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Cu NUCLEAR QUADRUPOLE RESONANCES OF SEVERAL COMPLEXES OF COPPER(I) HALIDES WITH TRIPHENYLPHOSPHINE

Tsutomu OKUDA, Morio HIURA, Koji YAMADA, and Hisao NEGITA
Department of Chemistry, Faculty of Science, Hiroshima University,
Hiroshima 730

The ^{63}Cu nuclear quadrupole resonances have been observed in $(CuX)_nL_m$ (X=Cl, Br, I; L=triphenylphosphine; n:m=1:1, 2:3, 1:2). Two characteristic frequency ranges were observed: the resonance frequencies of the three-coordinated Cu atoms are far above those of the four-coordinated.

It is well-known that copper(I) halides forms various complexes with phosphine such as $(CuX)_nY_m$, in which Y is a monodentate phosphine ligand. Their crystal structures have been studied by means of X-ray diffraction, and the coordination types of Cu atoms are found to be versatile. Recently, a few reports on Cu NQR have been published for the complexes between copper halides and neutral ligands.[1,2] So we examined the bondings of the Cu atoms in the complexes of copper(I) halides with triphenylphosphine (abbreviated as L) by means of NQR.

The complexes were prepared by the methods described in literature.[3,4] A super-regenerative oscillator with frequency modulation was used for recording NQR signals. Each ^{63}Cu NQR line was identified by the pair of resonance frequencies due to ^{63}Cu and ^{65}Cu, and the results are listed in Table 1. The molecular structures of these complexes have been determined by the X-ray diffraction.[4-10] Although they are complicated, the coordination types of the Cu atoms are roughly classified into (a)-(d) as shown in Fig. 1. In some cases the complexes were obtained as solvated crystals. As listed in Table 1, however, the resonance frequency is little affected by the solvent molecule in the crystal.

$(CuClL)_4$ has a cubane-like structure,[7,8] and the Cu atoms are of the coordination type (a). In this case, two closely situated resonance lines were observed near 13

MHz. $(CuBrL)_4$ and $(CuIL)_4$ have a chair-like structure, and the Cu atoms are grouped into two kinds of coordination types (a) and (c).[9,10] Accordingly, two resonance lines are to be expected, but only one weak resonance line was detected in a frequency region different from that of $(CuClL)_4$. This must be assigned to the Cu atom of the coordination type (c).

In the crystals of $(CuCl)_2L_3$, two Cu atoms are held together by Cl bridges, and two of the three phosphine ligands are bonded to one of the Cu atoms and the rest to the other.[5,6] Owing to the presence of the two kinds of Cu atoms, which are of coordination types (b) and (c), two well-separated resonance lines were found. Similar two resonance lines were observed also for $(CuBr)_2L_3$ and $(CuI)_2L_3$, the crystal structures of which have not been determined yet. Since the ^{63}Cu resonance frequencies in these complexes decrease monotonously from the chloride to the iodide, the molecular

Table 1. ^{63}Cu NQR Frequencies in the Complexes of CuX with L (=triphenylphosphine) at Room Temperature

Complex		Frequency
CuX:L	Formula	MHz
1:1	$(CuClL)_4$	13.76
		12.98
	$(CuBrL)_4\cdot 2CHCl_3$	28.09
	$(CuIL)_4\cdot 2CHCl_3$	26.09
2:3	$(CuCl)_2L_3\cdot C_6H_6$	30.37
		14.54
	$(CuCl)_2L_3\cdot \frac{1}{2}CHCl_3$	29.94
		14.56
	$(CuBr)_2L_3$	28.36
		14.31
	$(CuBr)_2L_3\cdot CHCl_3$	28.65
		14.39
	$(CuI)_2L_3\cdot \frac{1}{2}C_2H_4Cl_2$	27.39
		14.27
1:2	$CuClL_2\cdot \frac{1}{2}C_6H_6$	33.17
	$CuBrL_2\cdot \frac{1}{2}C_6H_6$	32.16

structures of $(CuBr)_2L_3$ and $(CuI)_2L_3$ may be similar to that of $(CuCl)_2L_3$. The higher resonance line in $(CuX)_2L_3$ (X=Cl, Br, I) can be assigned to the Cu atom of the coordination type (c) from the results of $(CuXL)_4$ (X=Br, I).

Figure 2 shows the relationship between the resonance frequency and the kind of halogen atom in $(CuX)_2L_3$ (X=Cl, Br, I). In the case of the same coordination type, ^{63}Cu resonance frequency decreases in the order Cl > Br > I, and the inclination of the curve is larger for the series of the coordination type (c) than that for (b). This must be caused by the influence of halogen atoms on the electric field gradient (EFG)

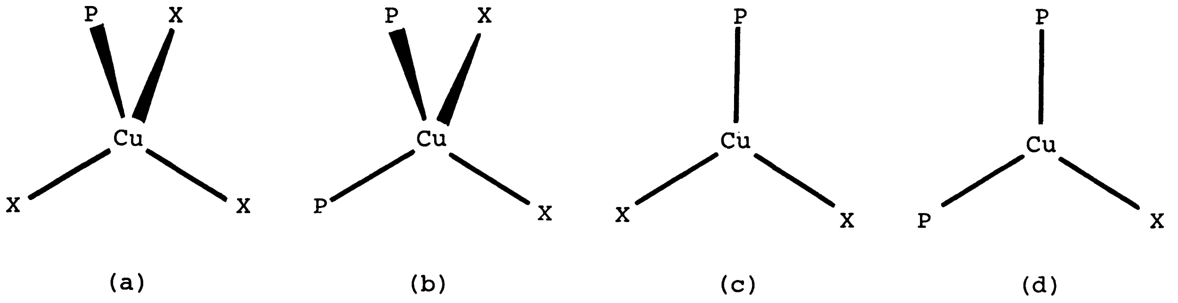

Fig. 1. The coordination types of the Cu atoms in the complexes of CuX with L (=triphenylphosphine).

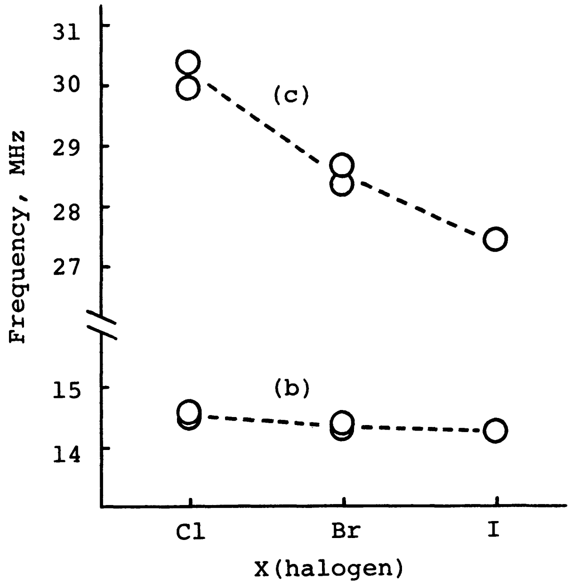

Fig. 2. Relationship between the ^{63}Cu NQR frequency and the kind of halogen atom in $(CuX)_2L_3$ (L=triphenylphosphine).

of the central Cu atom. The relative number of halogen atoms in the coordination sphere is larger for the Cu atom in (c) than in (b). Furthermore, the Cu-X distance of the coordination type (c) is shorter than that of (b). Therefore, the EFG of the Cu atom in (c) may be much more affected by the halogen atom than that in (b), and these combined effects should be responsible for the difference of the gradients between the two curves (b) and (c).

In the crystals of $CuBrL_2$, Cu atoms have the coordination type (d)[4] and one resonance line was observed in a considerably high frequency region. The molecular structure of $CuClL_2$ has not been established, but from the observed resonance frequenc it must take the monomeric form like $CuBrL_2$, not the dimeric.[11]

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