Thermodynamics of ammonium halopallidates

I. Heat capacity and thermodynamic properties of \((\text{NH}_4)_2\text{PdCl}_6\) at temperatures from 6 K to 350 K

JANE E. CALLANAN,
Callanan Associates, 2888 Bluff, Suite 429, Boulder, CO 80301, U.S.A.

RON D. WEIR, a
Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ontario K7K 5L0, Canada

and EDGAR F. WESTRUM, JR.
Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, U.S.A.

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The heat capacity of ammonium hexachloropallidate \((\text{NH}_4)_2\text{PdCl}_6\) was measured at temperatures from 6 K to 350 K by adiabatic calorimetry. The heat-capacity curve is smooth and without anomalies. It rises rapidly from \(T \to 0\) to \(T = 150\) K where the \(C_p, m\) value is 26.62 \(R\) \((R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\). Above \(T = 150\) K, the increase to 32.41 \(R\) at 350 K occurs more slowly. Values of the standard thermodynamic quantities are tabulated to \(T = 350\) K.

1. Introduction

The ammonium hexahalogenated metallates \((\text{NH}_4)_2\text{MX}_6\) (M denotes a polyvalent ion, and X denotes a halogen) usually crystallize at room temperature into a cubic antifluorite structure of space group Fm\(\overline{3}m\) and are ideal models for studying molecular motion in solids. The \(\text{NH}_4^+\) ion, located at a tetrahedral lattice site, is able to overcome the low barrier to rotation about its threefold axis. At room temperature, \(\text{NH}_4^+\) experiences classical hindered rotation and, at \(T < 40\) K, quantum-tunnelling.\(^{(1)}\) Some salts in this family undergo structural phase transitions and change into a phase of lower symmetry as the temperature is lowered.\(^{(2)}\) Some

a To whom correspondence should be sent.
salt pairs, e.g. K$_2$SnCl$_6$, (NH$_4$)$_2$SnCl$_6$,$^3$ and K$_2$OsCl$_6$, (NH$_4$)$_2$OsCl$_6$, show evidence of a transition in the alkali salt but not in the ammoniated salt. The (NH$_4$)$_2$PtCl$_6$, (ND$_4$)$_2$PtCl$_6$, pair is an example where a structural transition occurs only in the deuterated analogue. However, in the tellurium salts, there is a single structural transition in (NH$_4$)$_2$TeCl$_6$, (9) but there are two additional transitions in (ND$_4$)$_2$TeCl$_6$.,$^{10,11}$

Low barriers to rotation of 342. $R \cdot K$ and 307. $R \cdot K$ have been reported$^{12}$ for NH$_4^+$ in (NH$_4$)$_2$PtCl$_6$ and (NH$_4$)$_2$PdCl$_6$, respectively, which have attracted interest in determining the rotational potential of NH$_4^+$ in these and related compounds.$^{13-16}$ Heat-capacity results, a knowledge of which should help in understanding the mechanism of molecular rotation, are not available for either (NH$_4$)$_2$PdCl$_6$ or its deuterated analogue. We have, therefore, measured the heat capacity of (NH$_4$)$_2$PdCl$_6$ at temperatures from 6 K to 350 K by adiabatic calorimetry as part of our ongoing work with ammonium salts, and the results are described below.

2. Experimental

The sample of (NH$_4$)$_2$PdCl$_6$ was supplied by the Aldrich Chemical Company as 99.99 mass per cent pure according to the Certificate of Analysis. The only other element detected by spectrographic trace analysis was Fe with mass fraction 6 \times 10^{-6}. The finely-divided red powder was used as supplied as there was no need to grind the sample further.

The Guinier-de-Wolff diffraction pattern of our sample was in perfect agreement with the standard pattern for this compound: No. 9-397 as determined by the Joint Committee for Powder Diffraction Standards.$^{17}$ The structure at room temperature is face-centred with a = (0.9819 ± 0.0006) nm, which compares with 0.9826 nm for the standard.$^{17}$

The molar heat capacity $C_{p,m}$ was measured from $T = 6$ K to $T = 350$ K by adiabatic calorimetry in the Mark XIII adiabatic cryostat described previously.$^{18}$ A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for the temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S., now NIST) against the IPTS-48 (as revised in 1960)$^{19}$ for temperatures above 90 K, against the N.B.S. (NIST) provisional scale from 10 K to 90 K, and by the technique of McCrackin and Chang$^{20}$ below 10 K. These calibrations are estimated to reproduce thermodynamic temperatures to within 0.03 K between 10 K and 90 K and within 0.04 K above 90 K.$^{21}$ The effects of changing the temperature scale to ITS-90 vary over the range 90 ≤ $T/K$ < 350 from 0.020 ≤ ($T_{90} - T_{48}$)/K ≤ −0.27, and for the range 14 ≤ $T/K$ ≤ 350 from −0.008 ≤ ($T_{90} - T_{55}$)/K ≤ 0.018.$^{22,23}$ The changes in heat capacity, enthalpy, and entropy resulting from the conversion from IPTS-68 to ITS-90 have been shown for a number of materials to lie within the experimental error of the measurements over the range from 16 K to 2800 K.$^{22}$ Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S.
HEAT CAPACITY OF (NH₄)₂PdCl₆

The heat capacities from about T = 6 K to T = 350 K were acquired with the assistance of a computer, which was programmed for a series of determinations. During the drift periods, both the calorimeter temperature and its first and second derivatives of temperature with respect to time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. While the calorimeter was operating, the heater current and potential difference as well as the duration of the heating interval were determined. Also recorded was the apparent heat capacity of the system, which included the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-99) with four internal vertical vanes and a central entrant well for (heater + thermometer) was loaded with (NH₄)₂PdCl₆. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that moisture was no longer present in the sample. After addition of helium gas to the vessel (p = 5.1 kPa at T = 300 K) to facilitate thermal equilibration, the calorimeter was then sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top with a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density of 2.492 g·cm⁻³ derived from the unit-cell edge of our sample. The mass of the (NH₄)₂PdCl₆ was 11.94644 g (~0.03363176 mol based on its molar mass of 355.2132 g·mol⁻¹).

The thermal history of the (NH₄)₂PdCl₆ is represented by the following linear array. The arrows denote either cooling or heating, which correspond to the acquisition of the heat-capacity results.

\[
\begin{align*}
300 K & \quad \rightarrow \quad 206 K \quad \rightarrow \quad 218 K \quad \rightarrow \quad 56 K \quad \rightarrow \quad 347 K \quad \rightarrow \quad 6 K \quad \rightarrow \quad 75 K.
\end{align*}
\]

3. Results and discussion

The experimental molar heat capacities for (NH₄)₂PdCl₆ are presented in table 1, where the temperature represents the midpoint of the temperature intervals. The measurements were made in three series covering the range from T = 6.0 K to T = 350 K. The estimated errors in our heat-capacity values vary from about 0.01 · Cₚ,m at T = 10 K to <0.005 · Cₚ,m at T > 25 K. The heat capacity of the sample represented about 0.53 to 0.84 of the measured total heat capacity. A plot of Cₚ,m/R against T from 6 K to 350 K is presented in figure 1. The curve is smooth and without anomalies. It rises rapidly from T → 0 to T = 150 K, above which the Cₚ,m rises more slowly.

Special care was taken with respect to particle size and thermal history of our (NH₄)₂PdCl₆ sample in view of the hysteresis in Cₚ,m encountered by other workers with various ammonium compounds, but not necessarily with ammonium hexachloropalladate. Reproducibilities of the heat-capacity of NH₄PF₆, RbPF₆, (NH₄)₂SnCl₆, K₂Cl₆, and Rb₂SnCl₆ were all dependent on particle size, which in turn was affected by thermal history. In an n.m.r. study of KPF₆ and
TABLE 1. Experimental molar heat capacity of (NH₄)₂PdCl₆
(M = 355.2132 g·mol⁻¹; R = 8.31451 J·K⁻¹·mol⁻¹)

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TABLE 2. Standard molar thermodynamic functions for (NH₄)₂PdCl₆
(M = 355.2132 g·mol⁻¹; p₀ = 101.325 kPa; R = 8.31451 J·K⁻¹·mol⁻¹; \( \Phi_m^{\text{def}} = -\Delta_f^\circ H_m^\circ / T + \Delta_f^\circ S_m^\circ \))
FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature $T$ for (NH$_4$)$_2$PdCl$_6$. The region $T < 25$ K is enlarged in the lower right-hand corner.

RbPF$_6$,$^{(29)}$ the temperature dependence of the fluorine resonance also depended on particle size and previous physical treatment. Reproducible results were obtained on samples in the form of fine powders. Those that were crystalline before their first cooling showed hysteresis and the process of cooling and warming broke up the crystallites into small particles, thereby eliminating the effects of hysteresis. Our sample of (NH$_4$)$_2$PdCl$_6$ was supplied as a finely divided powder. It was cooled to 206 K, and heat capacities were measured up to $T = 216$ K in Series I before the sample was cooled to 56 K. No hysteresis was apparent between the $C_{p,m}$ values determined in the overlap regions from Series I and II, and from Series II and III.

Integration of the smoothed values for heat capacity and enthalpy and entropy increments yielded the thermodynamic functions. Values of $C_{p,m}/R$ and the derived functions are presented at selected temperatures in table 2. The heat capacities below 6 K were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation with a plot of $C_{p,m}/T^3$ against $T^2$ extrapolated to $T \to 0$ (not
shown). Such a plot is also useful for identifying any non-vibrational contributions to the heat capacity at low temperatures. Although the quantity measured calorimetrically is $C_{\text{sat},m}$, it effectively equals $C_{p,m}$ for these solids. The pressure effect of the helium exchange gas (0.3 kPa of helium at 20 K) on the heat capacity of solid (NH$_4$)$_2$PdCl$_6$, i.e. $(\partial C_{p,m}/\partial p)_T$, is also negligible. In addition, the correction of $C_{p,m}$ to $C_{v,m}$, which is needed for analysis of any heat-capacity results, is negligible at these low temperatures so that the heat capacity of our (NH$_4$)$_2$PdCl$_6$ can be written as a power series:

$$C_{p,m} = C_{v,m} = aT^3 + bT^5 + cT^7 + \cdots.$$  \hspace{1cm} (1)

The coefficients $a$, $b$, and $c$ are directly related to the corresponding power series for the frequency spectrum at low frequencies.$^{(30)}$ Thus as $T \to 0$, the lattice heat capacity of the solid should become equal to that of an elastic continuum and, as such, can be described by the Debye $"T^3"$ law:

$$C_{v,m} = aT^3,$$  \hspace{1cm} (2)

and

$$\Theta_0^2 = (12\pi^4Lk/5a)^{1/2}.\hspace{1cm} (3)$$

The $\Theta_0^2$ is the Debye characteristic temperature derived from heat capacities. From the plot of $C_{p,m}/T^3$ against $T^2$ in the region $36 < (T^2/K^2) < 400$, the experimental heat capacities for (NH$_4$)$_2$PdCl$_6$ follow a curve similar in shape to that for Ar and suggest that only lattice vibrations make significant contributions to the heat capacity in this temperature range. Extrapolation of the points below $T^2 = 36 K^2$ to cut the $T^2 = 0$ axis at $a/R$ gives $10^4 \cdot a/R = (3.20 \pm 0.40) \cdot K^{-3}$ or $10^4 \cdot a = (26.6 \pm 3.3) J \cdot K^{-1} \cdot mol^{-1}$, which yields from equation (3) $\Theta_0^2 = (90.1 \pm 3.5) K$. This compares with 93.5 K for Ar.

Only limited ancillary information is available to help interpret the motion of NH$_2^+$ within (NH$_4$)$_2$PdCl$_6$. The absence of $\lambda$-shaped or other anomalies in our heat-capacity results suggests that the Fm$\bar{3}$m cubic structure is retained to $T = 6 K$, but crystallographic studies are unavailable to confirm this. The results of the measurements of the temperature dependence of the proton-spin relaxation times for polycrystalline (NH$_4$)$_2$PdCl$_6$ show that the NH$_2^+$ reorientation is the dominant relaxation mechanism above 56 K and the derived activation energy $\Delta^1U_m^0$ for NH$_4^+$ lies between 211 $\cdot R \cdot K$,\hspace{1cm} (31) and 307 $\cdot R \cdot K$.\hspace{1cm} (12) Above 140 K, PdCl$_6^{2-}$ reorientation begins to contribute significantly to the relaxation time.\hspace{1cm} (31) This picture parallels closely that of the NH$_4^+$ and PtCl$_6^{2-}$ in polycrystalline (NH$_4$)$_2$PtCl$_6$ where the $\Delta^1U_m^0$ for NH$_4^+$ reorientation lies between 191 $\cdot R \cdot K$,\hspace{1cm} (31) and 342 $\cdot R \cdot K$.\hspace{1cm} (12) and the heat capacities vary smoothly with temperature without anomalies.\hspace{1cm} (7) The calculated tunnelling frequencies for NH$_4^+$ in the salts of the family (NH$_4$)$_2$MC1$_6$ where M denotes Pd, Pt, Ir, Re, Sn, Pb, and Te, do not agree well with those measured experimentally.\hspace{1cm} (1) The main reason for the discrepancy arises from the assumption in the model of three-fold sinusoidal potentials, whereas the actual potential is more boxlike near the minimum and the barrier is narrower. The discrepancies are greatest for the Pd and Pt salts whose barriers to NH$_4^+$ reorientation are the lowest.
We thank Dr R. D. Heyding for determining the crystal structure of our sample just prior to loading and Mrs J. Hale for help with the calculations. Two of us (J.E.C. and R.D.W.) acknowledge the Department of National Defence (Canada) for financial support.

REFERENCES