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Heat Capacity and Standard Thermodynamic Functions of Bis(η^6-mesitylene)vanadium Fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ over the Range from T = (0 to 345) K

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ABSTRACT: Low-temperature heat capacities of the crystalline bis(η^6-mesitylene)vanadium fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}$-$[\text{C}_{60}]^{\bullet-}$ have been measured by a precision adiabatic vacuum calorimeter over the temperature range from T = (7 and 345) K for the first time. The experimental results have been used to calculate the standard (P° = 0.1 MPa) thermodynamic functions: molar heat capacities $C^\circ_{p,\text{m}}$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and Gibbs energy $G^\circ(T) - H^\circ(0)$ of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ over the range from T = (0 to 345) K. The low-temperature (T < 50 K) dependence of the heat capacity was analyzed on the basis of Debye's heat capacity theory of solids and its fractal variant. Following that, the characteristic temperatures as well as the fractal dimension were determined, and some conclusions about the structure topology were made. The standard entropy of formation at T = 298.15 K of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ (cr) was calculated. The standard thermodynamic properties of tested fulleride and previously studied C_{60} fullerite were compared.

INTRODUCTION

The discovery of the method for producing C_{60} fullerenes in macroquantities[1] has laid the new field of research. Thus, different properties of functional fullerene derivatives with valuable characteristics have been extensively investigated. The study of donor—acceptor complexes of fullerenes where the latter play the role of relatively strong acceptors is dictated by the search for new unique materials. Such materials exhibit interesting optical, electrical conductivity, and magnetic properties.[2−9] Most often, fullerene complexes with aromatic hydrocarbons as donor partners were synthesized, and their properties were studied.[2,10−19] A similar fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$[12] was investigated using characterization tools including eletron paramagnetic resonance (EPR), NMR, and superconducting quantum interference device (SQUID) magnetic measurements and high resolution X-ray powder diffraction.

The calorimetric study of properties was carried out mainly for fullerides with organochromium compounds such as $[(\eta^6\text{-MePh})_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$,[11] $[(\eta^6\text{-Ph}_2)_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$,[15] $[(\eta^6\text{-}t\text{-BuPh})_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$,[16] $[(\eta^6\text{-}o\text{-Me}_2\text{Ph})_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$,[17] and $[(\eta^6\text{-EtOPh})_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$.[18]

There have been no data about heat capacity and thermodynamic properties of crystalline bis(η^6-arene)vanadium fulleride in the literature. Those are, however, necessary as the fundamental data for new functional derivatives of C_{60} and to detect the influence of organoelement groups on the thermodynamic characteristics. With regard of the foregoing, the thermodynamic study of one of the representatives of bis(η^6-mesitylene)vanadium fulleride, $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$, is actual and urgent. The presence of the values of these functions at some temperature values will allow to estimate the possibility of different chemical processes with bis(η^6-mesitylene)vanadium fulleride in defined conditions.

The purpose of the present study is to measure the low-temperature heat capacities by adiabatic calorimetry over the temperature range T = (7 to 345) K of the crystalline bis(η^6-mesitylene)vanadium fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$, to calculate the standard thermodynamic functions: molar heat capacities $C^\circ_{p,\text{m}}$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and Gibbs energy $G^\circ(T) - H^\circ(0)$ of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}$-$[\text{C}_{60}]^{\bullet-}$ (cr) over the range from T = (0 to 345) K, to determine the characteristic temperature, fractal dimension D and to establish the structure topology, to calculate the standard entropy of formation at T = 298.15 K of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}$-$[\text{C}_{60}]^{\bullet-}$ (cr), and to compare the thermodynamic characteristics of the fulleride under study and C_{60}.[20]

EXPERIMENTAL SECTION

Synthesis and Characterization of Crystalline Bis(η^6-mesitylene)vanadium Fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$. The twice-sublimated fine-crystalline powder of fullerite (not more than 0.0002 mass fraction of impurities) produced by the Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod was used as the starting material. Bis(η^6-mesitylene)vanadium fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}$-$[\text{C}_{60}]^{\bullet-}$ (gross formula $\text{C}_{78}\text{H}_{24}\text{V}$) was synthesized by the method described elsewhere.[21] The solution of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^0$

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(access) in toluene was added to the saturated solution of C_{60} in toluene at room temperature. Half of the solvent volume was removed in vacuo, and the rest was cooled. The resulting sediment was decanted and then washed by hexane and dried in vacuum. The derived microcrystalline black bis(η^6-mesitylene)vanadium fulleride is insoluble in hexane, sparingly soluble in PhMe, and soluble in PhCN. The elemental analysis yielded the V composition at 4.91 % which compares with 5.04 % calculated for $C_{78}H_{24}V$. The mesitylene and equimolar mixture of fullerene with vanadium was quantitatively formed at thermodecomposition.

The ion structure of fulleride was approved by results of electron and EPR spectra and by magnetic measurement data. The EPR spectra were recorded on a Bruker EPX radiospectrometer and electron spectra on a PerkinElmer Lambda25 spectrometer. The magnetic susceptibility was measured only at 293 K by the Gouy method with use of techniques described in the literature.[22] The visible spectroscopy of bis(η^6-mesitylene)vanadium fulleride in PhCN has shown the presence of an absorption band which is characteristic for $C_{60}^{\bullet-}$ at $\lambda = 1079$ nm. The crystalline bis(η^6-mesitylene)vanadium fulleride, in difference from starting bis(mesitylene)vanadium(0), is EPR-silent at 293 K. The magnetic moment of the crystalline bis(η^6-mesitylene)vanadium fulleride is close to 3.6 μ_B at 293 K, which corresponds to three electron spins. Thus, taking into account that the $[(\eta^6\text{-sim-Me}_3H_3C_6)_2V]^{\bullet+}$ cation has two electron spins, bis(η^6-mesitylene)vanadium fulleride is the salt-like, ion-radical fulleride $[(\eta^6\text{-sim-Me}_3H_3C_6)_2V]^{\bullet+}[C_{60}]^{\bullet-}$.

The tested sample is relatively unstable in the air, and therefore, all operations related to its preparation for calorimetric measurements were carried out in a chamber in a flow of high-purity argon.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range $7 \le (T/K) \le 345$. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[23,24] All of the measurements were performed with a computer-controlled measuring system comprised of an analog-to-digital converter, a digital-to-analog converter, and a switch. The calorimetric cell is a thin-walled cylindrical vessel from titanium of $1.5 \cdot 10^{-6}$ m^3. Its mass is (2.040 ± 0.005) g. A miniature iron—rhodium resistance thermometer (with the nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on ITS-90 by the Russian Metrology Research Institute. The difference in temperature between the ampule and an adiabatic shield was controlled by a four-junction copper—iron—chromel thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3}$ K, with the analog-to-digital converter of 0.1 μV. The energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded and processed online by a computer. The speed of the computer-controlled measuring system was 10 measurements per second.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard materials (K-2 benzoic acid and α-Al_2O_3)[25,26] prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation were measured over the temperature range of $7 \le (T/K) \le 345$. The sample masses were (0.768 and 1.500) g, respectively. It was established that the apparatus and the measurement technique enable the determination of the heat capacities of substances with an uncertainty not exceeding ± 2 % over the temperature range $7 \le (T/K) \le 15$, ± 0.5 % between T = (15 to 40) K, and ± 0.2 % over the temperature range $40 \le (T/K) \le 345$. The uncertainty of the phase transition temperatures is within about ± 0.01 K, and that of the enthalpies of transitions is ± 0.2 %.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were controlled at 0.01 K·s^{-1} and (0.5 to 2 K). The heating duration was about 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within 0.01 K·s^{-1} during the acquisition of all heat capacity results. Liquid helium and nitrogen were used as coolant. The ampule with the substance was filled with dry helium as a heat exchange gas to the pressure of 4 kPa at room temperature. The sample mass used for calorimetric measurement was 0.2124 g, which was equivalent to 0.000210 mol in terms of its molar mass, M = 1011.96 g·mol^{-1}. The molar mass of the object under study was calculated from the International Union of Pure and Applied Chemistry (IUPAC) table of atomic weights.[27] The experimental values of $C^{\circ}_{p,m}$ (180 points) were obtained in two series reflecting the sequence of experiments. The first series of measurements was completed over the temperature range of $7 \le (T/K) \le 86$. The second series of $C^{\circ}_{p,m}$ measurements was carried out between T = (84 to 345) K. The heat capacity of the sample was between (20 and 40) % of the overall heat capacity of the calorimetric ampule with the substance under temperature changing from (7 to 345) K.

RESULTS AND DISCUSSION

Heat Capacity. All experimental results of the molar heat capacity of $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ over the range from T = (7 to 345) K are listed in Table 1 and plotted in Figure 1. The heat capacity $C^{\circ}_{p,m}$ of $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}$-$[C_{60}]^{\bullet-}$ rises gradually with temperature increase. It was shown that the structure of the compound was stable over the temperature range between T = (7 and 345) K; that is, no phase change, transformation, association, or thermal decomposition occurred.

The experimental points of C°_p in the temperature range between T = (7 and 345) K were fitted by means of the least-squares method, and the polynomial equations of the C°_p versus temperature is the following: for the range from T = (7 to 19) K, T = (16 to 51) K, T = (45 to 102) K, T = (90 to 201) K, and T = (192 to 345) K:

$$\begin{aligned}C^{\circ}_p &= A + B(T/30) + C(T/30)^2 + D(T/30)^3 \\ &\quad + E(T/30)^4 + F(T/30)^5 + G(T/30)^6 + + H(T/30)^7 \\ &\quad + I(T/30)^8 + J(T/30)^9 + K(T/30)^9 \qquad (1)\end{aligned}$$

The corresponding coefficients (A, B, C, etc.) for eq 1 are given in Table 2.

Their standard deviations from the smoothed $C^{\circ}_p = f(T)$ curve are listed in Figure 2.

As Figure 1 illustrates, an orientation phase transformation and glass-like transition of the G-type which are seen for the initial fullerite C_{60} over the range from T = (185 to 275) K and T = (81.0 to 88.5) K are absent in the $C^{\circ}_{p,m} = f(T)$ plot of the tested fulleride, which testifies to the fully bonded fullerene fragments in the complex.[20] The nature of these transitions is described sufficiently in ref 20.

Table 1. Experimental Molar Heat Capacities of Crystalline Bis(η^6-mesitylene)vanadium Fulleride $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ (M = 1010.94 g·mol^{-1}, p^o = 0.1 MPa)

T / K	$C^o_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C^o_{p,m}$ / J·K^{-1}·mol^{-1}	T / K	$C^o_{p,m}$ / J·K^{-1}·mol^{-1}
Series 1					
6.75	6.58	10.43	21.7	43.64	114.6
6.83	7.09	10.67	22.2	45.62	118.7
6.91	7.48	10.94	23.3	47.52	122.1
6.99	8.00	11.14	23.9	49.42	125.7
7.09	8.52	11.39	24.6	51.31	128.8
7.19	8.98	11.79	25.9	53.19	131.5
7.28	9.50	11.94	26.3	55.08	135.0
7.36	9.9	12.23	27.4	56.96	138.7
7.45	10.3	12.74	29.0	58.86	142.3
7.57	10.7	13.03	30.3	60.75	146.3
7.64	11.1	13.71	33.0	62.65	151.1
7.70	11.5	14.41	35.2	64.54	155.8
7.83	12.0	14.72	36.4	66.43	160.6
7.96	12.5	15.55	39.1	67.38	163.1
8.11	13.0	16.08	41.00	68.33	165.9
8.24	13.5	17.62	46.00	70.23	171.0
8.37	14.1	19.03	50.31	72.11	176.1
8.45	14.4	20.81	56.17	74.20	181.3
8.56	14.9	22.64	61.50	75.85	186.2
8.71	15.4	24.46	67.60	77.50	190.6
8.91	16.0	26.60	73.88	79.58	196.4
9.02	16.5	28.66	79.74	81.00	200.0
9.13	16.9	30.66	85.01	82.14	203.6
9.32	17.6	32.40	89.70	83.70	208.7
9.50	18.3	34.27	93.90	84.29	210.0
9.71	19.0	36.00	97.60	85.18	213.1
9.81	19.4	38.03	102.0	86.53	217.4
10.07	20.4	39.92	106.0		
10.30	21.0	41.82	110.3		
Series 2					
84.29	210.0	118.21	332.0	157.40	493.9
85.18	213.1	120.84	342.8	161.89	511.7
86.53	217.4	123.44	353.3	165.78	526.2
87.91	222.5	126.07	365.1	170.65	544.0
89.00	226.1	128.70	377.0	175.00	559.7
90.30	230.9	129.91	381.9	176.08	563.8
91.60	235.5	131.32	388.3	181.12	583.9
93.50	243.5	132.47	393.2	183.00	587.0
95.10	249.3	133.93	398.7	187.00	603.0
97.08	256.5	135.08	404.7	192.80	626.4
99.73	265.9	137.70	414.9	195.92	640.6
102.37	274.6	140.00	425.8	198.65	651.2
105.02	284.2	142.20	435.0	201.50	662.8
107.66	293.4	145.52	449.3	202.44	666.1
110.30	302.9	148.12	459.0	206.22	682.7
112.94	312.2	150.72	469.2	210.00	697.4
115.58	321.9	153.97	481.8	215.50	720.6
217.51	728.6	269.70	950.3	313.60	1178
221.24	744.8	272.88	966.5	316.20	1193
224.96	759.7	276.26	980.6	318.30	1206
228.65	775.5	279.60	996.8	321.60	1227
232.33	789.4	282.96	1012	324.30	1243
235.97	807.6	286.29	1029	324.90	1245
239.61	821.6	289.59	1045	326.40	1255
243.24	837.9	292.87	1062	328.80	1269
244.89	843.6	296.00	1078	331.70	1283
248.42	858.2	298.76	1093	332.87	1291
251.97	874.4	299.93	1100	335.61	1310
255.52	888.5	301.94	1111	338.33	1327
259.30	904.8	305.20	1129	341.01	1341
262.55	918.2	309.10	1150	345.80	1371
265.99	933.6	310.90	1162		

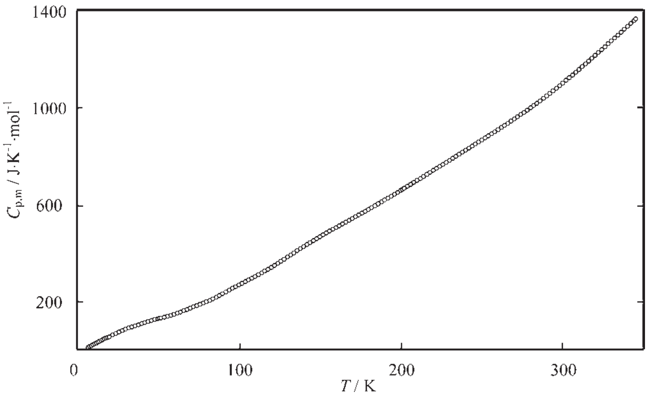

Figure 1. Curve of experimental molar heat capacities of $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ versus temperature (T).

For a similar fulleride $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$[12] in the interval of low temperatures, the X-ray diffraction study did not reveal any structural changes which were observed for $[(\eta^6\text{-MePh})_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$[11] and afterward for $[(\eta^6\text{-Ph}_2)_2Cr]^{\bullet+}\text{-}[C_{60}]^{\bullet-}$,[15] $[(\eta^6\text{-}t\text{-BuPh})_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$,[16] and $[(\eta^6\text{-EtOPh})_2\text{-}Cr]^{\bullet+}[C_{60}]^{\bullet-}$.[18] Authors[12] made the conclusion that in the range of low temperatures the formation of dimeric bond between fragments of fullerene C_{60} is impossible. The reason for the different behavior is to be found in the larger $C_{60}-C_{60}$ distances, induced by the larger chromium complex in $[(\eta^6\text{-sim-Me}_3H_3C_6)_2Cr]^{\bullet+}[C_{60}]^{\bullet-}$ which inhibits spontaneous dimer formation upon freezing of the C_{60} reorientation. It was assumed that the process of dimerization can occur as phase transition of higher order. In case of the studied fulleride $[(\eta^6\text{-sim-Me}_3H_3C_6)_2V]^{\bullet+}[C_{60}]^{\bullet-}$ the same behavior takes place.

The values of the fractal dimension D—the most significant parameter of the fractal version of Debye's theory of the heat capacity of solids[28−31]—were determined from the experimental results on the heat capacity of $[(\eta^6\text{-sim-Me}_3H_3C_6)_2V]^{\bullet+}[C_{60}]^{\bullet-}$ and literature data for C_{60} fullerite.[20] In the fractal version of Debye's theory of the heat capacity of solids, the exponent of T in

Table 2. Coefficients of Equation 1

		T/K				
		7 to 19	16 to 51	45 to 102	90 to 201	192 to 345
coefficients $\cdot 10^{-3}$	A	−7.785788	0.376776	14.9196	90.794507	−196.99699
	B	172.9036	−3.63756	−53.19435	−176.07444	162.38101
	C	−1662.819	15.2814	79.1032	146.98948	−56.83614
	D	9026.667	−34.6289	−62.21208	−68.966771	10.962789
	E	−30112.801	47.4598	26.6094	19.894606	−1.2571533
	F	62483.184	−40.2419	−4.900148	−3.5989075	0.085685964
	G	−75473.775	20.60505	−0.5708598	0.39157729	$-3.2135031 \cdot 10^{-3}$
	H	37706.69	−5.8306	0.4672054	−0.02123337	$5.1155261 \cdot 10^{-5}$
	I	20657.09	0.699405	−0.08687287	$-3.0099875 \cdot 10^{-5}$	
	J	−36506.026		0.005711339	$6.2551924 \cdot 10^{-5}$	
	K	13820.587			$-2.1853709 \cdot 10^{-6}$	

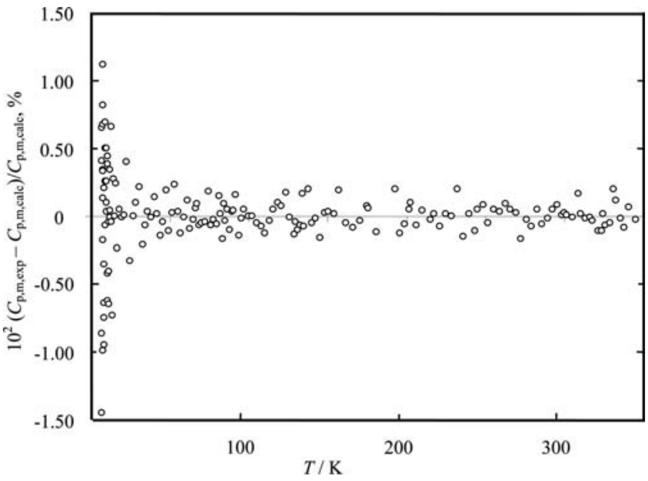

Figure 2. Deviations of experimental heat capacities $C^{o}_{p,m,exp}$ from values $C^{o}_{p,m,calc}$ calculated from eq 1.

the expression for heat capacity is referred to as fractal dimension D. The values of D allow one to estimate the topology of the structure. The values of D were estimated using the technique described, for example, in ref 31 with the use of eq 2:

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\Theta_{max}) \qquad (2)$$

where N is the number of atoms in a molecule, k is the Boltzmann constant, $\gamma(D+1)$ is the γ − function, $\xi(D+1)$ is the Riemann ξ-function, and Θ_{max} is the characteristic temperature.

It can be taken that isobaric and isochoric heat capacities are equal at temperatures below 50 K. Then, using eq 2, we find that, in the temperature range $20 \le (T/K) \le 50$, $D = 1.1$ and $\Theta_{max} = 200.1$ K for $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ and $D = 3$ and $\Theta_{max} = 231.6$ K for the C_{60}. According to refs 28 to 31, $D = 1$ corresponds to the solids with chain structure, $D = 2$ to those with a layered structure, and $D = 3$ to those with a spatial structure. Thus, it follows that $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ have a mixed, chain−layer structure topology, whereas C_{60} has a spatial structure.

As can be seen from the comparison of the values of characteristic temperature Θ_{max} that have been calculated for the temperature interval $20 \le (T/K) \le 50$, the $\Theta_{max}(C_{60}) > \Theta_{max}\{[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}\}$. Probably, it should be concluded that the examined fullerides have less hard structures in comparison with initial fullerite C_{60}.

The temperature dependence of heat capacity $C^{o}_{p,m} = f(T)$ in the low-temperature region ($T < 20$ K) is well-described by the limiting law $C^{o}_{p,m} = AT^3$ for the tested fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ as well as for fullerite C_{60}[20] which is characteristic of the solids of Debye's nature. Also, in the range (50 to 100) K, the heat capacity $C^{o}_{p,m}$ is a linear function versus T for the tested sample, which is typical of the solids having a structure of chain topology.

Standard Thermodynamic Functions of Crystalline Bis(η^6-mesitylene)vanadium Fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$. To calculate the standard thermodynamic functions in Table 3 of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$, their smoothed molar heat capacities $C^{o}_{p,m}$ were extrapolated from the temperature of the measurement beginning at approximately $T = (7 \text{ to } 0)$ K with the Debye law in the low-temperature limit:[32]

$$C^{o}_{p,m} = n\mathbf{D}(\Theta_D/T) \qquad (3)$$

where $n = 8$ is the number of degrees of freedom, $\mathbf{D}$ is the Debye function, and $\Theta_D = 56.3$ K refers to the Debye characteristic temperature. Using the above parameters,[32] eq 3 describes the $C^{o}_{p,m}$ values of the compound over the range $7 \le (T/K) \le 13$ with the uncertainties of ± 1 %. In calculating the functions, it was assumed that eq 3 reproduced the $C^{o}_{p,m}$ values of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ at $T \le 7$ K with the same uncertainties.

The calculations of $[H^{o}(T) - H^{o}(0)]$ and $S^{o}(T)$ were made by numerical integration of the curves with respect to T and ln T, respectively. The Gibbs energy $[G^{o}(T) - H^{o}(0)]$ was calculated from $[H^{o}(T) - H^{o}(0)]$ and $S^{o}(T)$ values at corresponding temperatures. The zero entropy of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ was assumed to be zero. The calculation procedure was described in detail in ref 33. The uncertainties determined for the function values are ± 2 % at $T < 15$ K, ± 0.5 % from (15 to 40) K, and ± 0.3 % from $T = (40 \text{ to } 345)$ K.

Using the value of the absolute entropy of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ in Table 3 and the elemental substances, namely, carbon,[34] hydrogen,[35] and vanadium,[35] the standard entropy of formation at $T = 298.15$ K was estimated to be $\Delta_f S^{o}_m(298.15, [(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}, \text{cr}) = -1152 \pm 2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Table 3. Smoothed Molar Heat Capacities and Thermodynamic Functions of Crystalline Bis(η^6-mesitylene)vanadium Fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{Cr}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ (M = 1010.94 $\text{g}\cdot\text{mol}^{-1}$, p° = 0.1 MPa)

T	$C^\circ_{p,\text{m}}$	$[H^\circ(T) - H^\circ(0)]/T$	$S^\circ(T)$	$-[G^\circ(T) - H^\circ(0)]/T$
K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$			
5	3.60	0.900	1.21	0.300
10	20.0	5.99	8.2	2.21
15	37.4	13.53	19.6	6.06
20	53.0	21.49	32.53	11.04
30	83.46	37.20	59.9	22.71
40	106.3	51.70	87.15	35.45
50	126.5	64.76	113.2	48.40
60	144.8	76.50	137.8	61.27
70	170.3	88.01	161.9	73.91
80	197.5	99.99	186.4	86.45
90	229.8	112.6	211.5	98.94
100	266.8	126.1	237.6	111.5
110	301.4	140.5	264.7	124.2
120	339.6	155.4	292.5	137.1
130	382.1	171.2	321.3	150.1
140	425.6	187.9	351.3	163.4
150	466.5	205.1	382	176.9
160	504.5	222.6	413.4	190.8
170	541.4	240.3	445.1	204.8
180	579.0	258.1	477.1	219.0
190	617.0	275.9	509.4	233.4
200	656.5	294.0	542	248.1
210	697.7	312.2	575	262.8
220	739.1	330.7	608.5	277.8
230	781.1	349.3	642.2	292.9
240	823.3	368.2	676.4	308.2
250	865.5	387.3	710.8	323.6
260	908.1	406.5	745.6	339.2
270	951.8	425.9	780.7	354.9
280	997.9	445.4	816.1	370.7
290	1047	465.2	852	386.6
298.15	1090	482.0	881.6	399.8
300	1100	485.7	888.4	402.7
310	1157	506.5	925.4	419.0
320	1216	527.5	963	435.3
330	1276	549.4	1001	452.1
340	1336	571.5	1040	468.8
345	1366	582.9	1060	477.1

The values obtained fit the equation

$$78\text{C(gr)} + 12\text{H}_2\text{(g)} + \text{V(cr)} \rightarrow [(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}\text{(cr)} \tag{4}$$

where gr, cr, and g are graphite, crystal, and gas, respectively.

CONCLUSIONS

This work reports low-temperature heat capacities measured by adiabatic calorimetry of the crystalline bis(η^6-mesitylene)vanadium fulleride $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$. Additionally, the standard thermodynamic functions of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ (cr) over the range from T = (0 to 345) K and the standard entropy of formation at T = 298.15 K were derived from these experimental results.

The low-temperature ($T \leq 50$ K) dependence of the heat capacity was analyzed on the basis of the heat capacity theory of solids of Debye and the multifractal variant, and as a result, a chain-layer structure topology was established. The thermodynamic characteristics of $[(\eta^6\text{-sim-Me}_3\text{H}_3\text{C}_6)_2\text{V}]^{\bullet+}[\text{C}_{60}]^{\bullet-}$ were compared with the corresponding data for C_{60}.

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