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Crystal Structure and ^{35}Cl NQR of Copper(II) Trichloroacetate Trihydrate

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The crystal structure of the title compound has been determined by means of X-ray diffraction. The crystal data and the final R value are: $Cu(CCl_3COO)_2 \cdot 3H_2O$, monoclinic $C2/c$, a=23.082(3), b=6.253(1), c=9.726(2) Å, β=94.67(1)°, Z=4, R=0.049. The structure consists of monomeric $Cu(CCl_3COO)_2(H_2O)_3$ molecules, which are linked together by intermolecular O-H···O hydrogen bonds to form a layer parallel to (100). Each Cu(II) atom is coordinated by five oxygen atoms which form nearly a square pyramid; two oxygen atoms of two carboxylate ions and two water molecules form its basal plane and the remaining water molecule occupies the apical position. The mean basal Cu-O length is 1.961 Å and the apical one 2.183 Å. The Cu(II) atom is displaced from the basal plane by 0.110 Å toward the apical oxygen. Thermal analysis (DSC) disclosed two phase transitions at 163 and 207 K, their estimated molar enthalpies being about 0.4 and 0.7 kJ mol^{-1}, respectively. At 77 K, 24 ^{35}Cl NQR signals are observed in the frequency range 38.7—40.3 MHz. The X-ray diffraction photographs for both low-temperature phases indicate the appearance of superstructures with less symmetrical space groups; the b spacing doubles below 207 K, while both b and c spacings double below 163 K.

One of the present authors studied ^{35}Cl nuclear quadrupole resonance (NQR) on a various salts of trichloroacetic acid with a view to obtaining structural informations.[1] Of these, the NQR spectrum of $Cu(CCl_3COO)_2 \cdot nH_2O$ was not consistent with that reported in the literature.[2] In order to solve this question, we investigated the crystal structure of the title compound. In course of this work, it was found that the ^{35}Cl NQR spectrum expected from the crystal structure determined at room temperature is quite different from that observed at 77 K. In fact, thermal analysis confirmed the occurrence of phase transitions at 163 and 207 K. Fortunately, undergoing of both phase transitions did not damage the crystal, and the structural changes could be followed by X-ray diffraction method at low temperatures. To get further information on the transitions the temperature dependence of the ^{35}Cl NQR frequencies were reinvestigated more accurately than in the earlier work.

The present paper deals with the crystal structures of the compound and the nature of the phase transitions newly found. Furthermore, the conformation of CCl_3COO^- group is discussed in detail especially in comparison with that recently found in $CCl_3COONH_4 \cdot 2.5H_2O$.[3]

Experimental

Material. Addition of dicopper carbonate dihydroxide hydrate to an aqueous solution of trichloroacetic acid in a stoichiometric ratio yielded a light blue precipitate at about 40 °C. The trihydrate crystal was obtained by recrystallization of the precipitate from water as a blue, flat plate characterized by perfect cleavage.

X-Ray Structure Determination. The density was measured by pycnometry with petroleum at 18 °C. The lattice parameters and the space group were first determined with a Weissenberg camera (Rigaku Denki Co.); reflection conditions hkl: $h+k=2n$ and $h0l$: $l=2n$ led to monoclinic $C2/c$ or Cc, the former space group being confirmed by successful refinements. A single crystal 0.2×0.3×0.3 mm in size was mounted with [010] coincident with the goniostat axis of an automated Rigaku four-circle diffractometer AFC-4, graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å), 40 kV-200 mA used. Unit cell parameters were refined by a least-squares method using 25 2θ values ($25° < 2\theta < 34°$). Intensity measurement in ω—2θ scan mode was made up to 2θ=55° ($-30 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 8$, $-12 \leqslant l \leqslant 12$), three standard reflections (040, 1604, $91\bar{5}$) were monitored every 50 reflections throughout the experiment. A total of 3210 reflections were measured. Lorentz-polarization and absorption effects were corrected, empirical absorption correction-factors on F less than 1.19.[4] Equivalent reflections were merged ($R_{av}=\sum||F_o|-<|F_o|>|/\sum|F_o|$=0.017), and of 1608 reflections remained 1441 with $|F_o|>3\sigma(F_o)$ were used for the structure determination.

The positional coordinates of Cu and Cl atoms were obtained by a direct method with MULTAN78[5] and confirmed by a three-dimensional Patterson synthesis. The other non-hydrogen atoms were located by successive Fourier syntheses. The structure was refined by block-diagonal least-squares with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were located by a difference Fourier synthesis and refined with isotropic thermal parameters. The quantity $\sum w(|F_o|-|F_c|)^2$ with $w=1/[\sigma^2(F_o)+0.13247|F_o|]$ was minimized for 1441 unique reflections and 96 variables. The final refinement including hydrogen atoms gave $R=\sum(||F_o|-|F_c||)/\sum|F_o|$=0.049, $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$=0.073 and goodness of fit $S=[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$=1.14, where m is the number of reflections and n the number of refined parameters. The maximum positive and negative electron densities $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ in the final difference Fourier synthesis were +0.9 and −0.9 e Å^{-3}, respectively. The maximum ratio of parameter shift to e.s.d. for non-hydrogen atoms, $(\Delta/\sigma)_{max}$, was 0.017. Neutral atomic scattering factors were used for all atoms and corrections for anomalous dispersion applied.[6] The computer programs used were MULTAN78, ORTEPII and UNICS-OSAKA.[5,7,8] The final atomic parameters are listed in Table 1.[9]

Crystal Data: $[Cu(CCl_3COO)_2(H_2O)_3]$, M_r=442.34, $C2/c$, a=23.082(3), b=6.253(1), c=9.726(2) Å, β=94.67(1)°, Z=4,

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Table 1. Fractional Coordinates and Equivalent or Isotropic Thermal Parameters (Å^2) with Estimated Standard Deviations in Parentheses

$B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$

Atom	x	y	z	B_{eq}/B_{iso}*
Cu	0	0.35222(12)	0.25	2.41(1)
Cl(1)	−0.20251(6)	0.30888(32)	0.31465(18)	5.55(3)
Cl(2)	−0.17847(7)	−0.08904(27)	0.44913(21)	5.67(4)
Cl(3)	−0.14626(8)	0.30503(38)	0.58822(16)	6.37(2)
O(1)	−0.0744(2)	0.3477(6)	0.3325(4)	3.89(6)
O(2)	−0.0630(2)	0.0075(7)	0.3807(6)	5.98(11)
O(W1)	0.0420(2)	0.3216(7)	0.4333(4)	4.37(6)
O(W2)	0	0.7014(8)	0.25	4.96(13)
C(1)	−0.0912(2)	0.1710(7)	0.3719(5)	2.71(6)
C(2)	−0.1524(2)	0.1721(7)	0.4285(5)	2.77(6)
H(1)	0.065(3)	0.423(14)	0.490(8)	5(2)*
H(2)	0.050(4)	0.203(14)	0.470(8)	6(2)*
H(3)	−0.019(5)	0.796(17)	0.318(10)	9(3)*

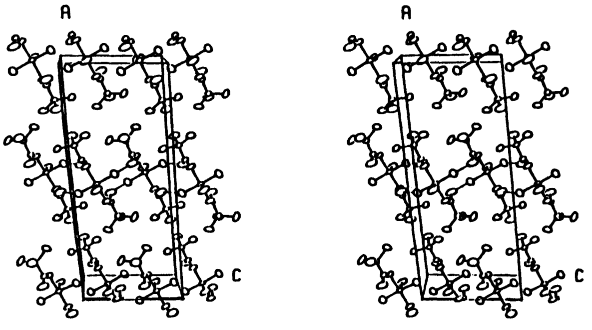

Fig. 1. A stereoscopic view of the crystal structure of $Cu(CCl_3COO)_2\cdot 3H_2O$ along the b axis. Thermal ellipsoids are shown at 50% probability level.

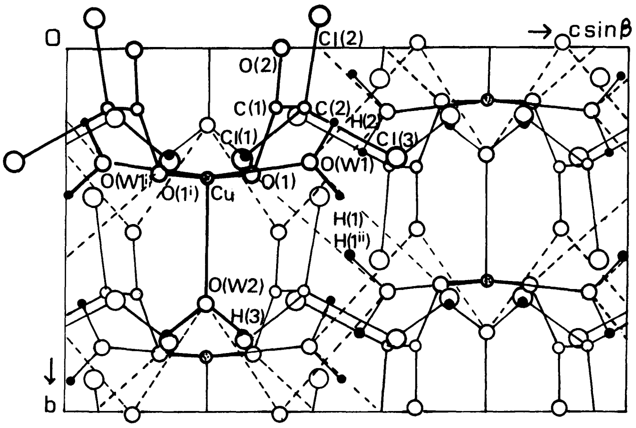

Fig. 2. The projection of crystal structure along the a axis with the atom numbering scheme.

D_m=2.08, D_x=2.10 Mg m^{-3}, μ(Mo $K\alpha$)=2.7 mm^{-1}, $F(000)$=868, T=291 K.

Thermal Analyses. Thermal gravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were carried out with two pieces of Rigaku "thermoflex" apparatus. The temperature ranges studied were 300—450 K for the former two and 100—300 K for the latter one. A relatively large single crystal (3×3×1 mm, about 16 mg) sealed in an aluminium cell under an atmosphere of nitrogen was used for DSC, because the transition enthalpies are too small to be detected with a powdered sample.

^{35}Cl NQR Experiment. The ^{35}Cl NQR frequencies were measured on a polycrystalline sample by use of a super-regenerative spectrometer with an accuracy of ±2kHz.[10]

Low-Temperature X-Ray Experiment. Oscillation and Weissenberg photographs were taken with a Cu $K\alpha$ radiation (40 kV, 150 mA) at 183 and 145 K. The specimen was kept at a desired temperature by controlling the flow rate of cold nitrogen gas and the current of a heater wound around an inner tube in which the gas flows. A flow of nitrogen-gas jetted through an outer tube formed a curtain to avoid formation of frost on the crystal during the experiment. A rather large single crystal (0.5 mm on edge) was chosen for the goniometric use at low temperatures.

Results and Discussion

Crystal Structure. A stereo pair of the crystal structure viewed along [010] and the projection along [100] with the atomic numbering scheme are shown in Figs. 1 and 2, respectively. Selected interatomic distances and angles are listed in Table 2. The structure of copper(II) trichloroacetate hydrate consists of discrete monomeric molecules, $[Cu(CCl_3COO)_2(H_2O)_3]$, in agreement with the prediction from the magnetic susceptibility[11] and ESR spectra.[12] The molecule has a crystallographic C_2 axis passing through the Cu and O(W2) atoms. Each copper(II) atom is coordinated by five oxygen atoms (two from monodentate trichloroacetato groups and three from water molecules) in a nearly square pyramidal arrangement. The four donor atoms, O(1), O(W1), O(1^i), O(W1^i), form a slightly distorted square and the water oxygen O(W2) occupies the apical position. The apical Cu-O(W2) distance (R_L=2.183 Å) is significantly longer than the mean basal Cu-O distance (R_s=1.961 Å), the tetragonality T^5(=R_S/R_L) being 0.90.[13] Such lengthening of the apical bond is quite common in copper(II) complexes with coordination numbers of 6 and even 5.[14] The four oxygen atoms in the CuO_5 chromophore is planar within 0.082(6) Å, and the central Cu atom is displaced from this plane by 0.110(2) Å toward O(W2). Although the second oxygen of each carboxylate ion

Table 2. Interatomic Distances (l/Å) and Angles (ϕ/°) with Standard Deviations in Parentheses

(1) CuO_5 chromophor					
Cu-O(1)	1.954(4)	Cu-O(W1)	1.968(4)	Cu-O(W2)	2.183(5)
[Cu-O(2)	2.946(6)]				
O(1)-Cu-O(W1)		90.7(2)	O(1)-Cu-O(W1$^{\rm i}$)		89.2(2)
O(1)-Cu-O(W2)		90.8(2)	O(W1)-Cu-O(W2)		95.6(2)
O(1)-Cu-O(1$^{\rm i}$)		178.3(2)	O(W1)-Cu-O(W1$^{\rm i}$)		168.8(2)
(2) CCl_3COO^- ion					
C(1)-O(1)	1.242(6)	C(1)-O(2)	1.212(8)	C(1)-C(2)	1.557(7)
C(2)-Cl(1)	1.757(5)	C(2)-Cl(2)	1.758(5)	C(2)-Cl(3)	1.758(5)
Cl(1)-C(2)-Cl(2)		108.1(3)	Cl(1)-C(2)-Cl(3)		109.2(3)
Cl(2)-C(2)-Cl(3)		110.0(3)	Cl(1)-C(2)-C(1)		110.4(3)
Cl(2)-C(2)-C(1)		111.4(3)	Cl(3)-C(2)-C(1)		107.7(3)
O(1)-C(1)-O(2)		126.4(5)	O(1)-C(1)-C(2)		114.9(4)
O(2)-C(1)-C(2)		118.4(5)			
O(1)-C(1)-C(2)-Cl(1)		48.1(5)	O(1)-C(1)-C(2)-Cl(2)		168.2(4)
O(1)-C(1)-C(2)-Cl(3)		−71.0(5)	O(2)-C(1)-C(2)-Cl(1)		−137.9(5)
O(2)-C(1)-C(2)-Cl(2)		−17.8(6)	O(2)-C(1)-C(2)-Cl(3)		102.9(5)
(3) Hydrogen bond					
O(W1)$\cdots$O(1$^{\rm ii}$)		3.122(6)	H(1)-O(W1)-H(2)		105(7)
O(W1)-H(1)		0.97(9)	O(1$^{\rm ii}$)$\cdots$O(W1)$\cdots$O(2$^{\rm iii}$)		89.8(2)
H(1)$\cdots$O(1$^{\rm ii}$)		2.24(8)	O(W1)-H(1)$\cdots$O(1$^{\rm ii}$)		150(7)
O(W1)$\cdots$O(2$^{\rm iii}$)		2.757(7)	O(W1)-H(2)$\cdots$O(2$^{\rm iii}$)		157(8)
O(W1)-H(2)		0.83(9)			
H(2)$\cdots$O(2$^{\rm iii}$)		1.97(8)			
O(W2)$\cdots$O(2$^{\rm iv}$)		2.774(8)	H(3)-O(W2)-H(3$^{\rm i}$)		108(9)
O(W2)-H(3)		1.0(1)	O(2$^{\rm iv}$)-O(W2)-O(2$^{\rm v}$)		92.7(3)
H(3)$\cdots$O(2$^{\rm iv}$)		1.8(1)	O(W2)-H(3)$\cdots$O(2$^{\rm iv}$)		159(10)

Symmetry code: (i) $-x$, y, $1/2-z$; (ii) $-x$, $1-y$, $1-z$; (iii) $-x$, $-y$, $1-z$; (iv) x, $1+y$, z; (v) $-x$, $1+y$, $1/2-z$.

group is situated at 2.946 Å from the Cu(II) atom, it is not regarded as bonded to Cu(II).

The bond lengths and angles in the trichloroacetato ligand are in agreement with those found in $CCl_3COONH_4\cdot 2.5H_2O$,[3] except for C-O distances and torsion angles. The lengths of 1.242 Å for C(1)-O(1) and 1.212 Å for C(1)-O(2) are significantly different owing to monodentative coordination of the ligand. More remarkable differences are seen in the torsion angles O-C-C-Cl, which are associated with the conformation of CCl_3COO^- ligand. In the most stable conformation of its free ion, the three torsion angles will be 90, 30, and 150°. In other words, one of the three C-Cl bonds will be perpendicular to the COO plane in the projection along the molecular axis C-C. As given in Table 2, the torsion angles deviate from these ideal values by 12—19° (the mean 15.3°) in contrast to the corresponding values of 0.3—3.0 (the mean 1.4°) for the NH_4 salt.[3] In both compounds, the CCl_3 groups are faced to each other with van der Waals contact and all the carboxylate oxygen atoms are participated in hydrogen bonds as acceptors. However, there exists a serious difference in coordination scheme between the two salts; in the Cu salt, one oxygen atom of the COO group coordinates also to a Cu(II) atom. It was therefore evidenced that the conformation of CCl_3COO moiety is largely affected by the bonding scheme with its surroundings.

As shown in Figs. 1 and 2, the $[Cu(CCl_3COO)_2(H_2O)_3]$ molecules are linked together by intermolecular hydrdogen bonds of O(W1)-H$\cdots$O(2), O(W1)-H$\cdots$O(1), and O(W2)-H$\cdots$O(2), forming a distinct layer parallel to (100). Thus, the terminal CCl_3 groups of trichloroacetato ligands face to each other with van der Waals contact between Cl(1) and Cl(2) (3.659 Å) and between Cl(1) and Cl(3) (3.582 Å) in interlayer space. Such a distinct layer structure is responsible for the perfect cleavage parallel to (100).

Thermal Properties and Phase Transitions. The DTA and TG experiments indicated that the dehydration of $Cu(CCl_3COO)_2\cdot 3H_2O$ proceeds in two steps; two water molecules were lost at about 338 K and the rest at about 404 K. On the other hand, two faint, but definite endothermic (exothermic) peaks were observed on heating (cooling) runs of DSC, providing a clear evidence for the presence of two phase transitions at 163 and 207 K. The transition enthalpies were estimated to be approximately 0.4 kJ mol^{-1} for the transition at 163 K and 0.7 kJ mol^{-1} for that at 207 K. These values are quite small and suggest very slight structural changes associated with the phase transitions. In fact, the single crystal remained unchanged in appearance after it experienced either phase transition many times. The three phases will be abbreviated as LTP, ITP, and RTP in order of increasing temperature, hereafter.

^{35}Cl NQR in LTP and ITP. The ^{35}Cl NQR frequencies at 77 K (the lowest temperature studied) are

Table 3. ^{35}Cl NQR Frequencies at 77 K and Their Temperature Coefficients at 110 K in $Cu(CCl_3COO)_2 \cdot 3H_2O$

Line No.	Frequency MHz	$(d\nu/dT)$ kHz K^{-1}	Line No.	Frequency MHz	$(d\nu/dT)$ kHz K^{-1}
ν_1	40.289	−6.71	ν_{11}	39.597	−4.19
ν_2	40.156$^{a)}$	−3.95	ν_{12}	39.549$^{a)}$	−7.92
ν_3	40.062$^{a)}$	−3.09	ν_{13}	39.536	−3.88
ν_4	40.005	−3.08	ν_{14}	39.411$^{a)}$	−4.72
ν_5	39.861$^{a)}$	−4.83	ν_{15}	39.322$^{a)}$	−4.94
ν_6	39.851	−3.36	ν_{16}	39.292	−7.12
ν_7	39.813$^{b)}$	−5.68	ν_{17}	39.213$^{a)}$	−5.89
		−4.18	ν_{18}	39.132$^{a,b)}$	−3.11
ν_8	39.807	−3.54			−3.29
ν_9	39.757$^{a)}$	−2.27	ν_{19}	39.044$^{a)}$	−4.65
ν_{10}	39.697$^{a,b)}$	−5.12	ν_{20}	39.041$^{a)}$	−4.54
		−6.85	ν_{21}	38.732	−2.87

a) These frequencies coincide with those reported for $Cu(CCl_3COO)_3 \cdot nH_2O$.[2] b) Two ^{35}Cl NQR lines superimpose by accident.

summarized in Table 3. At this temperature, 21 ^{35}Cl NQR lines were apparently observed, but three of them split into two lines at higher temperatures (see below). Therefore, there exist in total 24 NQR lines at 77 K. Twelve of these 24 frequencies coincide well with the 12 frequencies reported for $Cu(CCl_3COO)_2 \cdot nH_2O$.[2] The temperature dependences of the NQR frequencies are shown in Fig. 3. The lines at 39.813, 39.697, and 39.132 MHz at 77 K split into two lines as the temperature was raised. All of the 24 NQR signals faded out in the temperature range 115—170 K. Only a few signals could be observed still above about 160 K, and their frequency vs. T curves showed discontinuities around 163 K, as can be seen in Fig. 3(b). This observation confirms the presence of the phase transition at 163 K found by DSC.

The crystal structure of LTP has not been analyzed, but it is reasonable to expect that the difference in crystal structure between LTP and RTP is very slight. Therefore, one may discuss the ^{35}Cl NQR spectrum of LTP on the basis of the crystal structure of RTP. The ^{35}Cl NQR frequencies of LTP are distributed in a relatively wide frequency range from 38.7 to 40.3 MHz. This frequency splitting (at most 1.6 MHz) is too large to be attributed to mere crystal field effect. The geometry of the CCl_3 group is quite normal: Every C-Cl distance is typical of a single bond length and the angles between the three C-Cl bonds are close to the tetrahedral one. Thus, there seems to be no interaction of intramolecular origin through σ bonds that will be responsible for the frequency splitting. A possibility which could account for the frequency splitting is the rather peculiar configuration of the CCl_3COO group. Because its structure deviates considerably from the ideal one, Cl(2) and O(2) atoms are brought close together (2.863(6) Å) and this contact could contribute to shift the ^{35}Cl NQR frequency of the Cl(2).

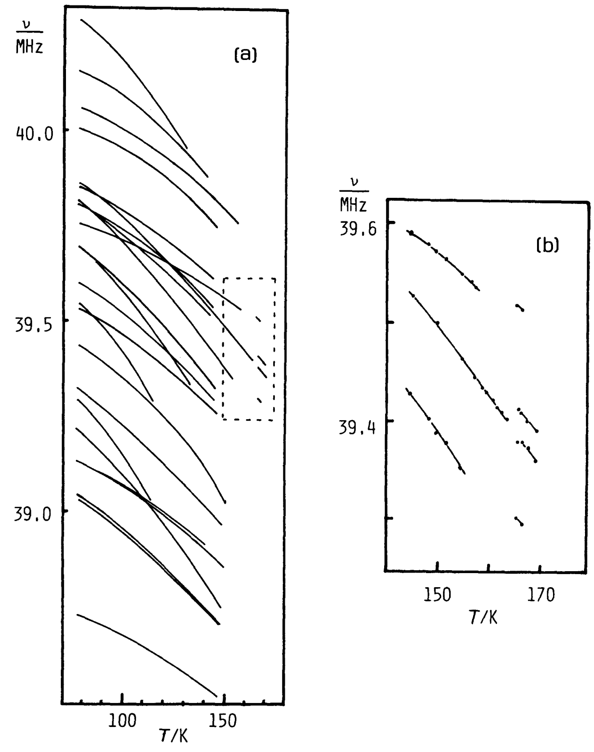

Fig. 3. (a) The temperature dependence of ^{35}Cl NQR frequencies in $Cu(CCl_3COO)_2 \cdot 3H_2O$; (b) enlargement of the region enclosed by dotted line in (a).

Another possibility which could explain the frequency splitting is the interactions between chlorine and water hydrogen atoms. The Cl(3)···H(1) distance 2.68(8) Å is shorter than the sum of the van der Waals radii (3.0 Å). In addition, H(3) is the second nearest hydrogen atom of the Cl(3) atom (3.6(1) Å), while H(2) and H(1) are the first and second nearest hydrogen atoms of the Cl(2) atom (3.10(8) and 3.36(8) Å). In contrast to these, the Cl(1) atom has no hydrogen neighbor closer than 3.9 Å. In an electrostatic model of hydrdogen bond, it is considered that a net positive charge is produced on the hydrogen atom participated in a hydrogen bond. In the present system, the positive charge on H(1), H(2), and H(3) can cause excess electric field gradients at the positions of Cl(3) and Cl(2) which could give rise to a shift of ^{35}Cl NQR frequency of about a hundred kHz. Thus, both effects of the hydrogen bonds and the Cl(2)···O(2) contact seem to be responsible for the frequency splitting.

Besides the large frequency splitting mentioned above, the extreme multiplicity is also characteristic of the ^{35}Cl NQR spectrum of LTP. According to the present X-ray analysis, RTP has only one crystallographically independent CCl_3 group in the unit cell. Therefore, the number of the ^{35}Cl NQR lines in RTP, if they were detected, should be three. In contrast, 24 ^{35}Cl NQR lines have been detected for LTP. Because the difference in the crystal structure between RTP and LTP is very slight, one may expect that the 24 NQR lines in LTP can be divided into three frequency groups each of which has 8 lines distributed in a narrow frequency region. However, the 24 lines are distributed almost uniformly and one fails to sort the lines in such a way. This indicates that the change in the crystal structure, though it is very slight, is quite effective to cause the shifts of the NQR frequencies to give a uniform distribution of lines. As shown in Table 3, the values of the temperature coefficients of the NQR frequencies are widely distributed and several of them are extremely large. These facts also suggest that the environment of each chlorine atom in LTP is considerably different from each other.

Structural Changes at Phase Transitions. The X-ray oscillation photographs, and zero- and first-layer Weissenberg photographs around [010] taken at 183 and 145 K provided valuable information on the crystal structures of ITP and LTP. The diffraction patterns of both phases were quite similar to those of RTP, except for extra spots superimposed on them. These additional sets of reflections had the spacings and very weak intensities indicative of the appearance of superstructures. It was therefore evidenced that the structural changes associated with the phase transitions are very slight, but the b spacing in RTP is doubled in ITP and the c spacing is also doubled in LTP. Moreover, the $(h1l)$ Weissenberg photographs for LTP phases suggested the lowering of the crystal symmetry from monoclinic to triclinic with the interaxial angles α' and γ' close to 90°. The observed reflection conditions, hkl: no and $h0l$: $l=2n$, led to monoclinic $P2/c$ or Pc for the superlattice in ITP, while the conditions, hkl: no and $h0l$: no did to triclinic $P\bar{1}$ or $P1$ for the superlattice in LTP.

The crystal data thus obtained are as follows:

$T=183$ K (ITP); $a'(=a)=23.13(5)$, $b'(=2b)=12.42(5)$, $c'(=c)=9.58(2)$ Å, $\beta'=95°$, $P2/c$ or Pc, $Z=8$,

$T=145$ K (LTP); $a'(=a)=23.09(6)$, $b'(=2b)=12.41(9)$, $c'(=2c)=19.04(5)$ Å, $\beta'=95°$, $P\bar{1}$ or $P1$, $Z=16$.

The numbers of ^{35}Cl NQR lines expected from these X-ray results are 12 or 24 for ITP and 48 or 96 for LTP, in contrast with the observations. The fade out of most or all signals in ITP or RTP may be due to rapid reorientation of CCl_3 groups about their threefold axes, in accord with the relatively large thermal parameters of Cl atoms (Table 1). On the other hand, the number of lines observed in LTP is just half of the expected one for more probable space group $P\bar{1}$. The further splitting may be too small to be detected.

In conclusion, the preliminary X-ray studies at low temperatures demonstrated that the positions of the heavy atoms in the three phases are not changed much. However, the appearance of superstructures in both ITP and LTP provided an evidence for some slight changes in geometries of CCl_3COO^- ligand and/or of (4+1) oxygen coordination around the Cu(II) atom, in particular with respect to the arrangements of the light atoms, O, C, and H. Such a mechanism would be supported by the very small enthalpy changes at the phase transitions. If in LTP the torsion angles in CCl_3COO^- groups are modified and consequently the water molecules form several kinds of hydrogen bonds, the interactions between Cl and O atoms and also between Cl and H atoms will be changed and hence the NQR frequencies of these chlorine atoms may shift from those of RTP. As a result, the splitting pattern in LTP will be different from that expected from the crystal structure of RTP.

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