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Motion of CF_3 Groups and Phase Transition in $[Cu_4(CF_3COO)_4]\cdot 2C_6H_6$ as Studied by ^1H and ^{19}F NMR Techniques

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The temperature variation of ^1H and ^{19}F nuclear spin-lattice relaxation times T_1 in $[Cu_4(CF_3COO)_4]\cdot 2C_6H_6$ was observed at different resonance frequencies. From the NMR experiments, it was found that this complex undergoes a first order phase transition at 130 K, which was confirmed by DTA measurements. In the room-temperature phase, ^1H gave normal exponential magnetization recovery curves and $\log T_1$ linearly decreased with increasing $10^3 T^{-1}$ whereas ^{19}F gave nonexponential magnetization recovery curves, from which long- and short-T_1 components could be derived. This indicates that the C_3 reorientation of CF_3 groups about their respective symmetry axis is responsible for ^{19}F T_1 and for ^1H T_1 as well through ^1H–^{19}F cross relaxation. This was confirmed from the coincidence of the $\log T_1$ *vs.* 10^3T^{-1} curve of the long component and that of ^1H T_1. A very small activation energy of 5.5 kJ mol^{-1} was obtained for the CF_3 reorientation. For the low-temperature phase, both ^1H and ^{19}F yielded nonexponential magnetization decay curves.

Recently, some Cu(I) complexes having capability to absorb and desorb CO, olefins, aromatic molecules *etc.* attract much attention from their usability as a carrier or a separator of those molecules.[1,2] Among these complexes, copper(I) trifluoroacetate is of interest in the formation of a fairly stable complex, $[Cu_4(CF_3COO)_4]\cdot 2C_6H_6$ by absorbing benzene vapor. It is so stable that we can investigate its solid state properties fairly in detail.[1,3,4]

According to Rodesiler and Amma,[3] this complex crystallizes in a monoclinic system $P2_1/n$ with $Z=4$. The structure can be described as a planar lozenge of four Cu atoms which are held together by bridging trifluoroacetate groups. Each CO_2^- group is approximately perpendicular to the Cu_4 plane but adjacent CO_2^- groups are on the opposite side of the plane. Two benzene molecules, between which the Cu_4 unit is placed, face each other. Although the Cu–C (in benzene) distances are longer than those determined in similar complexes,[5,6] all C atoms in each benzene ring having large thermal parameter are fairly definitely located. However, it is strange enough that no positional data of F atoms could be determined in their X-ray study. This suggests the presence of some disorder in the orientation of CF_3 groups and/or the occurrence of nearly free rotation of the groups. To clarify this point, the present investigation has been undertaken.

Experimental

Copper(I) trifluoroacetate synthesized by the method reported in literature[1] was purified by sublimation *in vacuo* at 140 °C. The compound was dissolved in benzene and the solvent was removed by vacuum distillation. The compound desorbs and adsorbs benzene molecules rather freely. The curve of the adsorption isotherm shows a plateau at 5 mmHg (1 mmHg=133.322 Pa) benzene vapor pressure, where the composition is determined as $[Cu_4(CF_3COO)_4]\cdot 2C_6H_6$. At higher benzene vapor pressure, the compound adsorbs additional benzene molecules physically giving $[Cu_4(CF_3COO)_4]\cdot nC_6H_6$ ($n>2$). Therefore, the number of "coordinated" benzene molecules was regulated by adjusting the equilibrium vapor pressure of benzene at 5 mmHg. The sample thus prepared was sealed in glass ampoules and employed for NMR and differential thermal analysis (DTA) measurements.

Two homemade pulsed NMR spectrometers[7,8] were employed for the determination of ^1H and ^{19}F nuclear spin-lattice relaxation times (T_1) at various temperatures using a conventional π-τ-$\pi/2$ pulse sequence. The experiments of DTA were carried out by means of a homemade apparatus.[9] Temperatures were determined by use of a copper-constantan thermocouple and were estimated to be accurate within ±1 K.

Results and Discussion

The $\log T_1$ values of ^1H observed at 20 and 45.500 MHz plotted against $10^3 T^{-1}$ for $[Cu_4(CF_3COO)_4]\cdot 2C_6H_6$ are shown in Fig. 1. Figure 2 shows a similar plot for the ^1H and ^{19}F nuclei determined at 45.500 and 42.804 MHz, respectively, under the same strength of applied magnetic field.

At room temperature, ^1H T_1 determined at 20 MHz yielded a fairly large value of *ca.* 30 s. With decreasing temperature, $\log T_1$ decreased linearly against $10^3 T^{-1}$ down to *ca.* 100 K, below which temperature the magnetization recovery curves became suddenly nonexponential and yielded long- and short-T_1 components as given in Fig. 1. The $\log T_1$ value determined at 45.500 MHz decreased with decreasing temperature along the same line as that obtained at 20 MHz down to *ca.* 100 K. Below this temperature, nonexponential magnetization recovery curves were also detected. The foregoing observation suggests the occurrence of phase transition.

To confirm this point, we carried out the experiments of DTA below room temperature. When the sample was cooled, an exothermic anomaly appeared at *ca.* 100 K, while an endothermic peak was recorded at 130 K with increasing the temperature from *ca.*

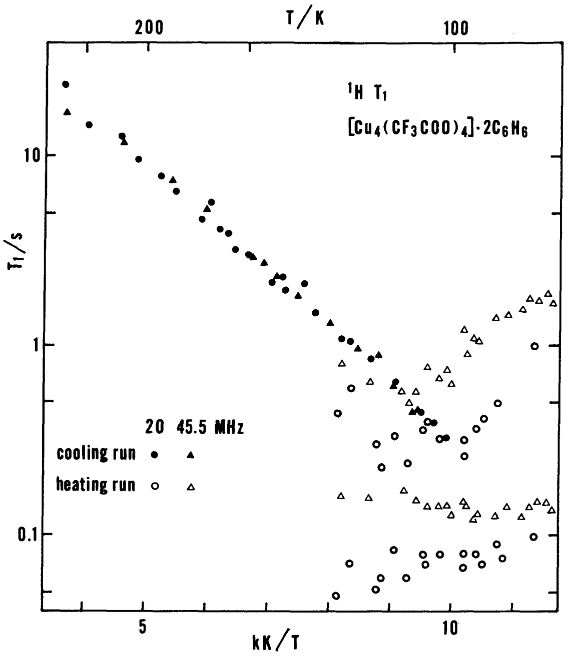

Fig. 1. Temperature dependences of ^{1}H T_1 in [Cu$_4$(CF$_3$COO)$_4$]·2C$_6$H$_6$ observed at 20 (●) and 45.500 (▲) MHz for the high-temperature phase and its supercooled one. For the low-temperature phase, long- and short-T_1 components observed with increasing temperature at the resonance frequencies of 20 (○) and 45.500 (△) MHz are plotted.

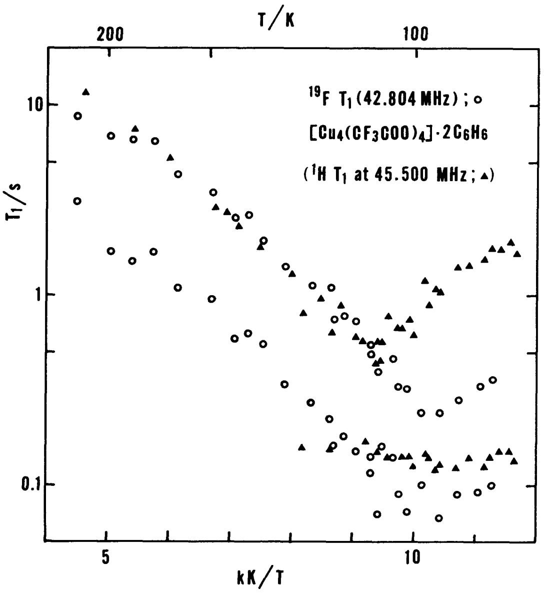

Fig. 2. Temperature dependences of ^{19}F T_1 in the complex observed at 42.804 MHz. The long- and short-T_1 components indicated by circles (○) observed for both phases are shown. Almost the same values were obtained for both cooling and heating runs. ^{1}H T_1 values determined at 45.500 MHz indicated by ▲ are shown for comparison.

80 K, showing the occurrence of thermal hysteresis. Accordingly, one can conclude that [Cu$_4$(CF$_3$COO)$_4$]·2C$_6$H$_6$ crystals undergo a first order phase transition at 130 K.

This complex contains ^{1}H and ^{19}F nuclei both of which have large magnetic moments and, therefore, it is expected that the T_1 values of both nuclei are governed by the motional process of benzene molecules and/or CF$_3$ groups through the mechanism of cross relaxation between them.[10] In solid benzene, the C_6 reorientation about the symmetry axis of the molecule is known to be activated near 100 K,[11] while Punkkinen *et al.* reported that CF$_3$ groups in solid CF$_3$COOAg perform the C_3 reorientation about their symmetry axis with the activation energy, E_a of 25 kJ mol^{-1}.[12] To obtain more detailed information about the motional process responsible for the ^{1}H T_1 values observed above, the T_1 measurements were performed on ^{19}F nuclei at the resonance frequency of 42.804 MHz. This frequency was selected so that the magnetic field where ^{19}F nuclei resonate at the above frequency was the same as that employed for the foregoing ^{1}H experiments.

It is characteristic for this complex that the magnetization of ^{19}F nuclei exhibits nonexponential recovery in both high- and low-temperature phases. The ^{19}F T_1 values of the former phase clearly belong to the hot side of the T_1 minimum because $\log T_1$ decreases linearly against $10^3 T^{-1}$ down to *ca.* 100 K. The magnetization recovery curves observed could be explained as arising from two long- and short-T_1 components. It is interesting to note that both components yielded no discernible discontinuity at both transformation temperatures (T_{tr}) from high- to low-temperature phase on the cooling run and also from low- to high-temperature phase on the heating run. The $\log T_1$ *vs.* 10^3 T^{-1} curve of the long component of ^{19}F T_1 in the high-temperature phase coincided with that of the ^{1}H T_1 as shown in Fig. 2. This indicates that the cross relaxation is operative between ^{1}H and ^{19}F nuclei and the same motional process governs the T_1 of both nuclei.

The existence of the short-T_1 component for the high-temperature phase in addition to the long one suggests that the motion responsible for the relaxation process of both nuclei is that of CF$_3$ groups, possibly the C_3 reorientation of the groups. The appearance of the nonexponential recovery curves for ^{19}F nuclear magnetization in the temperature region above its T_1 minimum can be interpreted in terms of cross correlation of ^{19}F–^{19}F dipolar interactions within a CF$_3$ group performing rapid reorientation about its C_3 axis. The nonexponential magnetization recovery curves explainable by the cross correlation have been found for ^{1}H T_1 in CH$_3$ groups of various organic compounds containing the group[13,14] and also for ^{19}F T_1 in CF$_3$COOAg.[12]

To confirm the C_3 reorientation of CF$_3$ groups activated in the present complex, we estimated the 2nd moment, M_2 of ^{19}F NMR from the analysis of free induction decay (FID) signals observed at 120 and 90 K. The FID curves $M_x(t)$ observed were assumed to be expressed as a function of time, t by[15)]

$$M_x(t) = M_x(0)\exp(-a^2t^2/2). \tag{1}$$

Here, a is a parameter determining the width of the Gaussian function. From this equation, M_2 can be given as

$$M_2 = a^2. \tag{2}$$

Least-squares-fitting calculation of Eq. 1 to the observed FID curves by use of SALS[16)] at the Computation Center of Nagoya University afforded the approximate M_2 values of 1.9 and 2.3 G^2 (1 G=10^{-4} T) at 120 and 90 K, respectively.

The rigid lattice M_2 value of isolated CF_3 groups can be calculated as 7.3 G^2 by use of the geometrical parameters of a CF_3 group determined for CF_3COOAg crystals.[17)] When isolated CF_3 groups perform the rapid C_3 reorientation, M_2 reduces the value to 1.8 G^2. In the present crystals, the ^{19}F M_2 value for the CF_3 group performing the C_3 reorientation is expected to become larger due to ^{19}F–^{19}F and ^{19}F–^{1}H dipolar interactions with ^{19}F in neighboring CF_3 groups and ^{1}H in neighboring benzene molecules, respectively. Accordingly, the above M_2 values estimated from FID observed indicate that the CF_3 groups perform the C_3 reorientation rapidly enough in the NMR time scale even at 90 K.

Figure 1 shows that ^{19}F T_1 detected by the spin-lattice relaxation of ^{1}H nuclei through cross relaxation between ^{19}F and ^{1}H in the high-temperature phase gives the same $\log T_1$ *vs.* 10^3 T^{-1} curve for the two different applied magnetic fields. This indicates that the observed ^{19}F T_1 can be interpreted in terms of usual dipolar interactions expressed by[18)]

$$T_1^{-1} = C[\tau/(1+\omega^2\tau^2)+4\tau/(1+4\omega^2\tau^2)], \tag{3}$$

where C, τ, and ω denote the motional constant for the CF_3 groups, the correlation time of the C_3 reorientation of the group, and the angular resonance frequency, respectively. Here, we assume an Arrhenius relationship between τ and the activation energy E_a, for the motional process as

$$\tau = \tau_0 \exp(E_a/kT), \tag{4}$$

where τ_0 denotes the correlation time at the limit of infinite temperature. From the gradient of the $\log T_1$ *vs.* 10^3 T^{-1} curves obtained for both ^{1}H T_1 and ^{19}F T_1 in the room-temperature phase, one can evaluate E_a for the C_3 reorientation of the CF_3 groups using Eqs. 3,4 as 5.5 kJ mol^{-1}.

The obtained E_a value is very small as compared with that of 25 kJ mol^{-1} reported for the same motional mode in CF_3COOAg crystals.[12)] Therefore, one can conclude that the CF_3 groups in the present complex are nearly free to rotate in the crystal. This is compatible with the result of X-ray analysis[3)] which was incapable of locating the positions of the F atoms, although there still remains a possibility that the CF_3 groups are statistically disordered and undergo C_3 reorientation almost freely. The C_6 reorientation of benzene molecules in this crystal could not be detected for the present investigation possibly because the motion may be so rapid that it gives very short correlation time at least in the room-temperature phase.

For the low-temperature phase, nonexponential magnetization recovery curves were observed for both ^{1}H and ^{19}F nuclei. This may be due to the dipolar cross relaxation between ^{19}F and ^{1}H nuclei because they are usually observed on the low-temperature side of T_1 minima when cross relaxation between heteronuclei is effectively operative.[19,20)] The T_1 values of both nuclei obtained for the low-temperature phase mostly belong to the cold side of T_1 minima. No further discussion for the results of T_1 measurements in this phase may be made because no structural data can be available.

It is noteworthy, however, that the ^{19}F T_1 value of both components changes almost smoothly with changing temperature across T_{tr} on both heating and cooling runs whereas the ^{1}H T_1 value changes drastically at T_{tr}. When the temperature was lowered, ^{1}H $\log T_1$ decreased linearly against 10^3 T^{-1} to *ca.* 100 K, where two T_1 values appeared suddenly. With increasing temperature in the low-temperature phase, two ^{1}H T_1 values were obtained up to 130 K, above which temperature the single ^{1}H T_1 of the high-temperature phase appeared. These facts suggest that the phase transition of this complex affects the motional state of the benzene molecules more strongly than that of the CF_3 groups.

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