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ORDERED AND DISORDERED HYDROGEN BONDS IN TIN(II) CHLORIDE DIHYDRATE FROM SINGLE CRYSTAL NEUTRON DIFFRACTION

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Single crystal neutron diffraction shows that the deuteron arrangements in $SnCl_2.2D_2O$ are ordered and disordered, respectively, below and above T_{tr}. In the high temperature phase four deuterons of two non-equivalent water molecules distribute among seven sites with individual occupancy factors.

Tin(II) chloride dihydrate, $SnCl_2.2H_2O$, exhibits a phase transition characterized by a strong dielectric anomaly at -55 °C.$^{1)}$ Our recent X-ray study has shown that no detectable change in structure occurs at the transition point, except for a slight discontinuity in the (100) spacing.$^{2)}$ Moreover, its spectra of proton and deuteron magnetic resonance (PMR and DMR) have provided a clear evidence for rapid reorientation of water molecules of crystallization above the transition temperature (T_{tr}). These results indicate that the ordering of the hydrogen atoms plays an important role in triggering the transition. We have also located the hydrogen atoms in the low temperature phase on the basis of PMR and DMR data for single crystals and of the crystal structure described by us.$^{3)}$ For determining the hydrogen positions the crystal structure of the deuterated analogue, $SnCl_2.2D_2O$, has now been analyzed by neutron diffraction both above and below T_{tr} (-39 °C). The present note will be chiefly concerned with the deuteron arrangements in the hydrogen bonded network.

Deuterated single crystals were used for the experiment, because the structure and also the lattice constants did not change upon deuteration. The intensity data were collected by use of a Rigaku neutron four-circle diffractometer at Research Reactor Institute of Kyoto University. The wavelength used was 0.994 Å and the flux density at the specimen was $7\times10^4 n/cm^2.sec$. A total of 311 independent reflections for the high temperature phase was measured at room temperature and 814 reflections for the low temperature one at liquid nitrogen temperature. A severe extinction effect was successfully corrected by taking into account some influence of crystal size on the diffraction intensity.

Prior to the ND experiment, the precise cell constants were determined in $SnCl_2.2H_2O$ by using an X-ray four-circle diffractometer (Table 1). All deuteron positions in $SnCl_2.2D_2O$ were located by Fourier and difference Fourier syntheses, starting from the X-ray data on the heavy atoms. The positional parameters were refined by full-matrix least-squares techniques with isotropic thermal parameters for the high temperature phase and with anisotropic thermal factors for the low temperature one. The final R values were 0.10 above T_{tr} and 0.07 below it. In these calculations the amount of H-substitution for D was first estimated from the low temperature ND data and then the occupancy factors for all deuteron sites were refined under a condition that the sum of two deuteron occupancies in each H-bond is constrained to unity. The atomic coordinates and the site occupancies thus obtained are given in Tables 2 and 3. The positional parameters of heavy atoms, namely Sn, Cl and O, in the high temperature phase agreed quite well with the X-ray result.[2)] Furthermore, it was found definitely that these parameters remain unchanged after the transition, whereas the deuteron arrangement changes from the disordered to the ordered one.

Table 1. Crystal Data of $SnCl_2.2H_2O$.

temperature	+24 °C	-185 °C
space group	$P2_1/c$	$P2_1/c$
Z	4	4
a (Å)	9.326(2)	9.158(2)
b (Å)	7.254(2)	7.156(3)
c (Å)	8.974(3)	8.942(3)
β (°)	114.91(5)	114.50(5)
V (Å^3)	550.4	533.3

Crystals of $SnCl_2.2D_2O$ have a predominantly layered structure, in which dichloroaquatin(II) complex molecules, $SnCl_2D_2O(1)$, form double layers and the second water molecules, $D_2O(2)$, are inserted between them. The most striking feature of the structure is that two types of water molecules are linked to each other by three hydrogen bonds in a two-dimensional network parallel to the (100) plane.

Figure 1 shows the deuteron-ordered structure in the H-bond sheet determined at -185 °C. The configuration of $D_2O(1)$ is type H and that of $D_2O(2)$ is type E, according to a classification by Chidambaram et al.[4)] In the former, one of the lone pairs of oxygen O(1) is directed toward the tin atom and the other toward the hydrogen donor oxygen O(2"), while in the latter the two lone pairs of O(2) are directed toward two donor oxygens O(1) and O(1"). Thus, three deuterons, D(2) and D(4) of the coordinated water molecule and D(5) of the non-coordinated one, form three normal O-D···O hydrogen bonds. The rest one D(7) of $D_2O(2)$ does not participate in any O-D···O bonding, but is directed toward one chlorine atom rather than two.[2)] These ordered, non-centric hydrogen positions are consistent with our PMR and DMR results. Geometrical features of these H-bonds are listed in Table 4(a).

As described earlier, the deuterated crystal undergoes the phase transition at -39 °C and above this temperature reorientation rates of both water molecules are high enough to affect their NMR spectra. The resulting, disordered structure was defined by the present ND study (Fig. 2). In the high temperature phase, two deuterons of $D_2O(1)$ distribute among three sites D(2), D(4) and D(6) with individual occupancy factors given in Table 3. In contrast to this, only one deuteron of $D_2O(2)$ behaves in a similar way and the other remains at the site D(7) with full occupancy.

This finding suggests that both kinds of water molecules reorient about Sn-O(1) and O(2)-D(7) axes, respectively, with three-fold symmetry. In that case it is expected that the deuteron occupancy factors would be 2/3 for $D_2O(1)$ and 1/3 for $D_2O(2)$. Values obtained for D(1) to D(4) agreed approximately with those, but the

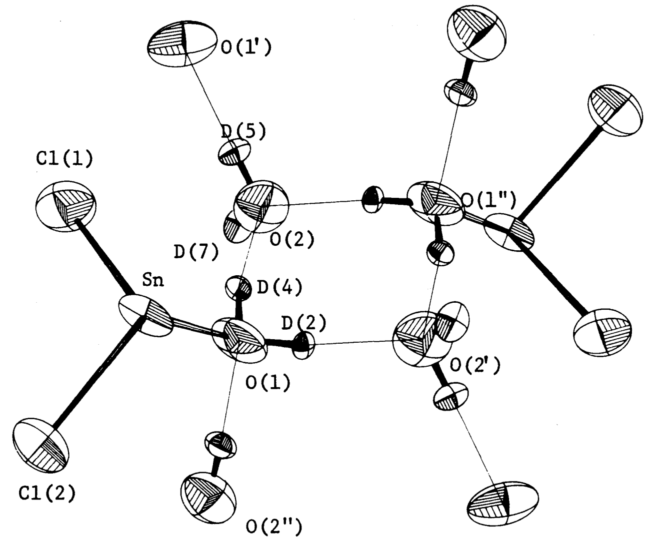

Fig. 1 The deuteron-ordered arrangement in the low temperature phase of $SnCl_2.2D_2O$. H-bonded distances are given in Table 4(a). Thermal vibration ellipsoids of the individual atoms are plotted.

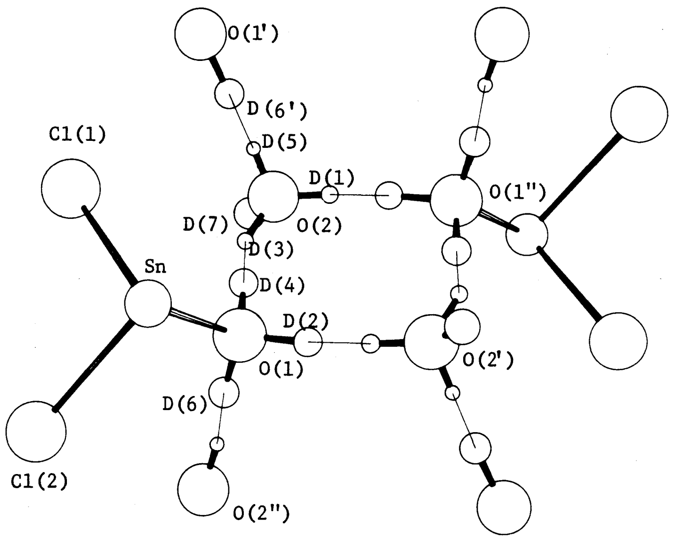

Fig. 2 The deuteron-disordered arrangement in the high temperature phase of $SnCl_2.2D_2O$. Bond lengths concerning H-bonds are given in Table 4(b). Each deuteron occupancy factor given in Table 3 is represented by the size of a circle.

Table 2. Atomic Coordinates and Site Occupancies in the Low Temperature Phase of $SnCl_2.2D_2O$ (Standard Deviations in Parentheses)

atom	site occupancy	x/a	y/b	z/c
Sn	1.0	0.3773(3)	0.2565(4)	0.5335(3)
Cl(1)	1.0	0.2830(2)	0.4899(3)	0.6836(2)
Cl(2)	1.0	0.3071(2)	0.5008(3)	0.3043(2)
O(1)	1.0	0.1096(4)	0.1685(5)	0.4156(4)
O(2)	1.0	-0.0683(4)	0.2058(5)	0.5931(4)
D(1)	0.0	-	-	-
D(2)	1.0	0.1014(4)	0.0331(5)	0.4056(4)
D(3)	0.0	-	-	-
D(4)	1.0	0.0502(4)	0.2004(6)	0.4847(4)
D(5)	1.0	-0.0117(5)	0.2509(7)	0.7022(5)
D(6)	0.0	-	-	-
D(7)	1.0	-0.1550(5)	0.2907(7)	0.5399(5)

Table 3. Atomic Coordinates and Site Occupancies in the High Temperature Phase (Standard Deviations in Parentheses)

atom	site occupancy	x/a	y/b	z/c
Sn	1.0	0.3755(8)	0.2595(15)	0.5351(7)
Cl(1)	1.0	0.2869(5)	0.4904(11)	0.6887(5)
Cl(2)	1.0	0.3075(6)	0.4982(15)	0.3052(5)
O(1)	1.0	0.1124(17)	0.1763(13)	0.4131(12)
O(2)	1.0	-0.0663(12)	0.2033(14)	0.5976(11)
D(1)	0.29(5)	-0.0869(42)	0.0878(31)	0.5982(32)
D(2)	0.71(5)	0.1097(31)	0.0337(21)	0.4065(21)
D(3)	0.25(5)	-0.0131(28)	0.2349(45)	0.5341(26)
D(4)	0.75(5)	0.0531(15)	0.2027(20)	0.4817(14)
D(5)	0.18(4)	-0.0258(47)	0.2412(55)	0.6886(42)
D(6)	0.82(4)	0.0472(12)	0.2249(18)	0.2985(12)
D(7)	1.0	-0.1480(18)	0.2861(25)	0.5468(16)

occupancy for site D(5) or D(6) deviated by three times its standard deviation. The sums consequently became 2.28 (more than 2) for the coordinated $D_2O(1)$, and 1.72 (less than 2) for the non-coordinated $D_2O(2)$, which suggests partial dissociation of water molecules in the crystal lattice. It does not seem surprising in the case of $SnCl_2 \cdot 2H_2O$ because of the pronounced protonic conduction found at and above the transition point and also of the so-called "solid acid" nature. In order to judge the significance of these deviations the occupancy factors are now in refinement under various bonding conditions.

In Table 4 hydrogen bond distances in the high temperature phase are compared with those in the low temperature one. It is noteworthy that the hydrogen bond in question O(2)···O(1'), differs again from the other two, that is, its distance (2.75 Å) in the high temperature form is shorter than that (2.81 Å) in the low temperature form in contrast with the others. It is therefore conceivable that this H-bond, O(2)-D(5)···D(6')-O(1'), should be the trigger of the phase transition.

In conclusion, it becomes clear from the present study that the phase transition of tin(II) chloride dihydrate is ascribed to the ordering of the hydrogen atoms without any change in the heavy atom arrangements. Raman spectra of single crystals of $SnCl_2 \cdot 2H_2O$ and $SnCl_2 \cdot 2D_2O$ have also provided some valuable information on the nature of the phase transition.[5)] To clarify the dynamical aspect of the disordered hydrogen atoms, pulsed PMR experiments are now in progress.

The details of the ND results will be reported soon.

Table 4. Hydrogen Bond Distances (Å) in High and Low Temperature Phases of $SnCl_2 \cdot 2D_2O$ with Their Standard Deviations in Parentheses

(a) The ordered structure below T_{tr}

O(1)-D(2)	0.973(5)	D(2)··O(2')	1.737(5)	O(1)··O(2')	2.702(5)
O(1)-D(4)	1.004(6)	D(4)··O(2)	1.730(6)	O(1)··O(2)	2.718(6)
O(2)-D(5)	0.952(5)	D(5)··O(1')	1.857(5)	O(2)··O(1')	2.808(4)
O(2)-D(7)	0.955(5)				

(b) The disordered structure above T_{tr}

O(1)-D(2)	1.036(18)	D(2)··O(2')	1.763(19)	O(1)··O(2')	2.783(14)
O(1)-D(4)	1.005(22)	D(4)··O(2)	1.816(20)	O(1)··O(2)	2.808(21)
O(1)-D(6)	1.012(13)	D(6)··O(2")	1.741(13)	O(1)··O(2")	2.752(13)
O(2)-D(1)	0.860(26)	D(1)··O(1")	1.928(24)	O(2)··O(1")	2.783(14)
O(2)-D(3)	0.929(32)	D(3)··O(1)	1.949(34)	O(2)··O(1)	2.808(21)
O(2)-D(5)	0.790(35)	D(5)··O(1')	1.972(33)	O(2)··O(1')	2.752(13)
O(2)-D(7)	0.925(19)				

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