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Copper Nuclear Quadrupole Resonance Spectra of Tris(tetramethylthiourea)copper(I) Tetrafluoroborate and Perchlorate

Yukio Hiyama, Noriyuki Watanabe, and Eiji Niki

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113

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^{63}Cu, ^{65}Cu NQR spectra of tris(tetramethylthiourea)copper(I) tetrafluoroborate ([Cu(tmtu)$_3$]BF$_4$) and tris(tetramethylthiourea)copper(I) perchlorate ([Cu(tmtu)$_3$]ClO$_4$) have been observed. The resonance frequencies are 27.390 MHz and 25.341 MHz in the BF$_4$ compound, 27.390 MHz and 25.340 MHz in the ClO$_4$ compound (23.0 °C). These results indicate that the crystal structure of [Cu(tmtu)$_3$]ClO$_4$ is very similar to that of [Cu(tmtu)$_3$]BF$_4$ and the copper valence has sp^2 hybridization with pπ–dπ bonding. The temperature dependence of ^{63}Cu NQR of [Cu(tmtu)$_3$]BF$_4$ has been studied from −100 to +100 °C. A discontinuous point has been discovered at −11 °C.

Recently, copper(I) coordination compounds have been studied because of biochemical or stereochemical interest.

Tris(thiourea)copper(I) tetrafluoroborate[4] is a sulfur-bridged dimer with tetrahedral Cu(I), while bis(thiourea)copper(I) chloride contains trigonal planar CuS$_3$ in a chain structure. Several copper NQR spectra[1–3] of these compounds, for example KCu(CN)$_2$, have been studied. [Cu(tmtu)$_3$]BF$_4$ is a trigonal planar Cu(I) monomer,[4] and its chemical bonding is also very interesting. So we synthesized [Cu(tmtu)$_3$]BF$_4$ and [Cu(tmtu)$_3$]ClO$_4$, and measured the copper NQR of these compounds. Furthermore, the temperature dependence of the resonance frequency in the BF$_4$ complex was carefully studied.

Experimental

Materials. Tetramethylthiourea and copper(II) tetrafluoroborate were commercially obtained. Copper(II) perchlorate was prepared from copper(II) carbonate and perchloric acid.

Preparation of Compounds. [Cu(tmtu)$_3$]BF$_4$ was prepared by a method given by Weininger and Amma.[4] [Cu(tmtu)$_3$]ClO$_4$ was prepared by the same method except for copper(II) perchlorate. These compounds are quite pale and polycrystalline.

Analysis. The composition of these compounds was ascertained by C–H–N analysis. [Cu(tmtu)$_3$]BF$_4$—Found: C, 33.22; H, 6.90; N, 15.69%. Calcd for C, 32.94; H, 6.63; N, 15.36%. [Cu(tmtu)$_3$]ClO$_4$—Found: C, 32.15; H, 6.57; N, 14.92%. Calcd for: C, 32.19; H, 6.48; N, 15.01%.

Spectrometer. The search spectrometer was a noisecontrolled superregenerative spectrometer that was built in our laboratory. The frequency measurement was made by use of the regenerative spectrometer that has been described[5] by Tsukada *et al.* The total error may amount to approximately 2 KHz.

Results and Discussion

^{63}Cu NQR spectra of [Cu(tmtu)$_3$]BF$_4$ are shown in Fig. 1. The observed resonance frequencies of the two compounds at 23.0 °C are given in Table 1.

Since ^{63}Cu or ^{65}Cu has a nuclear spin $I=3/2$, only a single NQR frequency $\nu=(e^2Qq/2h)(1+(\eta^2/3))^{1/2}$ is observed. Thus we cannot determine the coupling constant and the asymmetric parameter independently without a Zeeman study.

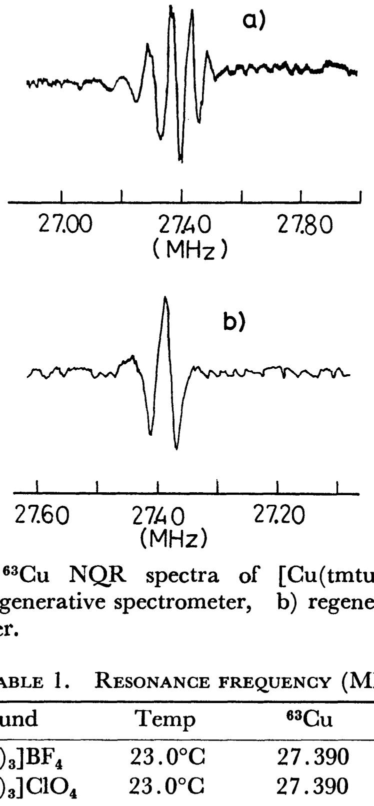

Fig. 1. ^{63}Cu NQR spectra of [Cu(tmtu)$_3$]BF$_4$. a) superregenerative spectrometer, b) regenerative spectrometer.

Table 1. Resonance frequency (MHz)

Compound	Temp	^{63}Cu	^{65}Cu
[Cu(tmtu)$_3$]BF$_4$	23.0°C	27.390	25.341
[Cu(tmtu)$_3$]ClO$_4$	23.0°C	27.390	25.340

According to the X-ray analysis by Weininger and Amma,[4] Cu(tmtu)$_3{}^+$ is distorted from a trigonal configuration. But we assume the asymmetric parameter η is zero for simplicity. On this assumption, we calculated the EFG (electric field gradient; q) of these compounds in Table 2. The EFG due to a 4p electron

Table 2. Value of the observed EFG

Compound	q($\times 10^{15}$ esu cm^{-3})	
[Cu(tmtu)$_3$]BF$_4$	4.80	$Q(^{63}\text{Cu}) = -0.16$ barn
[Cu(tmtu)$_3$]ClO$_4$	4.80	
4p electron[6)a)]	3.1	

a) determined from the constant of the magnetic hyperfine splitting, using the nuclear moment obtained by the nuclear induction method.

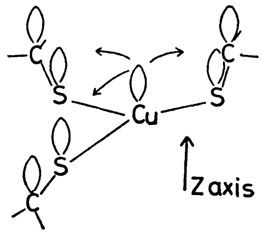

Fig. 2. $p\pi$—$d\pi$ bonding in $Cu(tmtu)_3^+$ ion. $3d_z{}^2$ (Cu) electron backdonates to π orbital (tmtu).

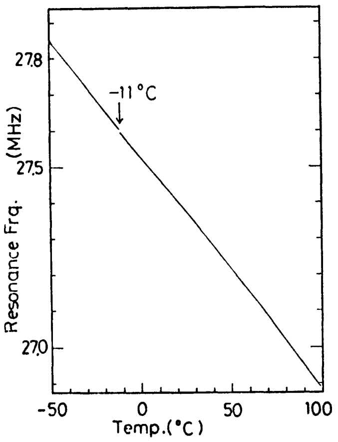

Fig. 3. Temperature dependence of ^{63}Cu NQR in $[Cu(tmtu)_3]BF_4$ (−50 to +100 °C). 28.763 MHz (−196 °C).

of the copper atom calculated by Korol'kov⁶⁾ is also shown in Table 2. So the EFG due to a sp^2 configuration (4s, 4p, $S=33\%$) is 3.1×10^{15} esu cm^{-3}. Since the BF_4^- ion is well separated from the copper atom, the EFG due to the negative ion is negligibly small.

The EFG observed around the copper atom in the $Cu(tmtu)_3^+$ is greater than that calculated for the sp^2 hybrid, quite covalent bond. We explain this by saying that the $3d_z{}^2$ electron of the copper backdonates to the π orbital of the ligands, and as a result the vacant $3d_z{}^2$ orbital enhances the EFG around the copper atom. Consequently we conclude that the EFG observed is due to sp^2 hybridization with $p\pi$–$d\pi$ bonding (Fig. 2).

The crystal structure of $[Cu(tmtu)_3]ClO_4$ has not yet been resolved. But we suggest that the crystal structure of the ClO_4 complex is close to that of the BF_4 complex, because of the similarity between the two EFG's.

Temperature Dependence. The temperature dependence of ^{63}Cu NQR in $[Cu(tmtu)_3]BF_4$ is shown in Fig. 3. The observed frequency gradient is very large ($d\nu/dT=-6.5$ kHz/°C) compared with that of Cu_2O (−3.3 kHz/°C). A discontinuous point has been discovered at −11 °C, but we could not ascertain any phase transition.

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