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Calorimetric and single crystal X-ray study of the phase transition of $(PyH)_2PdCl_4$

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Abstract

Polymorphic transition of pyridinium tetrachloropalladate(II) was investigated by heat capacity measurements and by single crystal X-ray structural analysis. A large λ-type anomaly was detected at 240 K in the temperature dependence of the heat capacity. The low-temperature phase (LTP) belongs to the triclinic space group $P\bar{1}$ with $a=6.856(1)$, $b=7.293(1)$, $c=7.721(1)$ Å, $\alpha=75.180(2)°$, $\beta=71.081(2)°$, $\gamma=81.109(3)°$ at 100 K, and the high-temperature phase (HTP) to the same space group $P\bar{1}$ with $a=7.217(2)$, $b=7.470(2)$, $c=7.880(2)$ Å, $\alpha=73.438(3)°$, $\beta=65.195(3)°$, $\gamma=82.727(4)°$ at 293 K. The pyridinium cations are ordered antiferroelectrically in LTP. In HTP, however, an orientational disorder of the cation was observed. The energy difference between potential wells for the reorientation of pyridinium ion in HTP is discussed referring to the results of the present single crystal X-ray and heat capacity as well as the previous ^1H NMR measurements. A five-site disorder model is shown to be consistent with both of the observations of ^1H NMR and X-ray study.

Keywords: D. Crystal structure; D. Phase transition; D. Specific heat; D. Nuclear quadrupole resonance (NQR); C. X-ray diffraction

1. Introduction

Many pyridinium salts reveal solid–solid phase transitions related to a change in the pyridinium ion dynamics. To understand the nature of the pyridinium ion in its different solid phases extensive studies have been reported so far including the recent ones of a ferroelectric family of pyridinium salts with tetrahedral anion such as IO_4^- [1,2], ClO_4^- [3,4], BF_4^- [5–8], ReO_4^- [9].

NMR studies [10–12] of various pyridinium halides showed that the high-temperature phase is disordered and the pyridinium ion performs reorientation about its pseudohexad C_6 axis. However, it was revealed by the calorimetric study [13] that the disorder of the pyridinium ion in pyridinium iodide can not be explained by the simple 6-fold disorder of orientation but 12 distinguishable orientations should be taken into account. Moreover, the short range order was suggested to be present even in the high-temperature phase.

The potential well for the pyridinium reorientation in the low-symmetric crystal phase, has been discussed by the model of reorientation between inequivalent potential wells [12,14–18]. Kozak et al. showed by NMR study that the energy difference, which characterizes the inequivalence of the wells, is a function of temperature in pyridinium hexafluorophosphate [16]. Our recent calorimetric study of pyridinium tetrabromoaurate(III) also revealed the temperature dependence of the energy difference through a cooperative effect of pyridinium orientation [18].

As briefly described above, the order–disorder process of pyridinium ion is a scientifically very rich interesting problem. In this paper, we will deal with the phase transition of pyridinium tetrachloropalladate(II), $(PyH)_2PdCl_4$, a pyridinium salt with the planar $PdCl_4^-$ anion having cation–anion ratio of 2–1.

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It is known from ^{35}Cl NQR and DTA/DSC measurements that pyridinium tetrachloropalladate(II) $(PyH)_2PdCl_4$ undergoes a phase transition at $T_c = 241$ K [19]. The temperature dependence of the NQR frequencies and a very broad thermal anomaly observed in DTA suggest a second order nature of the phase transition. ^{1}H NMR second moment M_2 shows a very gradual smooth decrease across T_c with increasing temperature. This suggests that inequivalence of potential wells for pyridinium motion remains even above T_c. In [19], assuming non-equivalent three-wells and two-wells potentials for $T > T_c$ and $T < T_c$, respectively, we have estimated the potential energy inequivalence ΔE in the respective phases from the temperature dependences of ^{1}H M_2 and ^{35}Cl NQR spin-lattice relaxation time T_1, respectively.

In the present study we measured heat capacity C_p to determine entropy change ΔS through the transition, which was compared with the theoretical value expected from the potential change through T_c. The potential change estimated by the previous NMR/NQR study will be re-examined from a structural point of view by use of crystal data obtained by the present single crystal X-ray diffraction study.

2. Experimental

2.1. Preparation and identification

$(PyH)_2PdCl_4$ was prepared according to the method described in Gmelin's handbook [20]. Five grams (28 mmol) of $PdCl_2$ was dissolved in 50 mL hydrochloric acid (6 mol L^{-1}) with heating. In this solution, a solution obtained by dissolving 12 g of pyridine (0.14 mol) into 30 mL of 6 mol L^{-1} hydrochloric acid, was added. The mixed solution was concentrated to ca. 50 mL by heating to 125 °C in oil bath. On standing the solution at room temperature dark brown prismatic crystals were obtained. The crystals were dried over NaOH in a vacuum desiccator. About 10 g of $(PyH)_2PdCl_4$ was obtained (yield 85%). The compound was identified by comparing X-ray powder diffraction patterns with that of the previous work [19] and by detecting DTA peak at 241 K.

X-ray powder diffraction patterns were measured using Cu Kα radiation employing a Rigaku RINT 2100S. Silicon powder was used as an internal standard for the diffraction angle. DTA measurements were made by use of a home-made apparatus with a copper vs. constantan thermocouple.

2.2. Heat capacity measurements

Heat capacity was measured in the temperature range between 17 and 280 K by use of an adiabatic calorimeter employing 3.631 g (8.890 mmol) of $(PyH)_2PdCl_4$. A Platinum resistance thermometer (Minco Products S1059, USA), which had a nominal resistance of 100 Ω at 273.16 K, was used after the temperature scale was transferred from the other thermometer calibrated on the ITS-90. The imprecision and inaccuracy of the heat capacity measurements with the apparatus were estimated previously to be less than 0.04 and 0.4%, respectively [21].

2.3. Crystal structure determination

Single crystal X-ray measurement of HTP was carried out at room temperature using a Rigaku AFC-5R diffractometer. A SMART 1000/CCD diffractometer (Bruker) with graphite-monochromated Mo Kα radiation ($2\theta < 55°$) was applied to the X-ray experiments for LTP at 100 K, as well as for HTP at 293 K. The crystal structures were solved by direct method and refined by full-matrix least-square

Table 1

Crystal data and details of the experiments and refinements

	Low-temperature phase	High-temperature phase
Formula	$(C_5H_6N)_2PdCl_4$	$(C_5H_6N)_2PdCl_4$
Formula weight	408.43	408.43
X-ray radiation	Mo Kα	Mo Kα
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.856(1)	7.217(2)
b (Å)	7.293(1)	7.470(2)
c (Å)	7.721(1)	7.880(2)
α (deg)	75.180(2)	73.438(3)
β (deg)	71.081(2)	65.195(3)
γ (deg)	81.109(3)	82.727(4)
Cell volume (Å^3)	351.9(1)	369.6(1)
Z	1	1
D_c (g cm^{-3})	1.927	1.835
μ(Mo Kα)	2.051	1.952
$F(000)$	202	202
Temperature (K)	100	293
Crystal form	Prismatic	Prismatic
Crystal color	Brown	Brown
Crystal size (mm^3)	0.45×0.30×0.28	0.45×0.30×0.28
Theta range (deg)	2.86–26.87	2.85–27.12
Index range	$h -6$ to 8 $k -5$ to 9 $l -9$ to 9	$h -9$ to 9 $k -6$ to 9 $l -9$ to 10
Reflections collected	1542	2082
Reflections unique	1171	1425
R_{int}	0.0133	0.0204
Reflections ($I > 2\sigma(I)$)	1168	1407
$R_1(F)$ ($I > 2\sigma(I)$)	0.0320	0.0360
$wR_2(F^2)$ for all reflection	0.0972	0.0949
Number of parameters	103	73
Goodness of fit for all reflections $S(F^2)$	0.812	1.048
Weighting scheme	$w^{-1} = [\sigma^2(F_o^2) + (0.1002p)^2 + 0.8929p]$, $p = (F_o^2 + 2F_c^2)/3$	$w^{-1} = [\sigma^2(F_o^2) + (0.0517p)^2 + 0.4833p]$, $p = (F_o^2 + 2F_c^2)/3$
Max. shift/esd	0.001	0.001
ρ_{max} (e Å^{-3})	1.012	0.577
ρ_{min} (e Å^{-3})	−1.264	−0.632