

Thermodynamics of ammonium halogenated tellurides

I. Heat capacity and thermodynamic properties of $(\text{NH}_4)_2\text{TeCl}_6$ at temperatures from 5 K to 350 K

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The heat capacity of ammonium hexachlorotellurate $(\text{NH}_4)_2\text{TeCl}_6$ was measured at temperatures from 5 K to 350 K. The heat-capacity curve shows a small anomaly around 86 K and a broad peak extending from 100 K to 280 K. The small anomaly reaches its greatest divergence from the lattice curve at 86.5 K and is coincident with the known transition from cubic Fm3m structure to trigonal R3. The low values of enthalpy and entropy of transition are consistent with the subtle change in orientation of the anions involved in the rotational displacive transition: $\Delta_{\text{trs}}H_m^\circ = (5.97 \pm 1.74) R \cdot K$ and $\Delta_{\text{trs}}S_m^\circ = (0.071 \pm 0.028) R$, where $R = 8.31452 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Smoothed values of the standard thermodynamic quantities are tabulated up to 350 K.

1. Introduction

The ammonium hexahalogenated metallates $(\text{NH}_4)_2\text{MX}_6$ (M denotes a transition metal or polyvalent ion, and X denotes a halogen) normally crystallize at room temperature into a cubic antiferroite structure of space group Fm3m or No. 225 O_h^5 . The NH_4^+ ion, positioned at a tetrahedral lattice site, experiences a low barrier to rotation about its three-fold axis, which causes hindered rotation at room temperature and tunnelling motion of the H^+ ions near $T \rightarrow 0$.⁽¹⁾ Some members of this family undergo structural phase transitions and change into a phase of lower symmetry as temperature is decreased. Other members show no hint of a transition

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even though one may be present in the alkali-metal analogue.⁽²⁻⁴⁾ Heat-capacity measurements recently completed⁽⁵⁾ on ammonium hexachloroplatinate $(\text{NH}_4)_2\text{PtCl}_6$ showed no anomaly or transition in the curve of heat capacity against temperature from 6 K to 348 K. However, in the deuterated salt $(\text{ND}_4)_2\text{PtCl}_6$, one λ -shaped transition was found at 27.2 K as well as two anomalies at 251.1 K and 276.8 K.⁽⁶⁾ When the relatively small atom of the transition element Pt is replaced by the significantly larger non-transition element Te, a structural transition is induced in $(\text{NH}_4)_2\text{TeCl}_6$ around 85 K; this is based upon results from experiments with Raman scattering and chlorine nuclear-quadrupole-resonance (n.q.r.).^(7, 8) The absence of published heat-capacity measurements from 5 K to 350 K by adiabatic calorimetry for $(\text{NH}_4)_2\text{TeCl}_6$ led us to determine these and the enthalpy and entropy of transition.

2. Experimental

The sample of $(\text{NH}_4)_2\text{TeCl}_6$ was provided by Professor J. Pelzl of Ruhr Universität, Bochum, Federal Republic of Germany, and is the same sample used for the neutron-diffraction studies⁽⁹⁾ at Atomic Energy of Canada Limited Research, Chalk River, Ontario. The Guinier-de Wolff diffraction pattern done on the $(\text{NH}_4)_2\text{TeCl}_6$ sample when received by us was in agreement with the standard pattern for this compound: No. 9-392 as determined by the Joint Committee for Powder Diffraction Standards.⁽¹⁰⁻¹²⁾ Its structure was found to be face-centred cubic at room temperature with $a = (1.0194 \pm 0.0002)$ nm.

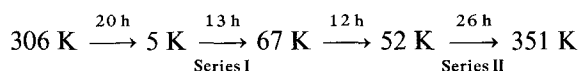
The molar heat capacity $C_{p,m}$ was measured at temperatures from 5 K to 350 K by adiabatic calorimetry in the Mark XIII adiabatic cryostat, which is an upgraded version of the Mark II cryostat described previously.⁽¹³⁾ A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S., now NIST) against the IPTS-1948 (as revised in 1960)⁽¹⁴⁾ for temperatures above 90 K, against the 1955 N.B.S. (NIST) provisional scale from 10 K to 90 K, and by the technique of McCrackin and Chang⁽¹⁵⁾ 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.⁽¹⁶⁾ The effects of changing the temperature scale to ITS-90 vary over the range $90 \leq T/\text{K} \leq 350$ from $+0.020 \leq (T_{90} - T_{48})/\text{K} \leq -0.27$, and for the range $14 \leq T/\text{K} \leq 90$ from $-0.008 \leq (T_{90} - T_{55})/\text{K} \leq 0.018$.^(17, 18) 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 14 K to 2150 K.⁽¹⁷⁾ Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S. (NIST). The heat capacities from about 5 K to 350 K were acquired with the assistance of a computer, which was programmed for a series of determinations.^(19, 20) During the drift periods, both the calorimeter temperature and the 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 $(\text{NH}_4)_2\text{TeCl}_6$. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that moisture was no longer released from the sample. After addition to a pressure of ≈ 32 kPa (at 300 K) of helium gas to the vessel to facilitate thermal equilibration, it 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 $2.360 \text{ g} \cdot \text{cm}^{-3}$ derived from the unit-cell dimensions of our sample. The mass of the $(\text{NH}_4)_2\text{TeCl}_6$ was 13.6554 g ($\hat{=}$ 0.0362795 mol based on its molar mass of $376.3932 \text{ g} \cdot \text{mol}^{-1}$ calculated from the 1985 IUPAC recommended list).⁽²¹⁾

The thermal history of the $(\text{NH}_4)_2\text{TeCl}_6$ is represented by the following linear array. The arrows denote either cooling or heating, which correspond to the acquisition of heat-capacity results.



3. Results and discussion

The experimental molar heat capacities for $(\text{NH}_4)_2\text{TeCl}_6$ are presented in table 1 in order of increasing temperature. The measurements were made in two series beginning at 5.2 K and ending at 351.0 K. The probable errors in the heat capacity decrease from about $0.01 \cdot C_p$ at 10 K to less than $0.0015 \cdot C_p$ at temperatures above 30 K. The heat capacity of the sample represented about 0.56 to 0.89 of the measured total heat capacity.

The sample was supplied as a fine yellow powder (diameter: ≈ 0.5 mm) and was judged not to require further grinding. Particle size and thermal history are factors that influence hysteresis effects in some ammonium compounds.⁽²²⁻²⁴⁾ Once loaded into the calorimeter, our sample of $(\text{NH}_4)_2\text{TeCl}_6$ was cooled directly from 306 K to 5 K in 20 h when the measurements began. No differences are apparent between the heat-capacity values in the region of overlap from our two series of measurements.

A plot of experimental values of $C_{p,m}/R$ against T from 5.9 K to 348 K is shown in figure 1. The two noteworthy features are the anomaly near 86 K and a broad peak extending from 100 K to 280 K.

The small anomaly around 86 K is expanded in figure 2 with the background lattice heat capacity shown by the broken line. This heat-capacity curve for the anomaly rises gradually beginning around 68 K, is continuous, and reaches its greatest divergence from the lattice curve at 86.5 K. It merges again with the lattice heat capacity at 98 K. There was no evidence of long equilibration times through the

TABLE 1. Experimental molar heat capacity of $(\text{NH}_4)_2\text{TeCl}_6$
($M = 376.393 \text{ g} \cdot \text{mol}^{-1}$; $R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		36.86	9.348	75.57	20.43	167.83	29.24	266.21	31.94
5.92	0.1710	38.95	9.989	79.35	21.17	172.97	29.56	271.38	32.08
6.86	0.3352	41.15	10.75	83.31	21.90	178.12	29.81	276.50	32.00
8.32	0.5803	43.58	11.63	87.48	22.63	183.27	30.11	281.66	32.04
9.57	0.7047	46.16	12.38	91.88	22.95	188.40	30.40	286.85	32.09
10.60	0.9687	48.74	13.29	96.56	23.28	193.63	30.53	292.02	32.10
12.06	1.240	51.24	14.18	101.44	23.78	198.87	30.80	297.04	32.19
13.36	1.625	53.77	14.96	106.46	24.39	204.08	31.06	302.14	32.26
14.78	2.059	56.43	15.66	111.50	24.90	209.27	31.18	307.17	32.41
16.24	2.467	59.24	16.44	116.58	25.49	214.47	31.30	312.24	32.43
17.77	2.884	62.18	17.19	121.66	25.93	219.62	31.47	317.36	32.65
20.16	3.557	65.28	18.06	126.74	26.45	224.84	31.59	322.53	32.80
22.63	4.327			131.83	26.93	230.06	31.65	327.69	32.90
24.55	4.923	Series II		137.01	27.43	235.24	31.71	332.92	33.07
26.71	5.672	56.85	15.71	142.19	27.69	240.43	31.83	338.13	33.28
28.77	6.336	59.38	16.42	147.29	28.05	245.58	31.91	343.32	33.33
30.72	7.143	62.29	17.27	152.39	28.41	250.63	31.94	348.42	33.34
32.75	7.794	65.36	17.97	157.52	28.73	255.78	31.95		
34.79	8.523	68.60	18.72	162.66	29.03	260.99	31.88		
		72.00	19.51						

region of the anomalies. For this reason and because the sample was cooled 65 K below the lower anomaly, we have no reason to believe that the sample was not in the equilibrium low-temperature phase. The excess molar enthalpy and entropy associated with the anomaly amount respectively to $\Delta_{\text{trs}}H_m^\circ = \Delta_{68\text{K}}^{98\text{K}}H_m^\circ = (5.97 \pm 1.74) R \cdot \text{K}$ and $\Delta_{\text{trs}}S_m^\circ = \Delta_{68\text{K}}^{98\text{K}}S_m^\circ = (0.071 \pm 0.028) R = R \cdot \ln(1.07)$. The error in these quantities is due to the uncertainty in the positions of the experimental heat-capacity curve and the lattice heat-capacity curve through the region of the anomaly.

Measurements of the n.q.r. frequency of the ^{35}Cl and of Brillouin scattering for $(\text{NH}_4)_2\text{TeCl}_6$ from which the elastic constants were derived suggest a structural transition in which the room-temperature cubic $\text{Fm}3m$ structure with space group O_h^5 changes below 85 K,^(7,8) or 89 K,⁽²⁵⁾ to trigonal $\text{R}3$ with space group C_{3i}^2 . Rotations of the anion octahedra about their 3-fold axis are thought to be involved. That this is the case is confirmed by neutron-diffraction studies. Not only was ferrorotation of the TeCl_6^{2-} by a few hundredths noted, but a small distortion of the lattice with a slight displacement of the NH_4^+ along the 111 direction was also detected. This finding is consistent, since tetrahedral ions such as NH_4^+ cannot be located within a structure having trigonal symmetry without some degree of distortion. In the light of this trigonal distortion along the cubic 111 direction and the slight change in the angle of orientation for the TeCl_6^{2-} , the low values of $\Delta_{\text{trs}}H_m$ and $\Delta_{\text{trs}}S_m$ for the anomaly found in our study are not surprising. That this slight realignment of the anion causes no discontinuity in the curve of heat capacity against temperature is also not surprising. However, a second-order phase transition at 89 K

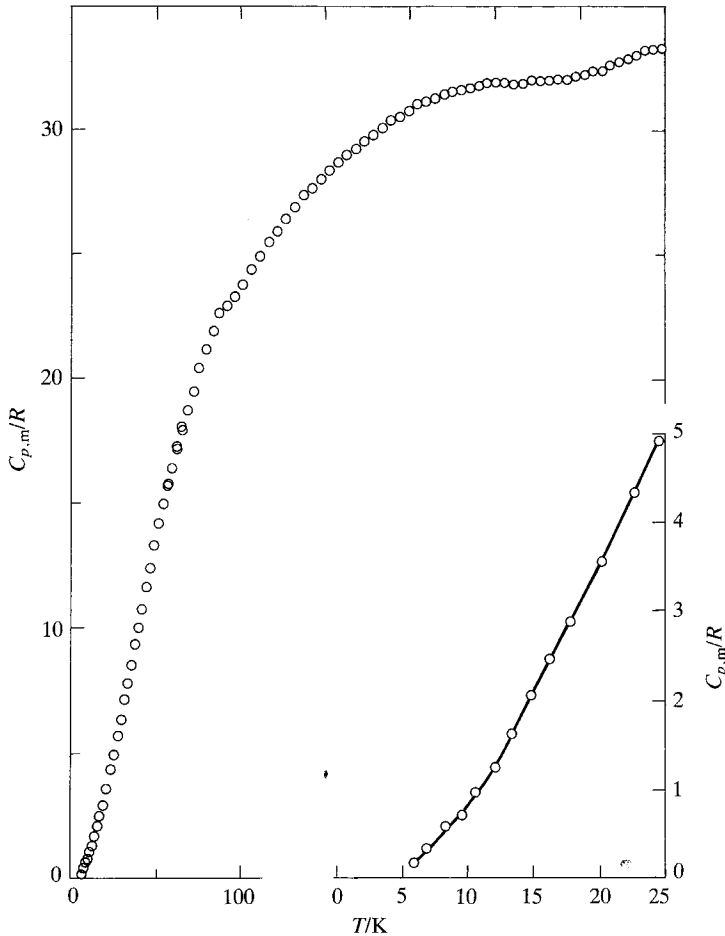


FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature T for $(\text{NH}_4)_2\text{TeCl}_6$. The region below 25 K is enlarged in the lower right-hand corner.

is reported⁽²⁴⁾ to have been detected by Kume *et al.*, but the results are unpublished (see reference 26, p. 14).

The broad maximum from 100 K to about 280 K reaches its peak at 250 K and is reminiscent of the broad peak observed in the heat-capacity curves of several other salts. That peak in the tetragonal ammonium scheelites,⁽²⁷⁻³⁰⁾ NH_4ReO_4 , ND_4ReO_4 , NH_4IO_4 , and ND_4IO_4 , reaches a maximum heat capacity near 200 K, and in the orthorhombic ammonium tetrafluoroborates,^(31, 32) NH_4BF_4 , and ND_4BF_4 , the peak maximum is around 150 K. In all these materials, the anisotropic thermal expansivities are responsible for the broad maximum. For $(\text{NH}_4)_2\text{TeCl}_6$, it is not clear what is happening. No attempt has been made to estimate the excess enthalpy or entropy for this anomaly because of the large uncertainty of the estimated baseline. Thermal expansivities are unknown, but in any case the lattice is apparently

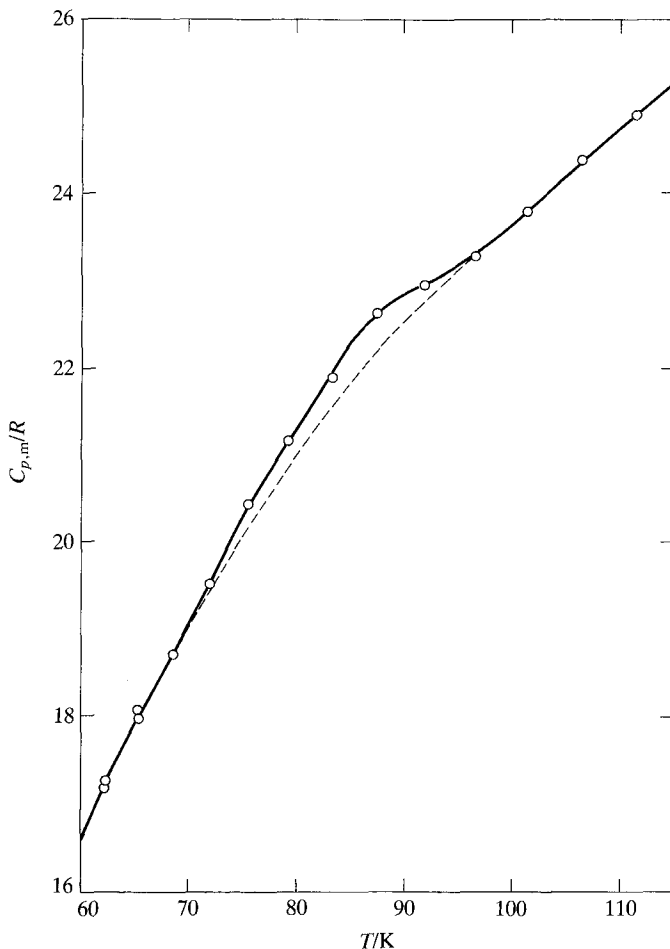


FIGURE 2. Experimental molar heat capacities at constant pressure $C_{p,m}$ plotted against temperature T through the region of the anomaly from about 85 K to 95 K for $(\text{NH}_4)_2\text{TeCl}_6$. ---, The lattice heat capacity.

cubic over the temperature range under consideration. The elastic constant C_{11} and the ^{35}Cl n.q.r. frequency change smoothly with temperature between 100 K and 300 K.^(7, 26) Above about 280 K, the quadrupolar spin-lattice relaxation time decreases sharply, which results from the onset of rapid reorientational motion of the TeCl_6^{2-} .^(26, 33)

Integration of the smoothed experimental heat capacities and for the enthalpy and entropy increments through the anomalies 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 of $(\text{NH}_4)_2\text{TeCl}_6$ below 5 K were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation using a plot of $C_{p,m}/T^3$ against T^2 and extrapolating to $T \rightarrow 0$. Such a plot is also useful for

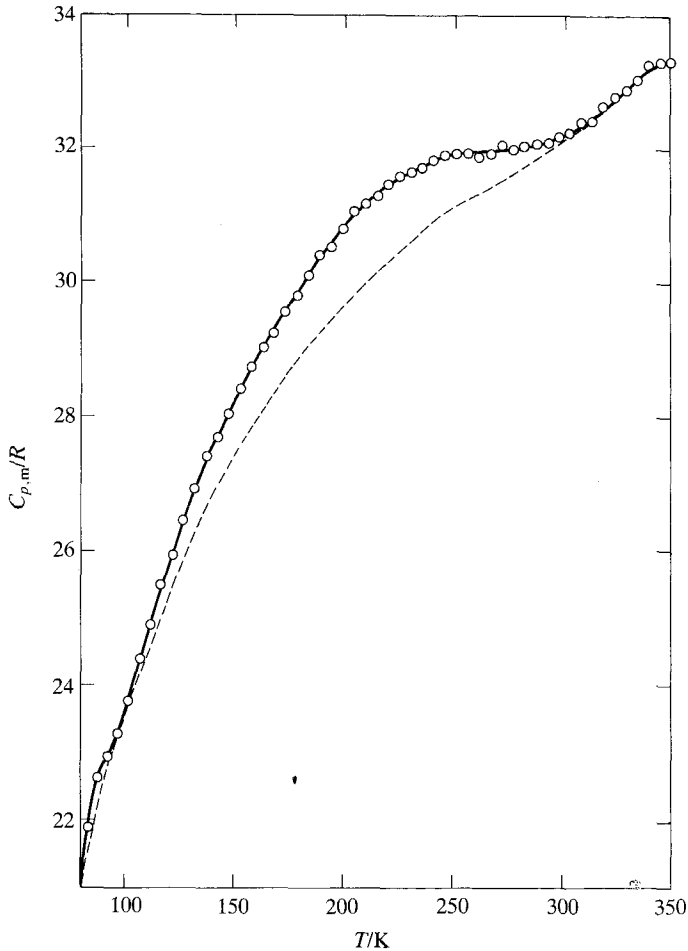


FIGURE 3. Experimental molar heat capacities at constant pressure $C_{p,m}$ plotted against temperature T through the region of the broad peak from about 100 K to 300 K for $(\text{NH}_4)_2\text{TeCl}_6$. ---, The estimated lattice heat capacity.

picking out any non-vibrational contributions to the heat capacity at low temperature. The quantity measured calorimetrically is $C_{\text{sat},m}$ which for these solids equals $C_{p,m}$ and at these low temperatures also $C_{v,m}$. Thus for our $(\text{NH}_4)_2\text{TeCl}_6$ insulators, the heat capacity can be written as a power series.

$$C_{p,m} = C_{v,m} = aT^3 + bT^5 + cT^7 + \dots \quad (1)$$

The parameters a , b , and c are related directly to the corresponding power series for the frequency spectrum at low frequencies.^(3,4) As $T \rightarrow 0$, the lattice heat capacity of the solid should equal that of an elastic continuum and can be approximated by the Debye “ T^3 ” law: $C_{v,m} = aT^3$ and $\Theta^\circ = (12\pi^4 Lk/5a)^{1/3}$. The Θ° is the Debye

TABLE 2. Standard molar thermodynamic functions for $(\text{NH}_4)_2\text{TeCl}_6$

$$\{M = 376.393 \text{ g} \cdot \text{mol}^{-1}; p^\circ = 101.325 \text{ kPa}; R = 8.31452 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; \Phi_m^\circ \stackrel{\text{def}}{=} -\Delta_0^T H_m^\circ/T + \Delta_0^T S_m^\circ\}$$

T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R	T/K	$C_{p,m}/R$	$\Delta_0^T S_m^\circ/R$	$\Delta_0^T H_m^\circ/(R \cdot \text{K})$	Φ_m°/R
0	0	0	0	0	135	27.18	29.65	2160.1	13.65
5	(0.0925)	(0.0298)	(0.116)	(0.0067)	140	27.54	30.65	2296.9	14.24
10	0.796	0.260	1.982	0.062	145	27.90	31.62	2435.5	14.83
15	2.055	0.818	9.082	0.213	150	28.25	32.57	2575.9	15.40
20	3.525	1.611	23.05	0.459	160	28.88	34.42	2861.6	16.53
25	5.085	2.561	44.58	0.778	170	29.38	36.18	3152.8	17.64
30	6.785	3.635	74.25	1.160	180	29.87	37.88	3449.1	18.72
35	8.725	4.823	113.0	1.594	190	30.38	39.51	3750.3	19.77
40	10.34	6.096	160.8	2.076	200	30.92	41.08	4056.7	20.79
45	11.96	7.407	216.5	2.595	210	31.21	42.59	4367.4	21.80
50	13.74	8.758	280.8	3.143	220	31.46	44.05	4680.8	22.78
55	15.30	10.14	353.6	3.716	230	31.66	45.46	4996.5	23.73
60	16.63	11.53	433.3	4.310	240	31.81	46.81	5314.1	24.67
65	17.91	12.92	519.8	4.918	250	31.91	48.11	5632.5	25.58
70	19.05	14.28	612.2	5.539	260	31.97	49.36	5951.9	26.47
75	20.14	15.64	710.2	6.167	270	32.01	50.57	6271.8	27.34
80	21.26	16.97	813.7	6.801	280	32.04	51.73	6592.1	28.19
85	22.23	18.29	922.4	7.438	290	32.11	52.86	6912.8	29.02
90	22.85	19.58	1035.3	8.077	300	32.19	53.95	7234.4	29.83
95	23.19	20.83	1150.4	8.716	310	32.42	55.01	7557.4	30.63
100	23.59	22.02	1267.3	9.351	320	32.70	56.04	7883.0	31.41
105	24.22	23.19	1386.8	9.983	330	33.02	57.05	8211.6	32.17
110	24.79	24.33	1509.3	10.61	340	33.28	58.04	8543.3	32.92
115	25.32	25.44	1634.6	11.23	350	33.33	59.01	8876.4	33.65
120	25.82	26.53	1762.4	11.85					
125	26.29	27.60	1892.7	12.45	298.15	32.18 ± 0.03	53.75 ± 0.06	7174.8 ± 7.1	29.69 ± 0.03
130	26.75	28.64	2025.3	13.06					

characteristic temperature derived from calorimetric measurements. The L and k are Avogadro's and Boltzmann's constants, respectively. From the $C_{p,m}/T^3$ against T^2 plot (not shown), and extrapolation of the points below $T^2 = 45 \text{ K}^2$ to intersect the $T^2 = 0$ axis at a/R gives $10^4 \cdot a/R = (4.00 \pm 1.00) \text{ K}^{-3}$ or $a \cdot 10^4 = (33.3 \pm 8.1) \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$. This yields $\Theta^\circ = (83.6 \pm 5.9) \text{ K}$ and compares with 93.3 K for argon,⁽³⁵⁾ 83.7 K for $(\text{NH}_4)_2\text{PtCl}_6$,⁽⁵⁾ and 92.1 K for $(\text{ND}_4)_2\text{PtCl}_6$.⁽⁶⁾

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