



Low-temperature heat capacity of $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$



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ABSTRACT

Iridium(I) (acetylacetonato)(1,5-cyclooctadiene) complex, $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$, was synthesized and characterized by elemental CH-analysis, NMR, X-ray spectroscopy. The heat capacity of compound $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$ has been measured by the adiabatic method within the temperature range (6–318) K. The thermodynamic functions: entropy, enthalpy and reduced Gibbs energy have been calculated. They have the following values at 298.15 K: $C_p^\circ = (323.6 \pm 0.6) \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta_0^{298.15} S_m^\circ = (347.0 \pm 0.9) \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta_0^{298.15} H_m^\circ = (50.82 \pm 0.09) \text{ kJ mol}^{-1}$, $\Phi_m^\circ = (176.5 \pm 0.7) \text{ J K}^{-1} \text{ mol}^{-1}$. The value of the absolute entropy were used to calculate the entropy of formation of $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$ at $T = 298.15 \text{ K}$. An anomaly of heat capacity has been discovered with a maximum at $T_c = 287.20 \text{ K}$, which points to the phase transition of the complex. Anomalous contributions to entropy and enthalpy have been revealed.

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1. Introduction

The noble metal iridium has high melting temperature, excellent chemical stability, radiographic visibility, biocompatibility and good electrical conductivity. Due to these properties, the iridium films are used in several essential applications such as in catalysts [1], spark plugs [2], protective coatings [3,4] and implanted electrodes [5]. The thermal decomposition of metal–organic compound (precursor) vapors on heating surfaces (metal–organic chemical vapor deposition or MOCVD) is one of the most suitable methods to obtain thin film of refractory metals [6–8].

The investigation of thermodynamic properties of volatile precursors is demanded to optimize conditions of obtaining the target films by MOCVD. For example, the standard thermodynamic functions (enthalpy, entropy, etc.) are used in the programs of CVD diagram calculation predicting the deposited phase composition as a function of the deposition conditions such as deposition temperature, total pressure, gas-reagent type, the ratio between gas-reagent and precursor vapors, etc. [9,10]. The reliable calculation of such thermodynamic functions requires low temperature data on heat capacity. Currently, the experimental methods of investigation are the main source of information on the low temperature heat capacity of solids [11–13].

In the light of the foregoing, we have initiated studies the low temperature heat capacity of volatile iridium complexes. In particular, the accurate data were obtained for iridium(III) β -diketonate

namely iridium(III) acetylacetonate ($\text{Ir}(\text{acac})_3$, $\text{acac} = \text{CH}_3\text{C}(\text{O})\text{CH}(\text{O})\text{CH}_3$) as the most popular MOCVD precursor [14]. In recent times, the usage of metal–organic compounds of iridium (I) in MOCVD has been increasingly developed [8]. So, iridium(I) (acetylacetonato)(1,5-cyclooctadiene) ($\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$ or $\text{Ir}(\text{acac})(\text{cod})$) was chosen as an object to continue the investigations as perspective and accessible iridium (I) precursor [6,8,15] with fixed β -diketonate ligand (acac).

This paper presents the results of experimental study of $\text{Ir}(\text{acac})(\text{cod})$ heat capacity in the temperature range (6–318) K by adiabatic calorimetry. The data obtained were used to calculate $\text{Ir}(\text{acac})(\text{cod})$ thermodynamic functions (entropy, enthalpy, reduced Gibbs energy).

2. Experimental

$\text{Ir}(\text{acac})(\text{cod})$ was obtained into the two steps synthetic procedure through the isolation of $[\text{Ir}(\text{cod})\text{Cl}]_2$ [15]. All reagents and solvents used are presented in the Table 1. All synthetic manipulations were performed in an atmosphere of an inert gas using standard Schlenk technique. All solvents and 1,5-cyclooctadiene were degassed by distillation under an inert gas. Acetylacetone was degassed by freeze–thaw procedure. The other reagents were used as purchased. The elemental CH-analysis was performed on Model CARLO-ERBA-11008 elemental analyzer. The ^1H NMR spectra were recorded on Bruker Avance 500 spectrometer (^1H : 500.129 MHz, ^{13}C : 125.757 MHz). Chemical shifts (δ , 10^{-6}) were referenced to the signals of the solvent ($\delta_{\text{H}} = 7.26 \times 10^{-6}$ for CDCl_3).

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Table 1
Characterization of chemical samples used in this study.

Chemical name	Chemical formula	Source	State	Mass fraction purity
Dihydrogen Hexachloroiridate (IV) Hydrate	$\text{H}_2[\text{IrCl}_6] \cdot n\text{H}_2\text{O}$	“Krastsvetmet” JSC (Russia)	Solid	≥ 0.99
1,4-Hydroquinone	$\text{C}_6\text{H}_4(\text{OH})_2$	Sigma-Aldrich Co. LLC (USA)	Solid	≥ 0.99
Pentane-2,4-dione (acetylacetone, Hacac)	$\text{C}_5\text{H}_8\text{O}_2$	Dalchem (Russia)	Liquid	≥ 0.99
Potassium hydroxide	KOH	“Component-reaktiv” Ltd. (Russia)	Solid	≥ 0.98
1,5-Cyclooctadiene (cod)	C_8H_{12}	Dalchem (Russia)	Liquid	≥ 0.99
Methanol	CH_3OH	FSUE RSC “Applied chemistry” (Russia)	Liquid	≥ 0.995
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	“Kemerovskaya farmatsevticheskaya fabrika” JSC (Russia)	Liquid	≥ 0.95
Diethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	“Kuzbassorghim” Ltd. (Russia)	Liquid	≥ 0.98
Hexane	C_6H_{14}	“Reaktiv” JSC (Russia)	Liquid	≥ 0.98
Iridium(III) (acetylacetonato)(1,5-cyclooctadiene), Ir(acac)(cod)	$\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{12})$	Synthesis (purification – Soxhlet extraction)	Solid	≥ 0.998 (elemental CH-analysis)

2.1. Preparation of $[\text{Ir}(\text{cod})\text{Cl}]_2$

The solution of 1,4-hydroquinone (5.16 g, 46.86 mmol) in 40 mL ethanol/water (2:1 v/v) was added to the solution of $\text{H}_2[\text{IrCl}_6] \cdot n\text{H}_2\text{O}$ (iridium content 0.4003: 30.00 g, 62.47 mmol) in 900 mL ethanol/water (2:1 v/v). The mixture was refluxed for 1 h and then 1,5-cyclooctadiene (46.59 mL, 380.42 mmol) was added, and the reaction mixture was refluxed overnight. The resulting solution was filtered and ca. 500 mL of the solvent were distilled off until crystallization of a red–orange $[\text{Ir}(\text{cod})\text{Cl}]_2$ started. The mixture was cooled to the room temperature and the precipitate formed was filtered off, washed with cold methanol (3×15 mL) and dried *in vacuo*. Yield: 15.06 g (72%). Anal. Calc. for $\text{Ir}_2\text{C}_{16}\text{H}_{24}\text{Cl}_2$ (mass.%): C, 28.6; H, 3.6. Found: C, 29.1; H, 3.6%.

2.2. Preparation of $\text{Ir}(\text{acac})(\text{cod})$

$[\text{Ir}(\text{cod})\text{Cl}]_2$ (7.13 g, 10.62 mmol) was dissolved in diethyl ether (110 mL) and then Hacac (2.12 mL, 21.24 mmol) was added. The mixture was stirred for 5 min and 1 M solution of KOH (34 mL) was added. A yellow precipitate was formed immediately and the ether phase turned yellow-green. After that water (114 mL) was added and the resulted mixture was stirred overnight to complete the reaction. The ether was evaporated *in vacuo* and a resulting precipitate was filtered off and dried *in vacuo*. The product was purified by Soxhlet extraction with hexane. Yield: 8.23 g (97%). Anal. Calc. for $\text{IrC}_{13}\text{H}_{19}\text{O}_2$ (mass.%): C, 39.1; H, 4.8. Found: C, 39.4; H, 4.8%. ^1H NMR (CDCl_3 , 25 °C): δ 1.62 (m, 4H, endo- CH_2 , cod), 2.00 (s, 6H, CH_3 , acac), 2.26 (m, 4H, exo- CH_2 , cod), 3.97 (s, 4H, CH = CH, cod), 5.51 (s, 1H, C_γ -H, acac).

A sample of $\text{Ir}(\text{acac})(\text{cod})$ at room temperature is a yellow crystalline powder. The melting temperature of the sample was determined using a Setaram DSC 111 calorimeter (standard Joule effect calibration [15], temperature calibration using benzoic acid and indium as a standard compounds). During measurements of five experiments, heating rate (0.5–1.0) K min^{-1} , the substance investigated, sample mass (14–17) mg, was contained in an evacuated glass ampoule; the onset temperature was used as the melting temperature. The result obtained is 428.0 K (expanded uncertainty is ± 0.5 with a 0.95 level of confidence) and absolutely agrees with the data presented in [16]. The results of the chemical analysis of the purified compound are in a good agreement with the theory within the accuracy of the analysis (C, H – 0.3%). X-ray phase analysis (powder XRD) was performed using a Shimadzu XRD-7000 diffractometer using $\text{CuK}\alpha$ radiation, range $2\theta = (5–65)^\circ$. According to XRD data, the sample is a single phase; the structure of the crystals obtained corresponds to the $\text{Ir}(\text{cod})(\text{acac})$ structure determined in the paper [17] (298 K), with lattice parameters $a = (1.7523 \pm 0.0002)$ nm, $b = (0.7069 \pm 0.0001)$ nm, $c = (1.0245 \pm 0.0001)$ nm, $\beta = (94.28 \pm 0.01)^\circ$; volume of elementary cell $V = (1.26551 \pm 0.00001)$ nm³; $Z = 4$; space group $C2/m$. The

calculated X-ray density, according to the data of the paper [17], is 2.096 g cm^{-3} .

The heat capacity $C_{p,m}(T)$ of the sample of $\text{Ir}(\text{acac})(\text{cod})$ was measured by the adiabatic method on the installation described in reference [18]. The temperature of the calorimeter was measured by a standard platinum resistance thermometer ($R_{100}/R_0 = 1.3925$). The standard uncertainty for the temperature was $u(T) = 0.01$ K. Resolution of the thermometric apparatus was 5×10^{-5} K above 50 K falling to 1.5×10^{-3} K at 11 K. The adiabatic control system gave the temperature stability of the calorimeter vessel within 1×10^{-5} K min^{-1} . The results of heat capacity measurements for a standard substance (benzoic acid) deviate from data [19] by less than 1% over the range (5–20) K, by less than 0.3% over the range (20–80) K, and by less than 0.15% over the range (80–273) K. The sample of $\text{Ir}(\text{acac})(\text{cod})$ of 2.950 g was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula $\text{Ir}(\text{acac})(\text{cod})$ as 399.51 g mol^{-1} .

The heat capacity $C_{p,m}(T)$ has been measured at 92 points over the range (6–318) K. The values obtained are presented in Table 2. Within the range (240–300) K, the presence of a λ -shaped anomaly with a maximum at $T_c = (287.20 \pm 0.01)$ K (Fig. 1) is found. The appearance of the anomaly indicates that the compound exhibits a phase transition. Two experimental series have been carried out in the region of anomaly. The results from these two series do not show a regular deviation between them (no hysteresis phenomena).

In order to clarify the nature of anomaly observed, the single-crystal X-ray investigation has been carried out at the temperature below the phase transition point. The monocrystals of $\text{Ir}(\text{cod})(\text{acac})$ were obtained by Soxhlet extraction at the same conditions as the powder sample and then were kept at 248.15 K for several weeks. To obtain the unit cell parameters of $\text{Ir}(\text{acac})(\text{cod})$ at 150 K, 3 ϕ -scan were recorded on a Bruker Kappa Apex2 DUO diffractometer fitted with graphite monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.071073$ nm). As a result, 36 frames with the width of 0.5° have been received and the following crystallographic parameters have been obtained: monoclinic syngony, C centring, $a = (1.724 \pm 0.003)$ nm, $b = (0.688 \pm 0.002)$ nm, $c = (1.006 \pm 0.002)$ nm, $\alpha = \gamma = 90^\circ$, $\beta = (94.54 \pm 0.03)^\circ$, $V = (1.19000 \pm 0.00005)$ nm³ (standard uncertainties, type A); $Z = 4$; calculated X-ray density 2.231 g cm^{-3} . Thus, the unit cell parameters are the same as those obtained at 298 K [17]. Within the temperature decreasing, no changes in the crystal structure occur during the phase transition.

3. Results and discussion

3.1. Thermodynamic functions under standard conditions

The raw experimental values of heat capacity have been smoothed by the Rumshiskii method [20]. The root-mean-square

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