $5 \times 10^{23}$ mol$^{-1}$ arising from Au(II). The small but finite concentration of Au(II) or some other reason should be responsible for the fade out phenomenon and the large $\Delta v_Q$ observed.

**Key words:** $^{35}$Cl NQR Frequency, $^{35}$Cl NQR Spin-lattice Relaxation, Mixed Valence Gold Complex, Charge Transfer Interaction, ESR.

**Introduction**

Cs$_2$[Au$^I$Cl$_2$][Au$^{III}$Cl$_4$] crystallizes in the tetragonally distorted perovskite structure, space group I4/mmm with axes $a$ = 749.5 and $c$ = 1088.0 pm, $Z$ = 2 [1–3]. In the crystal, linear and symmetric [Au$^I$Cl$_2$]$^-$ and square planar [Au$^{III}$Cl$_4$]$^2-$ are stacked alternately, forming the chlorine bridged networks of Au$^I$-Cl–Au$^{III}$ along the c-axis and of Au$^{III}$-Cl–Au$^I$ in the plane perpendicular to the c axis, as shown in Figure 1. The reported rather long interatomic distances of Cl–Au$^{III}$ (315.9 pm) and Cl–Au$^I$ (300.5 pm) compared with the bond lengths of Au$^I$-Cl (228.1 pm) and Au$^{III}$-Cl (229.5 pm) suggest that the Au$^I$–Au$^{III}$ charge transfer interactions are weak [2]. Although the ordinary gold (I, III) complexes form colorless ([AuCl$_2$]$^-_$) or pale yellow ([AuCl$_4$]$^2-$) crystals, the title compound crystallizes in an astonishingly jet black color as described by the discoverer [4], indicating the Au$^I$–Au$^{III}$ interaction to be present in the crystal. Therefore the complex may be classified as a class II mixed valence compound [5].

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

Reprint requests to Prof. A. Sasane; Fax: +81-263-37-2559.

Since the discovery of super conductivity in perovskite type oxides, the mixed valence system R$_2$[Au$^I$X$_2$][Au$^{III}$X$_4$] (R = Cs, Rb; X = Cl, Br, I) has been extensive-
ly studied by workers including one of the present authors [6–8]. However, no study has been carried out about this system by NQR technique. The present experiments have been undertaken to clarify the charge distribution in [Au''Cl₂]⁻ and [Au'''Cl₄]⁻ and the lattice dynamics of the complex anions.

**Experimental**

A home made pulsed spectrometer was used for the observation of ³⁵Cl NQR [9]. The line shape of the resonances was determined by monitoring the dependence of the spin echo amplitudes on the rf frequencies. The pulse sequence $\pi/2 - \tau - \pi/2 - \tau_e - \pi$ was employed for the measurements of the spin-lattice relaxation time $T_{1Q}$, where $\tau_e$ was set to be ca. 350 µs throughout the experiments. The signal amplitudes decreased exponentially with $\tau$ in all measurements.

ESR spectra were recorded on a JEOL JES-FE1XP X-band spectrometer. The spectra were calibrated using the spectrum of Mn²⁺ diluted in MgO.

Magnetic susceptibilities were measured by a vibrating sample magnetometer VSM-5/5SC from Toei Industry.

Two kinds of polycrystalline samples were employed. One (I) was prepared by the Bridgman method [2] and successively purified in concentrated hydrochloric acid by the thermal diffusion method. The other (II) was prepared in a similar way as described in [4] and then purified by sublimation.

**Results and Discussion**

³⁵Cl NQR $v_Q$

At 77 K, two ³⁵Cl NQR spin echo signals arising from Cs₂[Au'Cl₂][Au'''Cl₄] were observed at $v_{Q1} = 17.28$ MHz and $v_{Q2} = 27.10$ MHz (Fig. 2), indicating that there are two kinds of nonequivalent chlorine atoms in the crystal. This agrees with the results of X-ray analyses [1–3]. (Two other signals, located at 13.61 and 21.34 MHz, were assigned to corresponding ³⁷Cl NQR.) The large difference between $v_{Q1}$ and $v_{Q2}$ suggests that the two kinds of chlorine have clearly distinguishable bonding characters in the crystal. Since the crystal consists of fairly isolated complex anions, linear and symmetric [Au'Cl₂]⁻ and square planer [Au'''Cl₄]⁻, one of the $v_Q$ should be assigned to the Au'Cl and the other to the Au'''-Cl chlorine. ³⁵Cl NQR studies [10–13] have been accompanied by X-ray analyses in a wide variety of tetrachloroaurates(III) (Table 1). When the reported ³⁵Cl NQR $v_Q$ are plotted against the Au(III)-Cl bond lengths $L$, a good linear correlation is obtained, as shown in Figure 3. The observed $v_{Q2} = 27.10$ MHz and reported $L = 229.5$ pm [2] corroborate this correlation. Therefore $v_{Q2}$ is attributable to the Au'''-Cl chloride. The signal at $v_{Q1} = 17.28$ MHz falls within the range of ³⁵Cl NQR $v_Q = 17–18$ MHz in the various linear dichloroaurates(I) [14, 15] and can be assigned to the Au' -Cl chloride.

The ionic characters $i$ of the Au' -Cl and Au'''-Cl bonds have been estimated as 0.63 and 0.42, respectively, by the Townes and Dailey method [16]. The central gold atom carries a fractional protonic charge $p$ of 0.26 in [Au'Cl₂]⁻ and 0.68 in [Au'''-Cl₄]⁻. The charge distribu-

![Fig. 2. ³⁵Cl NQR spectra for $v_{Q1}$ ([Au'Cl₂]⁻) and $v_{Q2}$ ([Au'''Cl₄]⁻) lines at 77 K.](image-url)
Table 1. Au(III)-Cl bond length $L$ and $^{35}$Cl NQR frequencies $v_Q$ at 77 K in tetrachloroaurates(III).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$L$/pm</th>
<th>Ref.</th>
<th>$v_Q$/MHz</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[AuCl$_4$] · 2 H$_2$O</td>
<td>226.0</td>
<td>a</td>
<td>29.47</td>
<td>[10, 11]</td>
</tr>
<tr>
<td></td>
<td>227.8</td>
<td>a</td>
<td>28.87</td>
<td>[10, 11]</td>
</tr>
<tr>
<td></td>
<td>228.3</td>
<td>a</td>
<td>28.00</td>
<td>[10, 11]</td>
</tr>
<tr>
<td></td>
<td>228.8</td>
<td>a</td>
<td>25.36</td>
<td>[10, 11]</td>
</tr>
<tr>
<td></td>
<td>228.6</td>
<td>b</td>
<td>27.65</td>
<td>[11]</td>
</tr>
<tr>
<td>K[AuCl$_4$]</td>
<td>228.5</td>
<td>c</td>
<td>27.76*</td>
<td>[11]</td>
</tr>
<tr>
<td>K[AuCl$_4$] · 2 H$_2$O</td>
<td>228.5</td>
<td>d</td>
<td>28.18</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>229.1</td>
<td>d</td>
<td>27.14</td>
<td>[11]</td>
</tr>
<tr>
<td>SeCl$_3$[AuCl$_4$]</td>
<td>226.6</td>
<td>e</td>
<td>32.67</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>228.9</td>
<td>e</td>
<td>26.98</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>229.4</td>
<td>e</td>
<td>26.92</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>230.1</td>
<td>e</td>
<td>24.04</td>
<td>[12]</td>
</tr>
<tr>
<td>guH[AuCl$_4$]</td>
<td>228.8</td>
<td>f</td>
<td>28.15</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>228.8</td>
<td>f</td>
<td>28.30</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>229.1</td>
<td>f</td>
<td>28.06</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>229.3</td>
<td>f</td>
<td>27.88</td>
<td>[13]</td>
</tr>
<tr>
<td>Cs$_2$[Au$^{1}$Cl$_2$][Au$^{III}$Cl$_4$]</td>
<td>229.5</td>
<td>[2]</td>
<td>27.10**</td>
<td></td>
</tr>
</tbody>
</table>

*Average value.
**Present study.

A. Ishikawa et al. - A $^{35}$Cl NQR Study on Cs$_2$[Au$^{1}$Cl$_2$][Au$^{III}$Cl$_4$]

Fig. 3. Relation between Au(III)-Cl bond length and $^{35}$Cl NQR frequency. Full circles represent Na[AuCl$_4$] · 2 H$_2$O, open circles SeCl$_3$[AuCl$_4$], full squares Rb[AuCl$_4$], open squares K[AuCl$_4$] · 2 H$_2$O, full triangles guH[AuCl$_4$], open triangle K[AuCl$_4$], and cross Cs[Au$^{1}$Cl$_2$][Au$^{III}$Cl$_4$].
Temperature Dependence of $v_Q$ and $T_{1Q}$

The temperature dependence of $^{35}\text{Cl}$ NQR $v_{Q1}$ and $v_{Q2}$, determined from the spin echo signals of Cs$_2$[AuCl$_2$][AuIICl$_4$], is shown in Figure 4. When the temperature was increased from 77 K, the spectra became gradually weaker without changing $\Delta v_Q$ (Figure 5). The echo signals were observable up to 243 K, although the frequencies were indeterminable above 215 K. The temperature coefficient of $v_{Q1}$ is roughly twice as large as that of $v_{Q2}$. This means that the libration of [AuCl$_2$]$^-$ is more easily exited in the crystal lattice. The temperature dependence of $v_Q$ can be expressed by the Bayer-Kushida equation [21]. By introducing the effective angular frequency $\omega_{\text{eff}}$ of the lattice vibration and the effective moment of inertia $I_{\text{eff}}$ associated with the vibration, in the high temperature approximation, the equation can be rewritten as

$$v_Q = v\left[1 - \frac{3kT}{2I_{\text{eff}}\omega_{\text{eff}}^2} - \frac{\hbar^2}{8I_{\text{eff}}kT}\right],$$  

where $v$ represents the NQR frequency in a fictitious vibrationless state. Applying (1) on the data shown in Fig. 4, $v = 17.64 \text{ MHz}$, $\omega_{\text{eff}}/2\pi = 154 \text{ cm}^{-1}$ and $I_{\text{eff}} = 1.6 \times 10^{-46} \text{ kg m}^2$ have been obtained for $v_{Q1}$ and $v = 27.25 \text{ MHz}$, $\omega_{\text{eff}}/2\pi = 168 \text{ cm}^{-1}$ and $I_{\text{eff}} = 5.4 \times 10^{-46} \text{ kg m}^2$ for $v_{Q2}$. The value of $I_{\text{eff}}$ for [AuIICl$_4$]$^-$ motion is about three times larger than $I_{\text{eff}}$ for [AuCl$_2$]$^-$ motion. The well separated values of $\omega_{\text{eff}}$ and $I_{\text{eff}}$ between the complex anions suggest that the associated motions are isolative. The smaller value of the effective force constant, $I_{\text{eff}}\omega_{\text{eff}}^2$ for [AuCl$_2$]$^-$ than for [AuIICl$_4$]$^-$ suggests that the interaction between the anions are stronger in the plane perpendicular to the $c$ axis than those along the $c$ axis, in accordance with the crystal structure [2, 6].

$^{35}\text{Cl} T_{1Q}$ was determined as 1.2 and 0.55 s for $v_{Q1}$ and $v_{Q2}$, respectively at 77 K on the center frequency of the resonance lines. Upon heating, the difference in the $T_{1Q}$
became small and nearly the same of 34 ms at 193 K, as shown in Figure 6. Above 193 K, the signal intensities were too weak to determine $T_{1Q}$. Below 153 K, $T_{1Q}$ was proportional to $T^{-n}$, where $n$ was determined as 2.1 for $v_{Q1}$ and 1.8 for $v_{Q2}$. The close value of the exponent $n = 2.0$ suggests that the lattice vibration of the complex anions is responsible to the relaxation [22]. Above 153 K, $T_{1Q}$ deviates from the proportionality suggesting the presence of other relaxation mechanisms. A rapid $^{35}$Cl NQR $r_{1Q}$ decrease, observed in CsPbCl$_3$ (perovskite structure) above 300 K, was attributed to the reorientation of [PbCl$_6$]$_2^-$ octahedra [23]. Sharp decreases of $^{35}$Cl NQR $T_{1Q}$ caused by the reorientation of the complex anions have been reported even at relatively low temperatures in various octahedral [24, 25] and square planer [26] metal complexes as well. The migration of the lattice defects also contributes to the reduction $T_{1Q}$ [27]. The $^{35}$Cl NQR $T_{1Q}$ above 153 K can be considered to be strongly affected by the rotational motion of the complex anions or/and the existence of paramagnetic sites as lattice defects.

Acknowledgement

We appreciate the experimental assistance of Mr. H. Enokibori and Mr. M. Ohta. We are also grateful to Mr. N. Kimura for recording the ESR spectra and to Dr. Y. Amako for measuring the magnetic susceptibilities.