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# $^{63}$Cu High Resolution NMR of Cu(I) Halides in Aqueous Solution and Suspension

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In an aqueous solution, $^{63}$Cu chemical shielding order ($[CuCl_4]^{3-} \simeq [CuBr_4]^{3-} < [CuI_4]^{3-}$) and line widths (10 to 30 kHz) for CuX-KX systems(where X=Cl, Br, I) have been obtained. The chemical shift(−694 ppm) between $[CuCl_4]^{3-}$ and $[Cu(CN)_4]^{3-}$ is interpreted by the paramagnetic term which depends mainly upon a 3d-hole on a Cu(I) atom by using perturbation theory with an average excitation energy approximation. The line-broadening of Cu(I) halide complexes in aqueous solution is explained dominantly by a Cu(I) nuclear quadrupole interaction with the electric field gradient which arises from a 3d-hole on a Cu atom. For the abnormal increasing metal shielding order of $[MX_4]^{(4-i)-}$($[MCl_4]^{(4-i)-} \leqslant [MBr_4]^{(4-i)-} < [MI_4]^{(4-i)-}$), a possibility of the heavy-atom effect in the metal shielding of $[CuI_4]^{3-}$(649 ppm, using the lowest excitation energy of the diatomic molecule) and $[CdI_4]^{3-}$(1941 ppm using the lowest excitation energy of the diatomic molecule), is evaluated.

It is known that copper(I) halides are photosensitive and semiconductive materials. We think that it is a useful step for determing new materials to study the electronic structure of metal complexes as well as the nature of the chemical bond between metal and ligand. Magnetic properties have long been powerful tools for studies of the electronic structures of transitionmetal complexes. Recently, there have been published a number of papers[1-4] on experimental NMR studies of metal complexes in solid and liquid solution. These studies can be approached from both experimental and theoretical points of view. As one part of a continuing investigation, we have reported $^{109}$Ag NMR and MO theoretical studies.[5,6] We now describe a $^{63}$Cu high-resolution NMR investigation of nuclear relaxation and chemical shifts for Cu(I) halides in aqueous solution, elucidating correlations with electronic structure in these complexes.

To our knowledge, there were several $^{63}$Cu and $^{65}$Cu NMR investigations[4a,4b,7,8] dealing with copper(I) halides. Of these studies, Guenther et al.[7] performed a detailed investigation on $^{63}$Cu spin-lattice relaxation for solid-state CuX. Lutz et al.[4b] observed that the Cu chemical shift in solid CuX indicates a remarkable increasing shielding order (CuCl ⩽ CuI < CuBr) which does not show a linear dependence on the atomic number of the halide ligand. There have, until now however, been no theoretical study reported for the Cu chemical shift in solid CuX of a repetitive zinc-blende structure. This is because immense time and funds are needed for computer calculations using the ab initio SCFMO method. Thus, first it is necessary to investigate the Cu chemical shift in gaseous and solution-state Cu(I) halides.

Nakatsuji et al.[6] studied the metal chemical shielding constants in Cu, Zn, Ag, and Cd complexes by the ab initio finite perturbation SCF method. For the metal complexes, whose electronic configurations are primarily $d^{10}s^{1-2}p^0$, the metal chemical shifts are due mainly to the paramagnetic term, which depends upon the electrons in the valence np orbital and the holes in the valence (n-1) d orbital. For the Cu complexes(CuCl, $[CuCl_4]^{3-}$, $[Cu(CN)_4]^{3-}$, $[Cu(NH_3)_2]^+$), the d orbital mechanism is predominant. To obtain a physical picture of the Cu shielding of Cu(I) complexes($[CuCl_4]^{3-}$, $[Cu(CN)_4]^{3-}$), a simplified calculation was performed using perturbation theory,[5,9] with an average excitation energy approximation.

This paper presents representative $^{63}$Cu NMR spectra obtained from aqueous solutions and suspensions of Cu(I) halides, and provides a theoretical interpretation of the Cu chemical shift and linewidth. We suggest from a qualitative perturbation theory that the Cu chemical shielding is governed by a paramagnetic term, which depends upon a 3d-hole of the Cu(I) atom. For the increasing metal shielding order of $[MX_4]^{(4-i)-}$, we propose the possibility of an effect due to the heavy atom on the metal shielding of $[CuI_4]^{3-}$ and $[CdI_4]^{2-}$. The line-broadening in aqueous solution can be interpreted dominantly by a Cu(I) nuclear quadrupole interaction with the electric field gradient which arises from a 3d-hole in the Cu(I) atom. Lastly, the Cu chemical-shielding difference($[CuCl_4]^{3-} <$ CuCl ⩽ CuI $< [CuI_4]^{3-}$) between a suspension CuX and solution $[CuX_4]^{3-}$ is discussed qualitatively from the standpoint of structure.

## Experimental

**Materials.** $[Cu(CH_3CN)_4]BF_4$ was prepared by a method described in the literature.[10] The compound was checked by elementary analysis and an optical absorption method with the aid of the absorbance at 440 nm of a derived bis(2,2′-bipyridine)copper(I) in acetone($\varepsilon_{max}$=4800 $M^{-1}\,cm^{-1}$ (1 M=1 mol $dm^{-3}$)). All chemicals except an NMR reference sample used here were commercially available.

**NMR Measurements.** All $^{63}$Cu spectra were measured at 71.50 MHz with a FX-270 spectrometer. Between 1000 and 10000 transients were accumulated using a 17.5 μs (90°) pulse; 16 K data points were collected over a band width of 50 kHz. These measurements were made at temperature of 30 °C.

Before we measured solutions and suspensions, the samples were bubbled with nitrogen gas for three minutes. The molar ratio of CuX to water for the CuX suspension was 1/28. All $^{63}$Cu spectra were externally referenced to liquid

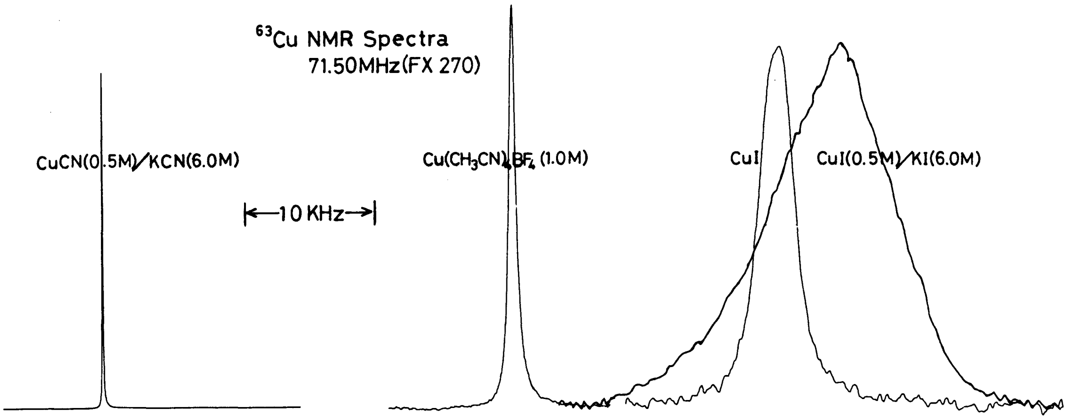


Fig. 1. $^{63}$Cu NMR spectra for Cu(I) compounds in aqueous solution and suspension at 71.50 MHz.

Table 1. Chemical Shifts and Linewidths for $^{63}$Cu Resonance and Mole Fraction of Cu(I) Complexes for Cu(I) Halides in Aqueous Solution and Suspension at 30 °C

| Cu(I) salt | Chemical shift$^{a)}$ (ppm) | linewidth (Hz) | Mole fraction(%) CuX(s) | Cu$^+$ | [CuX$_2$]$^-$ | [CuX$_3$]$^{2-}$ | [CuX$_4$]$^{3-}$ | X$^-$ (M) |
|---|---|---|---|---|---|---|---|---|
| CuCl(suspension) | −331 | 3500 | 100 | | 0 | 0 | 0 | |
| CuCl(0.5M)/KCl(4.0M) (aqueous solution) | −200 | 28000 | 0 | 0 | 3.4 | 22.3 | 74.3 | 2.7 |
| CuBr(suspension) | −388 | 3800 | 100 | 0 | 0 | 0 | 0 | |
| CuBr(0.5M)/KBr(4.0M) (aqueous solution) | −200 | 21000 | 0 | 0 | 0 | 2.0 | 98.0 | 2.5 |
| CuI(suspension) | −330 | 2700 | 100 | 0 | 0 | 0 | 0 | |
| CuI(0.5M)/KI(6.0M) (aqueous solution) | −434 | 12500 | 0 | 0 | 0.3 | 13.6 | 86.1 | 4.6 |
| [Cu(CH$_3$CN)$_4$]BF$_4$ | 0 | 600 | | | | | | |
| CuCN(0.5M)/KCN(6.0M) (aqueous solution) | 494 | 70 | 0 | 0 | 0 | 0.4 | 99.6 | 4.5 |

a) More positive values refer to lower shielding. The reference sample is a 1.0 molar solution of [Cu(CH$_3$CN)$_4$]BF$_4$ in CH$_3$CN.

1.0 M [Cu(CH$_3$CN)$_4$]BF$_4$ in CH$_3$CN. All chemical shifts for $^{63}$Cu are defined by

$$\Delta\delta_{\mathrm{sam}} = (\nu_{\mathrm{sam}} - \nu_{\mathrm{ref}})/\nu_{\mathrm{ref}},$$

where $\nu_{\mathrm{sam}}$ is the resonance frequency of a sample and $\nu_{\mathrm{ref}}$ is the reference frequency. Shifts defined in this manner are positive for lower shielding. The linewidth was evaluated from the widths at half-height. The line shape of the Cu spectra in a suspension and liquid solution is assumed to be Gaussian and Lorentzian, respectively.

## Results and Discussion

**Spectra of Solution Cu(I) Complexes.** Figure 1 shows a typical $^{63}$Cu spectra for Cu(I) complexes in an aqueous solution and suspension; Table 1 gives chemical shift and linewidth data. The total range of chemical shifts is in excess of 900 ppm. Such large variations in shielding are due to a domination of the shielding constant by local paramagnetic contributions.[5,6,9] Note that the shifts and linewidths given in the figure and table represent weighted averages of the shifts and linewidths for various species in equilibrium in the solution. In order to determine the mole fraction of the Cu(I) species in each NMR sample in Table 1, we utilized the solubility products and stability constants[11,12] for Cu(I) salts in Table 2, and performed numerical calculations.

Table 2. Solubility Products and Formation Constants of Cu(I) Complexes (30 °C)

| Cu(I) salt | $-\log K_{\mathrm{sp}}$ | $\log\beta_1$ | $\log\beta_2$ | $\log\beta_3$ | $\log\beta_4$ |
|---|---|---|---|---|---|
| CuCl | 6.73 | * | 5.4 | 5.8 | 5.9 |
| CuBr$^{a)}$ | 8.28 | * | 5.16 | 6.65 | 7.95 |
| CuI | 12.03 | * | 8.20 | 9.26 | 9.40 |
| CuCN | 19.5 | * | 24.0 | 28.6 | 30.3 |

The formation constant has not been obtained. a) The formation constant of [CuBr$_4$]$^{3-}$ has been obtained by the potential $E_{\mathrm{Cu}}$ measurement.[12]

**Cu Chemical Shift of Cu(I) Complexes.** Table 3

Table 3. The Change in AO Populations of Copper(I) Complexes

| Orbital | $[CuCl_4]^{3-}$ | $[Cu(CN)_4]^{3-}$ | |
|---|---|---|---|
| Copper | | | |
| $3d_{xx+yy}$ | 0.000 | 0.000 | |
| $3d_{zz}$ | 0.000 | 0.000 | |
| $3d_{xy}$ | −0.079 | −0.164 | |
| $3d_{xz}$ | −0.079 | −0.164 | |
| $3d_{yz}$ | −0.079 | −0.164 | |
| 4s | 0.217 | 0.292 | |
| $4p_x$ | 0.302 | 0.357 | |
| $4p_y$ | 0.302 | 0.357 | |
| $4p_z$ | 0.302 | 0.357 | |
| Ligand | | | |
| | $Cl^-$<br>$(Cl-n=3)$ | $CN^-$<br>$(C-n=2:N-n=2)$ | |
| ns | −0.020 | −0.494 | 0.000 |
| $np_x$ | −0.040 | −0.119 | 0.256 |
| $np_y$ | −0.040 | −0.119 | 0.256 |
| $np_z$ | −0.040 | −0.119 | 0.256 |

In our MO calculation, the AO population of copper(I) ion is given as: AO population of 4s, $4p_x$, $4p_y$, and $4p_z$ was 0.000, that of $2p_x$, $2p_y$, and $2p_z$ in C and N of $CN^-$ was 1.000 (because of $(p\pi)_x$, $(p\pi)_y$, and $(p\pi)_z$ of $CN^-$) and that of others is 2.000, respectively.

summarizes the change in valence atomic orbital population of the Cu(I) ion and the $Cl^-$ and $CN^-$ ligands due to ligand addition by the ab initio SCF MO method.[5,6] In the table the population increases in the 4s and 4p AOs of Cu(I) atoms and the population decreases in the s and p AOs of ligands indicate an electron transfer from the ligand to copper. Also, a back donation to a ligand produces a hole in the 3d orbitals, coincident with the bonding axes of Cu(I) complexes.

As reported earlier for $^{109}Ag$, the chemical shifts of metal complexes for a ligand-metal(Ib and IIb) interaction system can be governed by the paramagnetic term. This will also be explained by the following Eq. 1 for Cu chemical shieldings:

$$\sigma_{\mathrm{para}}(\mathrm{Cu(I)}) \simeq \frac{-2\alpha^2}{3}\left(\frac{<1/r^3>_p}{E_{\mathrm{p}}}\cdot P_T^e + \frac{<1/r^3>_d}{E_d}\cdot 3D_T^h\right), \tag{1}$$

where $P_T^e$ and $D_T^h$ are the total populations of the p electrons and d holes, respectively.

The paramagnetic term for Cu shielding can be estimated from $E_{\mathrm{p,d}}$ and $<1/r^3>_{\mathrm{4p,3d}}$ as parameters in the equation. We assume that $E_{\mathrm{p}}=E_{\mathrm{d}}=E$, $<1/r^3>_{\mathrm{4p}}=$ 0.59 a.u. and $<1/r^3>_{3d}=5.0$ a.u. (The latter two terms are obtained from the SCF functions by Clementi et al.[13]) The results in Table 4 agree qualitatively with the observed value (Table 1, CuCl/KCl vs. CuCN/KCN). We can also see that the d-orbital contribution is much larger than the p-orbital contribution. This tendency corresponds well to the theoretical result using an ab initio finite-perturbation SCF method.[6]

**Possibility of an Effect of a Heavy Atom on Cu Shieldings.** In an aqueous solution, we observed an anomalous shielding order $[CuI_4]^{3-}$ (for (CuI 0.50M/KI 6.0M))>$[CuBr_4]^{3-}$ (for(CuBr 0.50M/KBr 4.0M))≃$[CuCl_4]^{3-}$ (CuCl 0.50M/KCl 4.0M)). For other metal-(Ag(I), Zn(II), Cd(II)) four coordinate halide complexes, the $^{109}Ag$ shielding order may be $[AgCl_4]^{3-}$>$[AgBr_4]^{3-}$>$[AgI_4]^{3-}$ (The $^{109}Ag$ signal for $[AgCl_4]^{3-}$ has not been observed),[5] while the $^{67}Zn$ and $^{113}Cd$ shielding order $[ZnI_4]^{2-}$>$[ZnBr_4]^{2-}$>$[ZnCl_4]^{2-}$ and $[CdI_4]^{2-}$ >$[CdBr_4]^{2-}$>$[CdCl_4]^{2-}$ were shown[1a,2] The same shielding order in $[ZnX_4]^{2-}$ and $[CdX_4]^{2-}$ has been observed for $^{13}C$ in $CX_4$.[14] Thus, the shielding in $[CuX_4]^{3-}$, $[ZnX_4]^{2-}$, and $[CdX_4]^{2-}$ can be explained in terms of the heavy atom effect ($\sigma_{\mathrm{LS}}$).[15] On the other hand, the $^{109}Ag$ shielding may be unaffected by the term but due mainly to the paramagnetic term.

The heavy atom effect has been related to a spin-orbit coupling parameter $\zeta$ which is especially large for Br and I in Table 6. The simplified equation for the metal four-coordinate halide complex is

$$\sigma_{\mathrm{LS}}^{\mathrm{xx}} \simeq -4\pi\zeta\alpha^2|\phi_{\mathrm{s}}(0)|^2\frac{1}{E^2}[\,2P_{\mathrm{yBsA}}P_{\mathrm{yBzB}}P_{\mathrm{zBsA}} - P_{\mathrm{yBsA}}^2(P_{\mathrm{zBzB}}-1) - P_{\mathrm{zBsA}}^2(P_{\mathrm{yByB}}-1)], \tag{2}$$

Table 4. Calculated $^{63}Cu$ Chemical Shielding Constants of Cu(I) Complexes

| | $[CuCl_4]^{3-}$ | $[Cu(CN)_4]^{3-}$ |
|---|---|---|
| *d*-Contribution<br>($(2\alpha^2/3E_{\mathrm{d}})$unit) | −3.52 | −7.31 |
| *p*-Contribution<br>($(2\alpha^2/3E_{\mathrm{p}})$unit) | −0.53 | −0.63 |
| Paramagnetic term<br>($(2\alpha^2/3E)$unit) | −4.05 | −7.94 |
| $\Delta\sigma$ | 0 | 3.89 |
| ($E$=0.20 a.u.) | 0 | −690 |
| $\Delta\sigma$(exptl)[a)](ppm) | 0 | −694 |

a) This value has been obtained from CuCl/KCl vs. CuCn/KCN in Table 1. In this table more negative values refer to lower shielding.

Table 5. Quantities which are Required for the Evaluation of $\sigma_{\mathrm{LS}}$

| | $[CuX_4]^{3-}$ | $[AgX_4]^{3-}$ | $[CdX_4]^{2-}$ |
|---|---|---|---|
| Density[a)] of $[MX_4]^{(4-i)-}$ | | | |
| $3p_{x,y,z}$(Cl) | 1.900 | 1.938 | 1.960 |
| ns(M)−$3p_{x,y,z}$(Cl) | 0.210<br>($n$=4) | 0.171<br>($n$=5) | 0.702<br>($n$=5) |
| 1st Ionization Potential<br>E[ (a.u.)] b)<br>Excitation Energy[b)] | [0.284<br>0.0905 | 0.278<br>0.141 | 0.330<br>0.135 ] |
| $|\phi_{\mathrm{s(M)}}(0)|^2$(a.u.)[c)] | 4.37<br>($^{63}Cu$) | 8.62<br>($^{109}Ag$) | 2.44<br>($^{111}Cd$) |

a) The densities were obtained from Ref. 6. b) The values were estimated from the diatomic molecule.[16] c) These values were calculated from the corrected hyperfine splitting constants given by Knight.[17]

Table 6. Experimental Metal(Ib,IIb) Chemical Shifts and Calculated $\sigma_{LS}$(M(I,II)) Shieldings of Metal-Four Coordinate Halide Complexes

| X | $\xi$ (a.u.) $\times 10^{-2}$ | Relative to $[MCl_4]^{(4-i)-}$ $[CuX_4]^{3-}$ (ppm) Obsd | $[CuX_4]^{3-}$ (ppm) Calcd | $[AgX_4]^{3-}$ (ppm) Obsd | $[AgX_4]^{3-}$ (ppm) Calcd | $[CdX_4]^{2-}$ (ppm) Obsd | $[CdX_4]^{2-}$ (ppm) Calcd |
|---|---|---|---|---|---|---|---|
| Cl | 0.266 | 0 | 7.6[c)]<br>75[d)] | f) | 7.4[c)]<br>29[d)] | 0[b)] | 37[c)]<br>225[d)] |
| Br | 1.11 | 0 | 32[c)]<br>315[d)] | 0[a)] | 31[c)]<br>120[d)] | 116[b)] | 157[c)]<br>941[d)] |
| I | 2.29 | 234 | 66[c)]<br>649[d)] | −115[a)] | 64[c)]<br>248[d)] | 424[b)] | 325[c)]<br>1941[d)] |

a) The values was obtained from Ref. 5. b) The value was obtained from Ref. 1a. c) The values was calculated from the ionization potential of metal atom. d) The value was estimated from excitation energy of the diatomic molecule. e) In this table more positive values refere to higher shielding. f) The value has not been obtained.

where $P_{\mu\nu}$ is the orbital density: $P_{yBsA}$ denotes the density of the $p_y$ orbital on the B (halogen) atom and an s orbital on the A (metal) atom. Other notations correspond to reference.[15)]

In order to estimate the LS shift, $\sigma_{LS}$, for $[CuX_4]^{3-}$, $[AgX_4]^{3-}$, and $[CdX_4]^{2-}$, we used the quantities shown in Table 5. There, the densities of the metal four-coordinate halide complexes were approximated by tetrachloride complexes instead of tetrabromide and tetraiodide, which we have not calculated by the ab initio SCFMO method.[6)] An inspection of Table 6 shows that the LS shift (using both the 1st ionization potential of the metal atom and the lowest excitation energy of the diatomic molecule) is $[CdX_4]^{2-} > [CuX_4]^{3-} \geqslant [AgX_4]^{3-}$. This tendency corresponds to the observed one. For $[AgX_4]^{3-}$, the observed shift shows the opposite shielding order. This indicates that the Ag paramagnetic term is much larger than the LS term.

**Line-Broadening for Cu(I) Halide Complexes.** In Table 1, we can see remarkably different line widths for Cu(I) complex species of Cu(I) halides in aqueous solution. The linewidths[18)] can be approximated by

$$\Delta\nu_{1/2} \simeq \frac{1}{10}\left(1+\frac{\eta^2}{3}\right)(e^2Qq/\hbar)^2\tau_c\,, \tag{3}$$

where we can assume the asymmetry parameter, $\eta$, is nearly 0 for CuX; the correlation time, $\tau_c$, of the complex $[CuX_4]^{3-}$ is estimated as $2\pi \times 10^{-11}$ s in nonviscous water from the Einstein-Stokes relationship, the quadrupole moment of $^{63}$Cu, Q, is given as $-0.16 \times 10^{-24}$ cm$^2$ and the electric field gradient around the Cu nucleus, q, is affected by any change of the p- and d- electron densities. These densities are considered to result from the lone-pair electrons of the ligand. The field gradient will, thus, be the dominant factor for $^{63}$Cu linewidths.

An estimation of $e^2Qq$ by Eq. 3 gives 40 and 4 MHz for the different linewidths of 10 and 0.1 kHz in Table 1, respectively. The term $e^2Qq$ can be rewritten as

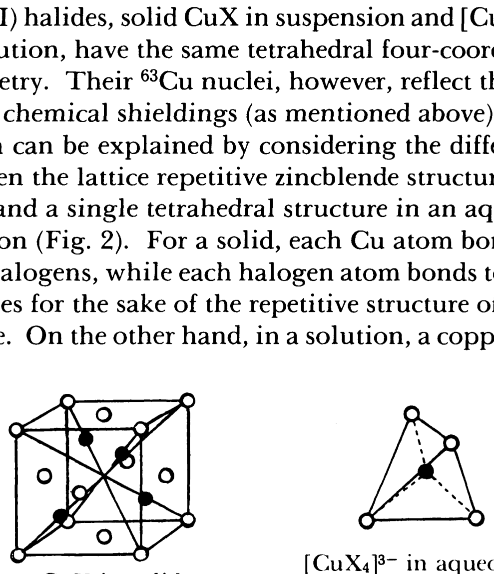
$$e^2Qq/\hbar = \frac{e^2}{\hbar}\frac{2L(L+1)}{(2L-1)(2L+3)}<1/r^3>Q\,. \tag{4}$$

We can evaluate $e^2Qq$ for the maximum case where the contribution arises from a single hole or electron on a 3d- or 4p-orbital. The value was estimated to be 110 or 12 MHz for a single 3d-hole or 4p-electron, respectively. It can, therefore, also be seen for the $^{63}$Cu observed linewidths (10 to 30 kHz) that the d-contribution (76 kHz) is larger than the p-contribution (0.9 kHz).

When we consider $^{63}$Cu linewidths from the sysmmetry of Cu(I) complexes in aqueous solution, the complex with a higher symmetry gives a sharper signal. The sharper signals of $[Cu(CN)_4]^{3-}$ and $[Cu(CH_3CN)_4]BF_4$ in solution are due to their tetrahedral symmetry. However, we observed broader signals for aqueous CuX-KX solution systems. This broadening may be partially attributed to a lower symmetry of $[CuX_3]^{2-}$ and a distortion of $[CuX_4]^{3-}$.

**The Difference between $^{63}$Cu Chemical Shieldings of Cu(I) Halides in Suspension and in Solution.** An inspection of Table 1 indicates that the Cu shift of CuX in suspension is in good accordance with a remarkable increasing shielding order (CuCl$\lesssim$CuI<CuBr) in solid, as reported by Lutz et al.[4b)] The $^{63}$Cu of $[CuCl_4]^{3-}$ in solution is more deshielded than that of solid CuCl in suspension (the shift between $[CuCl_4]^{3-}$ and CuCl is about 130 ppm), while the $[CuI_4]^{3-}$ in solution is more shielded than the solid CuI in suspension (the shift between $[CuI_4]^{3-}$ and CuI ($\geqslant$CuCl) is about −100 ppm). We can, thus, explain these anomalous shielding orders seen in the Cu(I) halides.

Cu(I) halides, solid CuX in suspension and $[CuX_4]^{3-}$ in solution, have the same tetrahedral four-coordinate symmetry. Their $^{63}$Cu nuclei, however, reflect the different chemical shieldings (as mentioned above). The reason can be explained by considering the difference between the lattice repetitive zincblende structure in a solid and a single tetrahedral structure in an aqueous solution (Fig. 2). For a solid, each Cu atom bonds to four halogens, while each halogen atom bonds to four Cu ones for the sake of the repetitive structure of zincblende. On the other hand, in a solution, a copper ion



CuX in solid

$[CuX_4]^{3-}$ in aqueous solution

Fig. 2. Zincblende structure of CuX in solid and a tetrahedral structure of $[CuX_4]^{3-}$ in aqueous solution.

has four halogens in a single tetrahedral complex. Then, in a solid, the electron donation from the halogen p orbital to the Cu(I) 4s and 4p orbitals and the back donation from the Cu(I) 3d orbital to the ligand may be much smaller than those in solution.

Here, in order to explain the observed $^{63}$Cu shielding order in $[CuX_4]^{3-}$ and CuX, we consider the paramagnetic, $\sigma_{para}$ (Cu(I)), and LS-shielding, $\sigma_{LS}$, terms. For Cu(I) chloride complexes, the shift between $[CuCl_4]^{3-}$ and CuCl is interpreted mainly by the diffrences between the paramagnetic terms in Eq. 1, because the contribution of the LS-shielding is ignored for the chloride complex (Table 6). Now, we assume that ($E_{p,d}$ solution)$\simeq$($E_{p,d}$ in solid) and ($\langle 1/r^3\rangle_{3d,4p}$ in solution) $\simeq$($\langle 1/r^3\rangle_{3d,4p}$ in solid) in Eq. 1. We can also take into account the population orders, $P_T$ ($[CuCl_4]^{3-}$)>$P_T$ (CuCl) and $D_T$ ($[CuCl_4]^{3-}$)>$D_T$(CuCl), as discussed above. Then, the observed deshielding order, $\sigma$($[CuCl_4]^{3-}$)>$\sigma$ (CuCl), is shown from the paramagnetic shielding order, $\sigma_{para}$ ($[CuCl_4]^{3-}$)>$\sigma_{para}$ (CuCl).

In the case of Cu(I) iodide complexes, both $\sigma_{para}$ (Cu(I)) and $\sigma_{LS}$ terms must be considered. For the $\sigma_{para}$ term, we may show the deshielding order, $\sigma_{para}$ ($[CuI_4]^{3-}$)> $\sigma_{para}$ (CuI) as well as $\sigma_{para}$ ($[CuCl_4]^{3-}$)>$\sigma_{para}$ (CuCl). For $\sigma_{LS}$, the difference between $\sigma_{LS}$ ($[CuI_4]^{3-}$ and $\sigma_{LS}$ (CuI) depends mainly upon the populations, $p_{zBzB}$ and $p_{yAyA}$ in Eq. 2. The populations in solid CuI are also assumed to be smaller than those in solution, for the sake of the repeat structure in solid. Thus, if ($\sigma_{LS}$($[CuI_4]^{3-}$)$-\sigma_{LS}$(CuI))>($\sigma_{para}$(CuI)$-\sigma_{para}$($[CuI_4]^{3-}$)) is pointed out, we can explain the observed shift between CuI and $[CuI_4]^{3-}$.

## Conclusion

In this paper, we presented representative $^{63}$Cu NMR spectra obtained from an aqueous solution and a pure solid of Cu(I) halides. Especially, a few tens of kHz of broader $^{63}$Cu spectra for CuX-KX systems (where X=Cl, Br, I) were shown. We provided a theoretical interpretation of the $^{63}$Cu line width and the chemical shielding. The line width and shielding were found to be due mainly to a 3d-hole in the Cu atom: The broadening is due to a Cu(I) nuclear quadrupole interaction with the electric field gradient, which arises from the 3d-hole. The shielding could be explained by the paramagnetic term which depends dominantly on the 3d-hole. Furthermore, for increasing metal shieldings of $[MX_4]^{(4-i)-}$, we evaluated the possibility of the heavy atom effect on the shielding of $[CuX_4]^{3-}$ and $[CdX_4]^{2-}$.

In a forthcoming paper, we hope to clarify the shielding order of $[CuX_4]^{3-}$ with the ab initio SCF MO method.

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