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NQR Zeeman Study of Bis(triphenylphosphine)copper(I) Bromide

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Zeeman effects of ^{63}Cu and ^{81}Br NQR spectra of bis(triphenylphosphine)copper(I) bromide, $CuBr(PPh_3)_2$, have been studied at room temperature. The asymmetry parameters and the quadrupole coupling constants (e^2Qq/h) have been found to be 0.113 and 64.58 MHz for ^{63}Cu and 0.518 and 105.91 MHz for ^{81}Br. The large asymmetry parameter of the ^{81}Br NQR line is caused by the π-bonding character of the copper-bromine bond. The bonding scheme between the copper and bromine atoms is discussed on the basis of the obtained directions of the electric field gradient axes.

A trigonal planar coordination is occasionally seen in copper(I) compounds, though it is rarely found in the other transition metal complexes. The X-ray analysis of $CuBr(PPh_3)_2 \cdot 0.5C_6H_6$ (PPh_3=triphenylphosphine) has shown that the $CuBr(PPh_3)_2$ molecule is monomeric and the coordination geometry about its copper atom is trigonal planar.$^{1)}$ NQR (nuclear quadrupole resonance) is very useful for the study of bonding character in copper(I) halide compounds, since both copper and halogen atoms have nuclear quadrupole moments. The ^{63}Cu NQR frequency in $CuBr(PPh_3)_2 \cdot 0.5C_6H_6$ has been reported.$^{2)}$

In the present study, both the ^{63}Cu and ^{81}Br NQR lines were observed for two compounds, $CuBr(PPh_3)_2$ and $CuBr(PPh_3)_2 \cdot 0.5C_6H_6$. Furthermore, since ^{63}Cu and ^{81}Br both have a nuclear spin $I=3/2$, a Zeeman study of NQR was carried out to determine the nuclear quadrupole coupling constant e^2Qq_{zz}/h, the electric field gradient (efg) principal axes x, y, z, and asymmetry parameter $(q_{xx}-q_{yy})/q_{zz}$. These can be used to describe more explicitly the nature of the bonding.

Experimental

$CuBr(PPh_3)_2 \cdot 0.5C_6H_6$ was prepared according to the method described by Davis *et al.*$^{1)}$ $CuBr(PPh_3)_2$ was obtained by recrystallization from the ethanol solution of $CuBr(PPh_3)_2 \cdot 0.5C_6H_6$. Found: C, 66.05; H, 4.38%. Calcd for $CuBrP_2C_{39}H_{33}$: C, 66.25; H, 4.56%. Found: C, 64.37; H, 4.66%. Calcd for $CuBrP_2C_{36}H_{30}$: C, 64.72; H, 4.54%. A single crystal of $CuBr(PPh_3)_2$ was obtained by the Bridgman-stockbarger method.

The NQR spectrometers used were super-regenerative oscillators employing a frequency modulation or a Zeeman modulation mode. The resonance lines due to four isotopes: ^{63}Cu, ^{65}Cu, ^{79}Br, and ^{81}Br were assigned on the basis of the known quadrupole moment ratios, $Q(^{63}\mathrm{Cu})/Q(^{65}\mathrm{Cu})=1.0806$ and $Q(^{79}\mathrm{Br})/Q(^{81}\mathrm{Br})=1.1974$. The Zeeman effect on the resonance line was examined by means of the zero-splitting cone method at room temperature with the magnetic field of about 2.5×10^{-2} T. The Zeeman-split signals were displayed on an oscilloscope. The magnetic field orientation for the zero-splitting was determined in polar coordinates (Φ, Θ), where Φ is the azimuthal angle and Θ is the polar angle.

Results and Discussion

The observed frequencies are listed in Table 1. The crystal structure for the benzene solvated compound $CuBr(PPh_3)_2 \cdot 0.5C_6H_6$ is available,$^{1)}$ but that for unsolvated $CuBr(PPh_3)_2$ is not. From the small difference in both ^{63}Cu and ^{81}Br NQR frequencies, however, it is reasonable to consider that the molecular structure of the unsolvated crystal is essentially the same as that in the solvated crystal, that is, the individual $CuBr(PPh_3)_2$ molecules are monomeric and have the trigonal planar coordinations in the unsolvated crystal.

The zero-splitting patterns obtained for both the ^{63}Cu and ^{81}Br nuclei of $CuBr(PPh_3)_2$ are shown in Fig. 1. From these zero-splitting patterns the asymmetry parameters (η) and the directions of the efg axes were obtained. The quadrupole coupling constant e^2Qq_{zz}/h can be calculated by substituting the value of η in the following relation:

$$\nu = (e^2Qq_{zz}/2h)(1+\eta^2/3)^{1/2}. \qquad (1)$$

The values of e^2Qq_{zz}/h derived in this way are listed in Table 1. For comparison, Table 1 includes the ^{63}Cu and ^{81}Br NQR frequencies of $(Bu_4N)CuBr_2$ (Bu=C_4H_9) reported by Bowmaker *et al.*$^{3)}$ $(Bu_4N)CuBr_2$ has a linear dibromocuprate(I) ion, so that the asymmetry parameters of Cu and Br atoms are assumed

Table 1. ^{63}Cu and ^{81}Br NQR parameters for bis(triphenylphosphine)copper(I) bromide and dibromocuprate(I) compounds

Compound	Nucleus	Frequency/MHz		η	$\frac{e^2Qq/h}{\mathrm{MHz}}$
		298 K	77 K		
$CuBr(PPh_3)_2$	^{63}Cu	32.36	33.93	0.113 ± 0.005	64.58 ± 0.02
	^{81}Br	55.28	56.63	0.519 ± 0.003	105.91 ± 0.02
$CuBr(PPh_3)_2 \cdot$	^{63}Cu	32.16	33.66		
0.5 C_6H_6	^{81}Br	52.88	55.53		
$(Bu_4N)CuBr_2$$^{a)}$	^{63}Cu	28.25	28.85	0$^{b)}$	56.50
	^{81}Br	60.35	62.6	0$^{b)}$	125.2

a) Ref. 3. b) The asymmetry parameter was assumed to be zero.

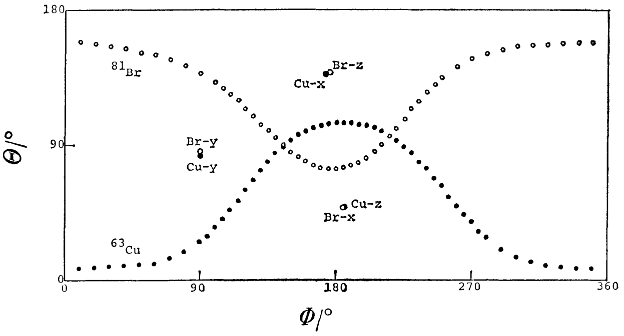

Fig. 1. The zero-splitting patterns of the ^{63}Cu and ^{81}Br NQR lines in $CuBr(PPh_3)_2$.

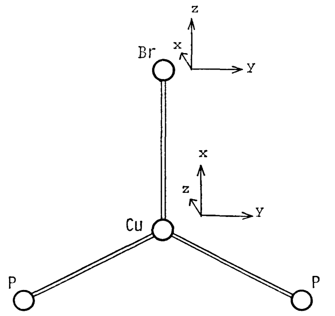

Fig. 2. The orientations of the efg principle axes for the copper and bromine atoms in the $CuBrP_2$ portion of the $CuBr(PPh_3)_2$ molecule.

to be zero.

One of the interesting features obtained from the Zeeman experiments is the large asymmetry parameter, 0.519, for the bromine atom. In this complex the bromine atom is considered to link to only one copper atom, as in the solvated compound. However, the obtained, asymmetry parameter is too large for a singly-bonded halogen atom. Accordingly, we can consider that the extraordinarily large asymmetry parameter results from the existence of the π-bond. Since the trigonal copper atom is considered to form sp^2-hybridized orbitals, the p_z orbital of copper is nonbonding, and can be used for π-bonding with ligands. In the previous NQR study and X-ray analysis of $Cu_2X_2(PPh_3)_3$ (X=Cl, Br, and I),[4,5] it was suggested that the p_π-p_π double bonding must occur in the bonds between copper and halogen atoms. In the present study, this suggestion has been confirmed by the large asymmetry parameter obtained for the bromine atom. The Zeeman study using a single crystal, furthermore, has revealed the relative orientations of the efg principal axes for both the ^{63}Cu and ^{81}Br atoms, *i.e.*, the efg x-, y-, and z-axes for the Br atom are along the z-, y-, and x-axes for the copper atom, respectively, as shown in Fig. 1. The z-axis of terminal halogen atom, in general, points along its bond direction. In the case of trigonal planar copper atoms it has become apparent from the Zeeman studies of $KCu(CN)_2$,[6] $Cu_2Cl_2(PPh_3)_3$, and $Cu_2I_2(PPh_3)_3$[4] that the efg z-axis of the three coordinated copper atom is perpendicular to the plane formed by three ligands. Therefore, both the y- and x-axes of the copper atom lie on the coordinate plane. On the basis of these results, the directions of the principal efg axes for both nuclei could be determined in a discrete molecule $CuBr(PPh_3)_2$, as shown in Fig. 2. The x-axis direction of the bromine atom is parallel to the z-axis direction of the copper atom, that is, it is perpendicular to the ligand plane. The y-axis direction of the bromine atom is normal to both its x-axis and its z-axis. This situation is similar to those of the trigonal planar species BBr_3 and BI_3,[7,8] which have p_π-p_π double bondings.

For the Cu–Br bond, one simple bonding model is proposed. The p_x, p_y, and p_z orbitals at the bromine atom are taken to be pointed toward the efg x-, y-, and z-axes, respectively. The p_z orbital forms a σ-bond with one of the sp^2-hybridized orbitals on the three-coordinated copper, and the p_x orbital can form a π-bond with the remaining p orbital on the copper atom. The p_y orbital is thought to have little interaction with the orbitals of the copper atom, so we can assume that the p_y orbital of the bromine atom does not take part in the Cu–Br bond formation. Then, e^2Qq_{zz}/h and the asymmetry parameter (η) are given by

$$e^2Qq_{zz}/e^2Qq_0 = N_z - (N_x+N_y)/2, \tag{2}$$

$$\eta = 3(N_x-N_y)/2[N_z-(N_x+N_y)/2], \tag{3}$$

where e^2Qq_0/h is the quadrupole coupling constant for one 4p electron of the ^{81}Br, and N_x, N_y, and N_z denote the number of electrons in the p_x, p_y, and p_z orbitals of the bromine atom, respectively. Assuming $N_y=2$, the occupation numbers N_x and N_z are calculated, to be $N_x=1.943$ and $N_z=1.807$. This N_z value is compared with the ^{81}Br NQR data of the centrosymmetric $CuBr_2^-$ ion,[3] in which $N_z=1.812$ at 298 K, assuming that the bromine atom is singly bonded to the copper(I) atom ($N_x=N_y=2$).

Bersohn[9] has shown that the Townes and Dailey analysis of the halogen coupling constants leads to the following relationship between the fractional π-bonding character, Π, and the coupling constants

$$\Pi = (2/3)(e^2Qq_{zz}/e^2Qq_0)(\eta). \tag{4}$$

The partial π-bonding character calculated according to this equation is 5.7%. This value is significantly smaller than the π-bonding character of the trigonal planar BBr_3 and BI_3 molecules: 13.3% and 15.6% for the boron-bromine and boron-iodine bonds, respectively,[7,8] although the asymmetry parameter of $CuBr(PPh_3)_2$, $\eta=0.519$, is slightly larger than those of the boron trihalides, $\eta=0.45$ for BBr_3 and $\eta=0.456$ for BI_3.[7,8] Thus, the small π-bonding character of the Cu–Br bond results from the fact that the e^2Qq_{zz}/e^2Qq_0 ratio of the bromine atom in $CuBr(PPh_3)_2$ is significantly smaller than those of BBr_3 and BI_3. Therefore, it is concluded that the ionic character of the copper-bromine bond is larger than those of the boron-bromine and boron-iodine bonds.

On the other hand, the Cu atom in $CuBr(PPh_3)_2$ has a larger value of e^2Qq_{zz}/h (64.58 MHz) than that of the three-coordinated copper atom in $Cu_2Br_2(PPh_3)_3$ (55.82 MHz at room temperature) in which the copper atom is linked by one triphenylphosphine and two bromine atoms. The e^2Qq_{zz}/h of an sp^2 hybridized copper atom is considered to be caused by the 4p valence electron donated from three ligands. It is well known that a triphenylphosphine ligand is a better donor than halogen atoms. Therefore, the larger value of e^2Qq_{zz}/h found in $CuBr(PPh_3)_2$ is explained by the increase in the number of the coordinate phosphine ligands, from one to two. In addition, although the efg y-axis was nearly along the Cu–P bonding direction in the case of $Cu_2Br_2(PPh_3)_3$, the y-axis direction in $CuBr(PPh_3)_2$ is normal to the bisector of the P–Cu–P angle. This finding is consistent with the idea that the copper(I) atom receives more electrons from the triphenylphosphine ligand than the halogen atom.

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