Thermodynamics of the Bis(η^{6} -*t*-butylphenyl)chromium Fulleride [Cr{ η^{6} -(*t*-BuPh)}₂] $^{\bullet+}C_{60}^{\bullet-}$

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In this work, the temperature dependence of heat capacity $C_{p,m}^{o} = f(T)$ of crystalline bis(η^{6} -t-butylphenyl)chromium fulleride between T = 6 and 360 K was measured for the first time by precision adiabatic vacuum calorimetry. Also, for the first time, the temperature dependence of EPR signal parameters of bis(η^{6} -t-butylphenyl)chromium fulleride in the range from 118 to 298 K was investigated by electron paramagnetic resonance. In the interval 170–210 K the reversible endothermic transformation was detected and its thermodynamic characteristics were estimated. This transformation was caused by dedimerization of fullerene fragments during heating. Based on the experimental data, the standard ($p^{\circ} = 0.1$ MPa) thermodynamic functions, namely, the heat capacity, enthalpy, entropy, and Gibbs function of heating were calculated for dimeric fulleride in the interval from $T \rightarrow 0$ to 170 K as well as for monomeric [Cr{ η^{6} -(t-BuPh)}]¹e⁺C₆₀⁶⁻ complex between 210 and 360 K. The standard thermodynamic properties of tested fulleride and previously studied C₆₀ fullerite and neutral dimer (C₆₀)² were compared.

The discovery of the method for producing C_{60} fullerenes in macroquantities¹ has laid a 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.^{2–4} Most often, fullerene complexes with aromatic hydrocarbons as donor partners were synthesized and their properties were studied.^{2,5–7}

As a result, on studying the thermal behavior of some bis(η^{6} -arene)chromium fullerides,^{6,8–11} the low-temperature dimerization of anion-radicals of the fullerene at cooling was detected. An analogy of reversible dimerization with the process occurring in the case of alkali metal fullerides was noted earlier.¹² The data about bonding strength between fullerene fragments in [Cr(Cp₂)]⁺C₆₀⁻•2C₆H₄Cl₂ complex are presented in Ref. 10 and it gives a chance for comparison with dissociation energy of bonds for the neutral dimer (C₆₀)₂.^{13–15}

The calorimetric study of the reversible dimerization process of fullerene molecules in crystalline complexes was carried out only for $[Cr(C_7H_8)_2]C_{60}^6$ and $[Cr(\eta^6-Ph_2)_2]^{\bullet+}C_{60}^{\bullet-9}$ (Ph₂ = biphenyl). However, the thermodynamic characteristics of the process as well as data about the thermodynamic functions for representatives of bis(η^6 -arene)chromium fullerides are given only by the authors of paper.⁹

There has been no data about heat capacity and thermodynamic properties of crystalline bis(η^{6} -t-butylphenyl)chromium fulleride in the literature. Those are however, necessary as fundamental data for new functional derivatives of C₆₀ and to understand the nature of low-temperature dimerization of fullerene fragments as well as to detect the influence of organoelement groups on the "hardness" and the stability of bonds between fullerene fragments in the low-temperature dimeric phase of C₆₀^{2–}. With regard to the foregoing, the thermodynamic study of one of representatives of bis(η^{6} arene)chromium fullerides, [Cr{ η^{6} -(t-BuPh)}]⁹+C₆₀^{6–}, is actual and urgent. The presence of the values of these functions at some temperature values will allow estimation of the possibility of different chemical processes with bis(η^{6} -tbutylphenyl)chromium fulleride in defined conditions.

The goal of this work is to calorimetrically study the temperature dependence of the heat capacity of the crystalline $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$ in the range from T = 6 to 358 K, to determine the temperature interval of transformation that was caused by dedimerization of fullerene fragments by heating, to estimate its standard thermodynamic characteristics; to calculate from the obtained data the standard ($p^\circ = 0.1$ MPa) thermodynamic functions heat capacity, enthalpy, entropy, and Gibbs function at heating for fulleride dimer in the range from $T \rightarrow 0$ to 170 K and for $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$ monomeric complex for the interval between 210 and 360 K; to compare the standard thermodynamic characteristics of the

complex under study, C_{60} fullerite, neutral dimer $(C_{60})_2$ as well as some previously studied fullerides.

Experimental

The tested sample of $bis(\eta^6-t-butylphenyl)$ chromium fulleride $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$ was synthesized by the method described in Ref. 16. The solution of $[Cr(\eta^6-(t-BuPh))_2]^0$ in toluene was added to the saturated solution of C₆₀ in toluene at room temperature. The resulting sediment was decanted and then washed with toluene and dried in vacuum. The elemental analysis yielded the Cr composition at 4.98% which compares with 5.00% calculated for C₈₀H₂₈Cr. The *t*-butylbenzene and equimolar mixture of fullerene with chromium was quantitatively formed at thermo-decomposition. The ion structure of fulleride was confirmed by results of EPR and ESR spectra. The EPR spectra were recorded on a Bruker EPX radiospectrometer and electron spectra on a Perkin-Elmer Lambda25 spectrometer. The EPR spectrum of $bis(n^6-t-butylphenyl)$ chromium fulleride in tetrahydrofuran (THF) at 293 K shows a line with typical for cation $[Cr(\eta^6-arene)_2]^{\bullet+}$ hyperfine structure, g = 1.986, $a_{\rm H} = 3.5$ G, $a_{\rm Cr} = 18.1$ G. Thus, bis(η^6 -*t*-butylphenyl)chromium is the cation-radical in fulleride. The visible spectroscopy of bis(η^6 -t-butylphenyl)chromium fulleride in THF has shown presence of an absorption band which is characteristic for $C_{60}^{\bullet-}$ at $\lambda = 1081$ nm. Thus, bis(η^6 -t-butylphenyl)chromium fulleride is the ion-radical salt: [Cr{ η^{6} -(t-BuPh) $_{2}^{\bullet+}C_{60}^{\bullet-}$.

The tested sample is relatively unstable in air and therefore all operations related to its preparation for calorimetric measurements were conducted in a special box in a flow of high-purity argon.

To study the temperature dependence of the heat capacity and temperatures of transformations of $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$ sample in the range from T = 6 to 360 K, an automatic thermophysical device, a BCT-3 low-temperature adiabatic vacuum calorimeter was employed. The calorimeter was manufactured at "Termis" JSC at the All-Russia Metrology Research Institute, Moscow region, Russia, its design and the operation procedure were described earlier.¹⁷ The reliability of the calorimeter operation was checked by measuring $C_{\rm p,m}^{\rm o}$ of standard samples of highly purified copper, standard synthetic corundum and K-2 benzoic acid¹⁸ prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation. The amounts of the indicated samples were 2.0000, 1.5000, and 0.7682 g respectively. It was established that the apparatus and the measurement technique enable determination of the heat capacity $C_{p,m}^{o}$ of substances with the error not exceeding $\pm 2\%$ near 15 K, $\pm 0.5\%$ between 15 and 40 K, and $\pm 0.2\%$ in the range from 40 to 360 K and measurement of the phase-transition temperatures within about ± 0.01 K and to measure the enthalpies of transformations within ±0.2%.

A sample of bis(η^{6} -t-butylphenyl)chromium fulleride with a mass 0.1240 g was placed in a thin-walled (1.5 cm³) cylindrical titanium ampoule. After pumping, the ampoule was filled with high-purity helium as a heat-exchange gas to a pressure of 6 kPa (at room temperature) and selected. The measurements of $C_{p,m}^{o}$ were made in the temperature range from 6 to 360 K. 169 experimental values of $C_{p,m}^{o}$ were obtained in three series reflecting the sequence of experiments. The first cycle of measurements was completed in the temperature range from 6 to 90 K. The second series of $C_{p,m}^{o}$ measurements was carried out between T = 80 and 360 K. The sample was cooled down to T = 160 K and a repeated cycle of $C_{p,m}^{o}$ measurements (third series) was conducted to T = 250 K. The heat capacity of the sample was between 15% and 30%

of the overall heat capacity of the calorimetric ampoule with the substance under temperature change from 6 to 360 K. The experimental C_p^o values were smoothed by means of a computer program in the form of degree and semi-logarithmic polynomials. As an example, the polynomials with the corresponding coefficients for ranges from 6 to 18 K and from 208 to 360 K are cited below. For fulleride in the interval between 6 and 18 K, the equation $C_{p,m}^o$ (T) = 7.428 · 10 - 1.413 · 10³ · (T/30) + 1.041 · 10⁴ · (T/30)² - 3.536 · 10⁴ · (T/30)³ + 6.33 · 10⁴ · (T/30)⁴ - 5.729 · 10⁴ · (T/30)⁵ + 2.066 · 10⁴ · (T/30)⁶ as well as the equation $C_{p,m}^o$ (T) = 1.43317421 · 10⁶ - 3.12766475 · 10⁶ · ln(T/30) + 2.71804584 · 10⁶ · (ln(T/30))² - 1.1751988 · 10⁶ · (ln(T/30))³ + 2.52755168 · 10⁵ · (ln(T/30))⁴ - 2.16201458 · 10⁴ · (ln(T/30))⁵ in the range from 208 to 360 K were used. In the above equations the $C_{p,m}^o$ is given in J K⁻¹ mol⁻¹.

The mean-square deviation of experimental $C_{p,m}^o$ points from the corresponding averaging $C_{p,m}^o = f(T)$ curve did not exceed $\pm 0.6\%$ in the range 6–20 K, $\pm 0.08\%$ between 20 and 170 K, and $\pm 0.05\%$ from 210 to 360 K. The molar mass of the object under study was calculated from the IUPAC table of atomic weights.¹⁹

Results and Discussion

Heat Capacity and Thermodynamic Characteristics of Transformation. The experimental values of molar heat capacity of $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet--}$ in the range 6– 360 K and the averaging $C_{p,m}^o = f(T)$ curve are presented in Figure 1. It can be seen that heat capacity of fulleride gradually increases with rising temperature until T = 170 K. In the temperature interval from 170 to 210 K, endothermic transformation occurs that manifest itself as a positive deviation from the normal trend of the temperature dependence of $C_{p,m}^o$ (Figure 1).

The heat capacity grows relatively rapidly from 508.25 $JK^{-1}mol^{-1}$ at T = 170 K until the p. C (Figure 1) and then it decreases down to $651.5 JK^{-1}mol^{-1}$ at T = 210 K. The above temperature region for the relation $C_{p,m}^{o} = f(T)$ is described by the BCD curve. The transition is reversible. It was reproduced on repeated cooling and heating (as it described above). The



Figure 1. The temperature dependence of heat capacity of the bis $(\eta^6$ -*t*-butylphenyl)chromium fulleride [Cr{ η^6 -(t-BuPh)}₂]^{•+}C₆₀^{•-}: AB: dimeric form, ED: monomeric form, BCD: apparent heat capacity in the transformation interval.

 $C_{\rm p,m}^{\rm o}$ values determined in the second and third series of measurements coincide in limiting error of their determination as the temperature drift is reproduced at register of heat capacity points. The transition enthalpy $\Delta_{\rm tr} H_{\rm m}^{\rm o} = (15.36 \pm 0.02) \, \rm kJ \, mol^{-1}$ was determined graphically as an area bounded by BCDB (Figure 1).

A similar transition was detected earlier for fulleride $[Cr(C_7H_8)_2]C_{60}^{8}$ over the range from 245 to 265 K and for $[Cr(\eta^{6}-Ph_{2})_{2}]^{\bullet+}C_{60}^{\bullet-9}$ in the range 270–320 K. The authors of Ref. 6 interpreted this transformation as the first-order equilibrium phase transition from a three-wedge low-temperature phase to a simple cubic high-temperature one on heating. It was shown^{6,8} that at T > 265 K the fulleride $[Cr(C_7H_8)_2]C_{60}$ existed in the form of a dynamically disordered anion of fullerene and bis(η^6 -toluene)chromium cation while at T < 245 K the sample was in the form of ordered dimers $(C_{60})_2$ with two cations of bis(η^6 -toluene)chromium. The authors came to these conclusions based on the structural data on the bond lengths and angles in [Cr(C7H8)2]C60 molecules at different temperatures and thus, the inference about the low-temperature dimerization of fullerene fragments in the fulleride was made.⁶ According to X-ray data,¹⁶ it was found that at room temperature bis(η^6 -biphenyl)chromium fulleride [Cr(η^6 -Ph₂)₂]^{•+}C₆₀^{•-} is a monomer with a fairly ordered cation $[Cr(\eta^6-Ph_2)_2]^{\bullet+}$ and a disordered anion-radical of fullerene in the structure whereas in a lower-temperature range (T = 100 K) the anion-radicals $C_{60}^{\bullet-}$ in this compound are ordered into the dimers via a single link.

As opposed to the authors of Ref. 8, we⁹ suggested to consider this transformation as superposition of the physical transition—the ordering of the structure on cooling—and the process of chemical nature, i.e., the association of an ion-radicals of fullerene by means of the formation of a single link between them. It taking into account as stated by us earlier⁹ it is impossible to estimate strictly thermodynamically equilibrium temperature of transition as well as its entropy by the second law as is often done for phase transitions.²⁰

For the sample tested in the present work, $[Cr{\eta^6}-(t-$ BuPh) $_{2}^{\bullet+}C_{60}^{\bullet-}$, the indicated endothermic transformation has the same nature as for fullerides $[Cr(C_7H_8)]_2C_{60}{}^{6,8}$ and $[Cr(\eta^6-Ph_2)_2]^{\bullet+}C_{60}^{\bullet-.9}$ According to electron paramagnetic resonance data, the EPR spectrum of the solid sample [Cr{ η^6 - $(t-BuPh)_{2}^{\bullet+}C_{60}^{\bullet-}$ at 298 K (Figure 2) is given by the symmetric singlet and has a g-factor equal to 1.9918, which is intermediate between those characteristic of $[Cr{\eta^6}-(t-$ BuPh)}₂]^{•+} (1.9860) and C₆₀^{•-} (1.9996–2.0000)²¹ because of strong exchange coupling between $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}$ and $C_{60}^{\bullet-}$. The EPR spectrum at 118 K (Figure 2) is a single line with anisotropy and g = 1.9821, which is characteristic of noninteracting paramagnetic $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}$. Such behavior is characteristic of [Cr(C7H8)]2C60 and [Cr(C6H6)]2C6011 and is related to dimerization of anion-radicals of fullerene on cooling. It should be noted that the value of EPR signal g-factor for fulleride $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$ changes abrupt in the range from 178 to 208K (Figure 3) under cooling. Such behavior points to dimerization of fullerene anion-radicals in $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$ composition in this temperature interval. The dedimerization of fullerene anions that are linked via single bond occurs when they are heated in the range



Figure 2. EPR spectra of the crystalline $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$ at different temperatures.



Figure 3. The temperature dependence of g-factor in EPRsignal of the crystalline $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$.

between 170 and 210 K and therefore the chemical nature of fulleride before and after transformation is not identical. Thus, the temperature dependence of heat capacity $C_p^0 = f(T)$ (Figure 1) characterizes the two different states: dimer $(C_{60}^{-})_2$ with two cations $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}$ until T = 170 K and $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$ after T = 210 K. In the range between 170 and 210 K it is a mixture of fulleride and monomeric complex.

Some peculiarities should be noted from the comparison of temperature intervals of dedimerization of fullerides $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$, $[Cr(\eta^6-Ph_2)_2]^{\bullet+}C_{60}^{\bullet-}$, $[Cr(C_7H_8)]_2C_{60}$, and the neutral dimer $(C_{60})_2$. First of all, in the case of dimer $(C_{60})_2^{15}$ the dedimerization of fullerides begins under heating at a distinctly lower temperature, the process occurs in a much closer (20–50 K) temperature interval and it is reversible.

Thus, the dedimerization of $(C_{60})_2$ occurs in the range from 380 to 490 K, but by contrast, for the complex under study it occurs in the range 170-210 K. The above differences are caused by the nature of fullerene fragments binding in the compounds. In a neutral dimer $(C_{60})_2^{15}$ the binding of C_{60} molecules by hard covalent bonds is realized via the [2 + 2]cyclo-addition mechanism. In fullerides low-temperature dimerization of C₆₀ fragments is realized by means of a single bond and accompanied with the formation of dimeric dianions $(C_{60})_{2}$. It should be also noted that for the fullerides being considered in the present paper, the dedimerization process under heating begins at the lowest temperature (T = 170 K)for $[Cr{\eta^{6}-(t-BuPh)}_{2}]^{\bullet+}C_{60}^{\bullet-}$, which is indicative of its relatively lower thermal stability. Thus, the stability of dimeric dianions (C60)2 depends significantly on the nature of counter ions.

For the fulleride under investigation the *G*-type transition and orientation phase transition^{22–24} known for fullerite C_{60} are absent on the $C_p^o = f(T)$ curve (Figure 1), which testifies to the fully-bonded fullerene fragments in the complex.

The temperature dependence of heat capacity $C_p^o = f(T)$ in the low-temperature region (T < 20 K) is well described by the limiting law $C_p^o = AT^3$ for the tested complex $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$ as well as for fullerite C_{60} ,²⁴ neutral dimer $(C_{60})_2$,¹⁵ and fulleride $[Cr(\eta^6-Ph_2)_2]^{\bullet+}C_{60}^{\bullet-}$, earlier⁹ which is characteristic of the solids of Debye's nature. In the range 50–100 K, the heat capacity C_p^o is a linear function vs. *T* for the tested sample, dimer $(C_{60})_2^{15}$ and for fulleride $[Cr(\eta^6-Ph_2)_2]^{\bullet+}C_{60}^{\bullet-9}$ which is typical of solids having a structure of chain topology.

Thermodynamic Functions. The standard thermodynamic functions of the crystalline fulleride dimer (Table 1) were calculated from the $C_{p,m}^{o}(T)$ values in the range $T \rightarrow 0$ to 170 K and for the monomeric complex $[Cr{\eta^6-(t-BuPh)}_2]^{\bullet+}C_{60}^{\bullet-}$ in the range from 210 to 360 K (Table 2). The $C_{p,m}^{o}$ data over the range $T \rightarrow 0$ to 6 K were determined by the extrapolation of the $C_{p,m}^{o} = f(T)$ curve from the Debye's heat capacity function of solids:

$$C_{\rm p,m}^{\rm o} = nD(\theta_{\rm D}/T) \tag{1}$$

where *D* denotes the Debye's heat capacity function, n = 7 and $\theta_D = 45.0$ K are specially selected parameters. With such parameters, eq 1 describes the experimental $C_{p,m}^o$ values in the range from 6 to 12 K with the error $\pm 1.4\%$. It was assumed that from 0 to 6 K, eq 1 reproduces the values of $C_{p,m}^o$ with the same error.

The calculations of $H^{\circ}(T_2) - H^{\circ}(T_1)$ and $S^{\circ}(T_2) - S^{\circ}(T_1)$ were made by numerical integration of the curves $C_{p,m}^{\circ} = f(T)$ and $C_{p,m}^{\circ} = \ln f(T)$ respectively. The Gibbs function of heating $G^{\circ}(T_2) - G^{\circ}(T_1)$ was calculated from $H^{\circ}(T_2) - H^{\circ}(T_1)$ and $S^{\circ}(T_2) - S^{\circ}(T_1)$ values at respective temperatures. The calculation procedure was described in detail in Ref. 25. The determined errors of the function values are $\pm 2\%$ at T < 15 K,

Table 1. Standard Thermodynamic Functions of the Dimeric $Bis(\eta^6-t$ -butylphenyl)chromium(I) Fulleride $[Cr\{\eta^6-(t-BuPh)\}_2]^{\bullet+}C_{60}^{\bullet-}; M = 1041.1 \text{ g mol}^{-1}$

T/K	$C_{\rm p}^{\rm o}(T)$	$[H^{\circ}(T) - H^{\circ}(0)]$	$S^{\circ}(T)$	$-[G^{\circ}(T) - H^{\circ}(0)]$
	$/JK^{-1}mol^{-1}$	$/kJ mol^{-1}$	$/JK^{-1}mol^{-1}$	$/kJ mol^{-1}$
5	5.81	0.00721	1.91	0.00230
10	24.9	0.0850	11.9	0.0341
15	40.0	0.247	24.8	0.125
20	57.82	0.4911	38.71	0.2837
25	70.13	0.8120	53.05	0.5139
30	81.69	1.192	66.86	0.8138
40	106.9	2.136	93.85	1.618
50	126.8	3.311	120.0	2.688
60	141.1	4.654	144.4	4.012
70	155.2	6.133	167.2	5.571
80	173.9	7.774	189.1	7.353
90	200.1	9.638	211.0	9.353
100	227.8	11.78	233.5	11.58
120	285.9	16.90	280.1	16.71
140	361.2	23.33	329.5	22.80
160	456.7	31.48	383.8	29.92
170	497.9	35.30	407.1	33.08

Table 2. Standard Thermodynamic Functions of the Monomeric Bis(η^{6} -*t*-butylphenyl)chromium(I) Fulleride [Cr{ η^{6} -(*t*-BuPh)}₂]^{•+}C₆₀^{•-}; $M = 1041.1 \text{ g mol}^{-1}$

T/K	$C_{\rm p}^{\rm o}(T)$	$[H^{\circ}(T) - H^{\circ}(210)]$	$S^{\circ}(T) - S^{\circ}(210)$	$-[G^{\circ}(T) - G^{\circ}(210)]$
	$/{\rm J}{\rm K}^{-1}{\rm mol}^{-1}$	$/kJ mol^{-1}$	$/{ m J}{ m K}^{-1}{ m mol}^{-1}$	$/kJ mol^{-1}$
210	672.0	7.907	36.95	0.2226
230	704.6	14.79	67.52	0.7387
240	742.9	22.02	98.30	1.574
250	782.3	29.65	129.4	2.706
260	820.2	37.66	160.9	4.163
270	854.9	46.04	192.5	5.923
280	886.5	54.75	224.1	8.013
290	915.8	63.77	255.8	10.41
298.15	939.2	71.32	281.5	12.60
300	944.5	73.06	287.3	13.13
310	978.0	82.68	318.8	16.15
320	1013	92.62	350.4	19.50
330	1051	103.0	382.2	23.16
340	1093	113.7	414.2	27.15
350	1141	124.8	446.5	31.44
360	1194	145.4	503.7	35.13

 $\pm 0.5\%$ from 15 to 40 K and $\pm 0.2\%$ in the temperature range between 40 and 360 K.

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