H-Transfer Motions in an H-Bonded (Chloranilic Acid)-(1,3-Diazine) 1:2 Molecular Complex Studied by ^{35}Cl NQR and ^{1}H NMR

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^{35}Cl NQR and ^{1}H NMR relaxation times (T_{1Q}, T_{1H}) were measured in a hydrogen-bonded (chloranilic acid)-(1,3-diazine) 1:2 molecular complex in a temperature range of ca. 100–300 K. NQR frequencies observed were explained by the monovalent (1−) ionic structure of chloranilic acid, implying partial H-transfer to diazine molecules. This H-transfer was shown to be dynamic by observing a single T_{1H} minimum at ca. 120 K. Two new relaxation processes observed by NQR in high-temperature range, but undetected by NMR, were shown to be H-transfer motions between differently charged states of chloranilic acid molecules.

In our previous studies, we showed that NQR can be a new technique for detecting the hydrogen transfer through intermolecular H-bonds in solids by measuring temperature dependences of the ^{35}Cl NQR relaxation in *p*-chlorobenzoic acid[1] and 1:2 complexes of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone) with 1,4- and 1,2-diazines[2,3] (abbreviated to 1,4- and 1,2-complex, respectively). These studies revealed that the intermolecular H-transfer can be observed by the NQR technique more sensitively than by the familiar solid-state ^{1}H NMR method. In the multi-H-transfer systems cited above, respective transfer modes were clearly detected separately in the NQR measurements, whereas only a single relaxation process corresponding to the lowest-temperature mode was observed by ^{1}H NMR. This is because the intermolecular H-transfer results in a charge transfer between molecules that causes a marked fluctuation of the electric field gradient (efg) at NQR nuclei. On the other hand, the fluctuation of the magnetic field made by this motion is small and gives only a weak relaxation mechanism in ^{1}H NMR, because the migration distance of H-atoms in H-bonds is short, of the order of 10 pm.

In crystals of 1:2 complexes of chloranilic acid with 1,4- and 1,2-diazines,[4] two symmetric H-bonds are formed between chloranilic acid and diazine molecules. We have shown[3] that three kinds of H-transfer modes between two equivalent monovalent ionic structures of chloranilic acid, and also among neutral, monovalent and divalent species can take place. In good agreement with this prediction, the same number of relaxation processes were observed by the ^{35}Cl NQR relaxation measurement in 1,2-complex, where the most stable structure of chloranilic acid in crystal is the divalent ion. On the other hand, only two NQR relaxation processes were found in 1,4-complex where the monovalent ion was shown to be stable for chloranilic acid. For 1,2-complex, the correspondence between two possible excitation paths of H-transfer from the divalent ionic state and the observed two relaxation processes is difficult and not conclusive.

In the present study, we performed NQR and NMR measurements in an analogous chloranilic acid complex where 1,3-diazine, having a different hydrogen attractive force from those of the foregoing 1,2- and 1,4-derivatives, is introduced. The reported crystal structure of the complex with 1,3-diazine-(abbreviated to 1,3-complex)[5] is similar to those of 1,2- and 1,4-complexes, and contains three almost isolated symmetric molecular units bonded by OH···N hydrogen bonds with a short O···N distance (261.5 pm) comparable to 259.0[5] and 258.2 pm[4] in 1,4- and 1,2-complexes, respectively. We can expect the H-transfer in this system from this short O···N distance, and new H-transfer-mode sequences due to the different H-bond strengths from those in the foregoing complexes and a pK_a value (1.31)[6] of 1,3-diazinium in solution different from 2.25[6] and 0.57[6] in 1,2- and 1,4-diazinium ions, respectively. For these purposes, ^{35}Cl NQR, ^{1}H NMR, and thermal measurements were performed in crystalline (chloranilic acid)-(1,3-diazine) 1:2 complex, $[(C_6Cl_2O_2(OH)_2)(C_4N_2H_4)_2]$.

Experimental

A 1:2 molecular complex of chloranilic acid ($C_6O_2Cl_2(OH)_2$) with 1,3-diazine ($C_4N_2H_4$) was prepared according to the literature.[5] The dark purple crystals obtained were recrystallized from methanol. Samples used for the measurements were identified by elemental analyses: Calcd for C, 0.455; H, 0.027; N, 0.152. Found: C, 0.450; H, 0.028; N, 0.150. We also performed a single crystal X-ray diffraction analysis at room temperature and obtained a crystal structure in good agreement with reported data.[5]

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^{35}Cl NQR frequencies were measured by a Dean-type external quenching super-regenerative oscillator[7] with the Zeeman modulation, used in over a range of 115–290 K. The ^{35}Cl NQR relaxation time (T_{1Q}) was determined with a home-made pulsed spectrometer[8] in the same temperature range by applying the π–τ–$\pi/2$ pulse sequence. The ^{1}H NMR spin–lattice relaxation time (T_{1H}) was measured with a home-made pulsed spectrometer at a Larmor frequency of 54.3 MHz[9] over a range of 69–290 K by applying the saturation recovery method.

For detecting possible phase transitions, we employed the differential thermal analysis (DTA) with a home-made apparatus above 100 K up to room temperature using chromel-p-constantan thermocouples.

Results and Discussion

Temperature Dependence of ^{35}Cl NQR Frequencies. Temperature dependences of ^{35}Cl NQR frequencies in 1,3-complex are shown in Fig. 1. A single resonance line, consistent with the structural data[5] requiring that all chlorine atoms in crystals are crystallographically equivalent, was observed in the high-temperature range above 210 K. The resonance line disappeared below ca. 115 K and above ca. 290 K with cooling and heating the sample, respectively. The resonance signal was weakened and no signal was observed between ca. 205 and 210 K. In this temperature range, a frequency discontinuity of ca. 60 kHz was observed. By the measurement of DTA, we found a quite broad and weak heat anomaly with a peak around 202 ± 5 K, implying the presence of a phase transition in crystals. Over a temperature range of 115–160 K, another resonance line ca. 20 kHz higher, with nearly the same intensity but broader than that of the low frequency, was observed. This indicates that two nonequivalent Cl sites are formed in crystals below the phase transition temperature. Upon heating, both lines were gradually weakened and the high-frequency line disappeared around ca. 160 K. Observed resonance frequencies were 35.954 and 35.935 ± 0.001 MHz at 115 K, and 35.537 ± 0.001 MHz at 290 K.

By the extrapolation of the observed frequency to 77 K, ca. 36.0 MHz is obtained. Neutral chloranilic acid was reported to show a resonance line at 37.15 MHz at 77 K,[10] while divalent sodium chloranilate (2−) has an averaged value of 35.20 MHz at the same temperature.[10] Comparing these data with that in the present 1,3-complex, we can presume that chloranilic acid in the present system has a charge close to (1−), or takes the monovalent (1−) structure most of the time.

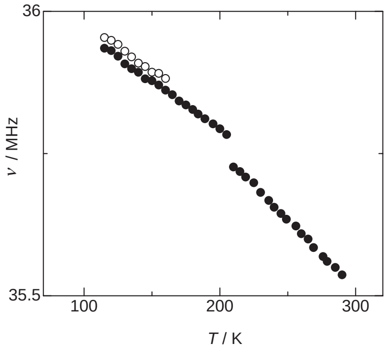


Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies (ν) in (chloranilic acid)-(1,3-diazine) 1:2 complex. A single resonance line observed at high temperatures is split into two lines, shown by closed and open circles below the phase transition at ca. 204 K. Resonance signals could not be observed below 115 K and above 290 K.

Table 1. Theoretical Values of ^{35}Cl Quadrupole Coupling Constants (e^2Qq), Asymmetry Parameters (η), and Resonance Frequencies (ν) in the Static Lattice of an Isolated Chloranilic Acid Molecule, and Mono- and Divalent Ionic States[11]

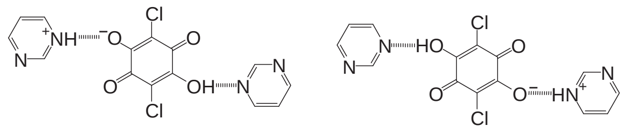
	e^2Qq/MHz	η	ν/MHz
Neutral (0)	−77.8	0.11	38.98
Monovalent (1−)	−72.3	0.09	36.20
Divalent (2−)	−64.4	0.12	32.38

Since the monovalent state of chloranilic acid has not been prepared, no NQR data on this state was reported. To confirm the above assignment of the observed frequency, Bailey[11] performed the theoretical calculation of quadrupole parameters in a neutral chloranilic acid molecule, and in mono- and divalent ions in the isolated state. The calculated values of quadrupole coupling constants (eQq) and asymmetry parameters (η), together with resonance frequencies (ν) derived, are given in Table 1. The absolute values themselves cannot be directly compared with the observed values, because no effects from thermal vibrations and charges in neighboring molecules in crystals are included in the calculation. If we note relative values, we can see that the monovalent ion gives a frequency at the middle of those found in neutral and divalent species supporting the present interpretation.

From the observed NQR frequencies given above, we can see that the formal charge of chloranilic acid in 1,3-complex is close to that in 1,4-complex, which gave ca. 36.40 MHz at 77 K.[2] The stability of the monovalent chloranilate in 1,3-complex can be expected from pK_a values of 1,3-diazinium ions of 1.31 in H_2SO_4[6] and pK_{a1} and pK_{a2} of chloranilic acid of 0.76 and 2.58, respectively, in an aqueous $NaClO_4$ solution.[6] The frequency order: 1,2-, 1,3-, and 1,4-complexes, agrees with that of pK_a values in these diadinium ions, giving 2.25, 1.31, and 0.6, in the same order, in aqueous solutions.[6] From these data, we can expect that diazine molecules in 1,3-complex will attract hydrogen to nearly the same extent but a little stronger than diazine molecules in 1,4-complex in agreement with a larger pK_a value in 1,3-diazinium ions, as given above. These differences in resonance frequencies caused by electric charges on chloranilic acid molecules can be explained by the Townes–Dailey approximation,[12] which predicts that more negatively charged chlorine atoms with electronic structures closer to a spherical ion will give lower resonance frequencies.

The most stable structure of the present 1,3-complex in crystals can, accordingly, be expressed as I and II given in Chart 1, where the equivalent mode of the H-transfer to the diazine molecule on the opposite side of the chloranilic acid molecule can be realized with the equal possibility.

^{1}H NMR Spin–Lattice Relaxation Time (T_{1H}). A temperature dependence of ^{1}H NMR T_{1H} observed at a Larmor frequency of 54.3 MHz is shown in Fig. 2. In the range of 69–290 K, a single T_{1H} minimum was observed at ca. 110 K, and a discontinuous change attributable to the phase transition



(I) (II)

Chart 1.

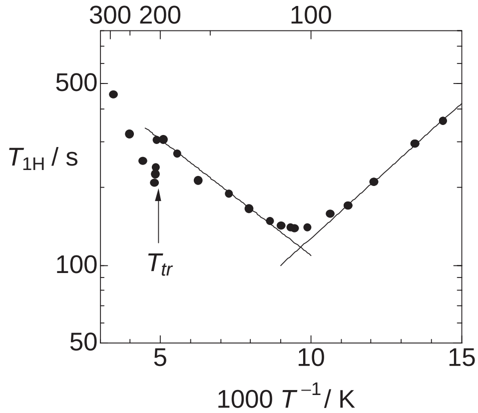


Fig. 2. A temperature dependence of ^{1}H NMR spin–lattice relaxation time (T_{1H}) observed in (chloranilic acid)-(1,3-diazine) 1:2 complex at a Larmor frequency of 54.3 MHz. Solid lines are best-fitted slopes giving activation energies drawn on both sides of the T_{1H} minimum. T_{tr} is the phase transition temperature.

was obtained within the range 205–210 K. Analogously to the analysis for T_{1H} in 1,2- and 1,4-complexes,[2,3] this T_{1H} minimum was explained by the H-transfer motion in the H-bonds between chloranilic acid and diazine molecules. From T_{1H} slopes in the high- and low-temperature sides of the minimum, activation energies of 2.1 and 2.3 ± 0.5 kJ mol^{-1}, respectively, for this motion were obtained. The low activation energy of ca. 2.2 kJ mol^{-1} compared with 3.8 and 3.2 kJ mol^{-1} determined for 1,2- and 1,4-complexes,[2,3] respectively, suggests that the protonic jump in 1,3-complex is easier than those in the other complexes. This result agrees with the order of T_{1H} minimum values, giving 150, 45, and 37 s in 1,3-, 1,4-, and 1,2-complexes, respectively, observed at the Larmor frequency of 54.3 MHz. Here, a longer T_{1H} value means a shorter jump distance of protons, because less averaging of the magnetic dipolar interactions is caused by this jumping.

From the most stable structure of 1,3-complex, shown above as structure I and II, the obtained H-transfer mode can be assigned to the simultaneous H-transfer of two H-atoms in a chloranilic acid molecule, as given by I ↔ II. This motion is most probable because the stable monovalent ionic structure of chloranilic acid derived from NQR frequencies is retained throughout the motion, and also because these activation energies are close to 3.2 kJ mol^{-1} determined for the same motional mode in 1,4-complex.[2]

From the fact that the NQR measurement revealed the presence of two kinds of crystallographically nonequivalent chlorine sites in the low-temperature phase, one may expect that the H-transfer mode given above is split into two modes at low temperatures. The fact that a single T_{1H} minimum was observed, however, implies that the expected crystal distortion in the low-temperature phase is quite small and thus only a single mode was observed. Accordingly, even though two different modes of H-transfer are formed in the low-temperature phase, they give almost the same relaxation effect. The quite small splitting of NQR frequencies observed in this phase also supports this interpretation.

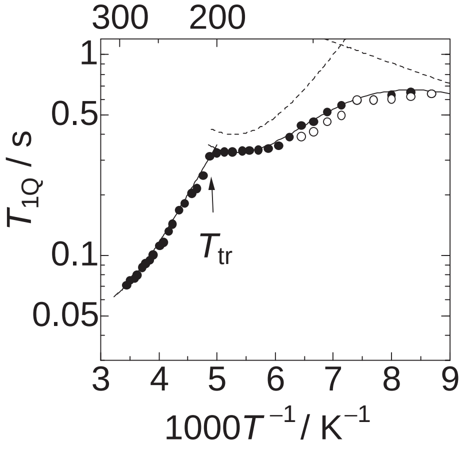


Fig. 3. A temperature dependence of ^{35}Cl NQR spin–lattice relaxation time (T_{1Q}) observed in (chloranilic acid)-(1,3-diazine) 1:2 complex. Broken and solid lines are calculated values for three motional modes and the best-fitted theoretical curve given by their summation, respectively. T_{tr} is the phase transition temperature.

^{35}Cl NQR Spin–Lattice Relaxation Time (T_{1Q}). Observed data of ^{35}Cl NQR T_{1Q} in a range of 115–290 K are shown in Fig. 3. Two resonance lines observed in the low-temperature phase afforded almost the same T_{1Q} values. The obtained temperature dependence was attributed to the three superimposed relaxation processes, each of which was assumed to be expressed by the Debye-type relaxation equation[13] given by

$$T_{1Q}{}^{-1} = C\left(\frac{\tau_c}{1+\tau_c^2\omega^2}\right), \tag{1}$$

where C, τ_c, and ω denote the motional constant, the motional correlation time, and the NQR frequency, respectively. We also assume that an Arrhenius-type equation for the activation of this motion can be given by

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right). \tag{2}$$

Here, E_a is the activation energy of the motion.

Applying these equations, we fitted three T_{1Q} curves to the observed data, where the lowest-temperature relaxation process was assumed to have the same E_a as that derived from T_{1H}. The best fitted T_{1Q} values and determined motional parameters are shown in Fig. 3 and Table 2, respectively.

The facts that three motional modes were observed in NQR, whereas only a single mode was observed in NMR, can be explained by the reason already reported.[2,3] Since no disordered position of atoms in crystal except acidic hydrogens in chloranilic acid was reported in the present complex at room

Table 2. Activation Energies (E_a), Pre-Exponential Factors (τ_0) of Motional Correlation Times, and Motional Constants (C) of H-Transfer Motions in (Chloranilic Acid)-(1,3-Diazine) 1:2 Complex Determined by ^{35}Cl NQR Spin–Lattice Relaxation Time Measurement in Three Temperature Ranges

Temp range	Low	Intermediate	High
E_a/kJ mol^{-1}	2.2 ± 0.5[a)]	7.6 ± 1.0	9.8 ± 1.0
$\tau_0 \times 10^{10}$/s	1.0 ± 0.5[b)]	0.35 ± 0.05	—
$C \times 10^{-9}$/s^{-2}	0.83 ± 0.05[b)]	1.1 ± 1.0	—

a) The value obtained by NMR was assumed. b) The T_{1Q} minimum temperature same as in T_{1H} was assumed.

temperature by the X-ray study,[5] we can expect that observed motions are due to the transfer of acidic protons as discussed for 1,2- and 1,4-complexes.[2,3]

As described above, the lowest-temperature T_{1Q} decrease observed below ca. 120 K was assigned to the correlated H-transfer of two hydrogen atoms keeping the monovalent structure of chloranilic acid given above as I ↔ II, because this relaxation was observed in the temperature range close to that in T_{1H}. Since the other two relaxation processes observed at high temperatures gave T_{1Q} values shorter than that in the lowest-temperature one, we can presume that the high-temperature motional modes fluctuate the efg at resonant chlorine atoms more than that by the lowest-temperature motion. Analogously to the motional modes reported in 1,2- and 1,4-complexes,[2,3] possible H-transfer motions are uncorrelated H-transfer modes which consist of proton interchanges between differently charged states of chloranilic acid molecules giving marked efg fluctuations compared with the lowest-temperature mode which keeps the monovalent charge on the molecule throughout the H-transfer process. The three expected kinds of H-transfer modes including the lowest-temperature motion are shown in Fig. 4, where mode ***A*** that keeps the monovalent ionic state of chloranilic acid is expected to contribute to T_{1H} and T_{1Q} in the lowest-temperature range, while mode ***B*** and mode ***C***, between mono- and divalent ions, and monovalent ions and neutral molecules, respectively, are observed by the NQR relaxation at higher temperatures. It should be emphasized that NQR can observe respective H-transfer modes separately, while ^{1}H NMR could not. This is because the NQR detection of the efg fluctuation caused by the intermolecular charge transfer is much more sensitive than the NMR measurement of the magnetic dipolar relaxation caused by a small displacement of protons in H-bonds.

The two relaxation processes observed at high temperatures cannot straightforwardly be corresponded to the expected modes ***B*** and ***C*** given in Fig. 4. In the present stage, we lack for any direct reasoning enabling us to assign definitely. Since the pK_a value of 1.31 for 1,3-diazinium is much higher than 0.65 for 1,4-diazinium and approaches 2.25 in 1,2-diazinium, we can expect that 1,3-diazine attracts hydrogen more strongly than 1,4-diazine, implying that the stability of divalent chloranilic acid in 1,3-complex is high compared with that in 1,4-analog. From NQR frequencies, an analogous tendency was obtained, namely, 1,3-complex gave the NQR frequency of ca. 36.0 MHz at low temperatures, being ca. 400 kHz lower than that in 1,4-complex; this value is close to ca. 35.2 MHz in divalent chloranilate salt.[10] It was noted before that the most stable structure in both 1,3- and 1,4-complexes should be the monovalent chloranilic acid ion. But, as is shown from the above discussion, the most stable structure in 1,4-complex is shifted to the neutral chloranilic acid, whereas that in 1,3-complex is shifted to the divalent ion.

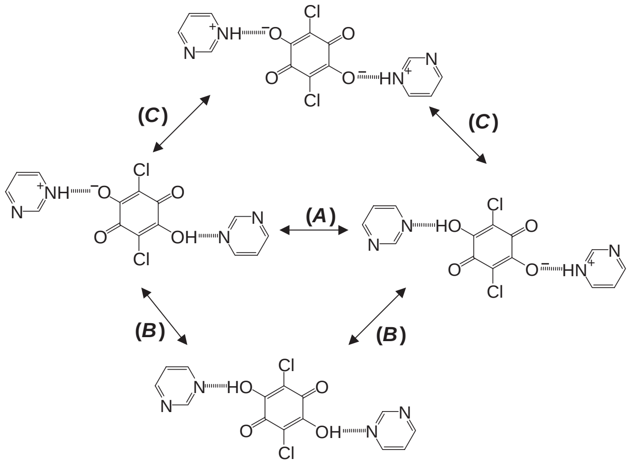


Fig. 4. Three kinds of hydrogen transfer modes expected in crystal of (chloranilic acid)-(1,3-diazine) 1:2 complex. ***A***, ***B***, and ***C*** indicate three expected kinds of H-transfer modes.

Temperature dependences of NQR frequencies also can provide information of stable structures of chloranilic acid molecules. The 1,2-complex consisting of the divalent acid as the stable form gave an unusual frequency increase with the temperature increase from 77 K.[3] This can be explained that the time being in the monovalent structure, which gives a higher frequency, increases upon heating. Both 1,3- and 1,4-complexes showed normal negative temperature coefficients of the resonance frequencies on heating, but the magnitude of the frequency decrease in the former was about double that in the latter,[2] although both have quite analogous arrangements of molecules in crystals.[5] 1,3-Complex afforded roughly a 400 kHz decrease of the frequency in a range ca. 110–290 K. This unusually large decrease is unexplainable only by lattice vibrations; it is attributable to the contribution from divalent ionic structure giving a low frequency. On the other hand, the structure of 1,4-complex is mostly contributed from neutral chloranilic acid molecules, which give a frequency higher than those in 1,3-complex containing ionic structures.

The above considerations clearly shows that the most stable structure of 1,3-complex consists of monovalent chloranilic acid ions at low temperatures. It is reasonable to assume that, upon heating, excitation motions to the divalent acid ion by H-transfers start first, then, motions to the neutral acid molecules occur at higher temperatures.

Effects from Phase Transition. From the NQR frequency jump observed at the phase transition of ca. 204 K, it is expected that this transition is first order. However, since the resonance signal became gradually weak and disappeared in the range of 205–210 K, the frequency might be continuous in this range. Furthermore, a very wide and weak heat anomaly was observed in our DTA measurements. These suggest that this first-order transition has a higher order nature as well.

No marked changes in the crystal structure at the transition seems to be expected, because of the quite weak heat anomaly observed and the very small NQR frequency splitting of ca. 20 kHz in the low-temperature phase.

It is noted that a clear T_{1H} decrease was observed at the transition. Since T_{1H} values in this temperature range were quite long, it is highly possible that only a subtle change in crystals gives such a marked anomaly. Detailed analyses of this T_{1H} decrease need further frequency dependent measurements of relaxations, and, in the present stage, we cannot comment on its mechanism. But some effect from lattice fluctuation in crystals in the neighborhood of the transition seems to be a possible explanation, if one considers the long tail of the heat anomaly observed on both sides of the transition temperature.

Conclusion

As shown in 1,2- and 1,4-complexes containing two kinds of intermolecular H-bonds in a complex, the ^{35}Cl NQR relaxation measurement in analogous 1,3-complex afforded new motional modes of H-transfers which were undetected by the ^{1}H NMR relaxation measurements. The present NMR and NQR data including the previous results show that the NQR method can provide a probe for detecting H-motions in multiply H-bonded solids more sensitively than the widely used NMR technique. Of course, since a marked advantage of NMR is the direct detection of H-motions, the combined application of both techniques is quite effective in studying intermolecular multiple H-transfer systems.

In the present 1,3-comlex, the most stable structure of chloranilic acid was determined to be a monovalent ionic state as in 1,4-complex. Three kinds of H-transfer motions detected by NQR could be assigned to three modes expected from the structure, i.e., the correlated transfers of two protons retaining the monovalent structure, uncorrelated transfers between monovalent and divalent ionic structures, and such transfers between monovalent ionic and neutral molecular states. ^{1}H NMR could show the presence of only the first mode. The correspondence of last two motions to the observed NQR relaxation processes is, however, not conclusive and further investigations will be required.

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