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Phase transition and proton exchange in 1,3-diazinium hydrogen chloranilate monohydrate

In the hydrate crystal of 1:1 salt with 1,3-diazine and chloranilic acid (H2ca), (1,3-diazineH)·H2O·Hca, an unique hydrogen-bonded molecular aggregate is formed. A single proton transfer from chloranilic acid to 1,3-diazine results in 1,3-diazinium cation, 1,3-diazineH+, and hydrogen chloranilate anion, Hca-, in the crystal. There exists hydrogen bond between 1,3-diazinium ion and water (H2O) of crystallization, and between the H2O and hydrogen chloranilate ion. X-ray crystal analysis [1] revealed proton disorder in the N-H···O hydrogen bond at 225 K (Fig. 1). In order to reveal dynamic aspect of this disorder, 35Cl NQR measurements were conducted. Fig. 2 shows temperature dependence of the NQR frequencies. Two resonance lines observed at 35.973 and 35.449 MHz at 321 K split into four lines below Tc = 198 K clearly showing occurrence of a solid-solid phase transition; 36.565, 36.357, 36.011, 35.974 MHz at 77 K. Temperature dependence of spin-lattice relaxation time T1 in high-temperature phase was observed to obey an Arrhenius-type relation with the activation energy of 8.5 kJ mol-1. This result leads to the conclusion that proton exchange in the N-H···O hydrogen bond takes place in the high-temperature phase. Below Tc the symmetry related N-H···O hydrogen bonds shown in Fig. 1 become non-equivalent and one of them falls in the ordered state [1]. Specific heat measurements by DSC resulted in the transition entropy of 1.3 J K-1 per 1 mole [(1,3-diazineH)·H2O·Hca]2 which is far less than 2R ln2 = 11.5 J K-1 mol-1. It may be expected that proton ordering is not complete even in LTP and proton exchange in the two hydrogen bonds does not occur independently but concertedly in the high-temperature phase.

[1] K. Gotoh, T. Asaji, and H. Ishida, Acta Cryst. C66 (2010) o114.

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