



Article Breaking through the Thermodynamics "Wilds" of Metal–Organic Chemical Vapor Deposition Precursors: Metal tris-Acetylacetonates

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Abstract: Metal acetylacetonates belong to the β -diketonate family and are considered as classics among precursors for metal-organic chemical vapor deposition (MOCVD). The success of film preparation is crucially dependent on the volatilization thermodynamics of the precursors used. Data on the volatilization thermodynamics of metal acetylacetonates are in huge disarray. We amassed and analyzed experimental data on the vapor pressures and on the enthalpies and entropies of fusion, vaporization, and sublimation of acetylacetonate tris-complexes of metals(III) (Al, Sc, Cr, Mn, Fe, Co, Ru, Rh, In, and Ir) available in the literary sources. In addition, saturated vapor pressures over crystalline Al(III), Cr(III), and In(III) acetylacetonates and corresponding thermodynamic sublimation properties were determined. New findings enabled us to arbitrate the conflict among literature data. The enthalpies and entropies of sublimation, vaporization, and fusion were adjusted to the reference temperature for a correct comparison using the empirically estimated differences in heat capacities. The heat capacity of the crystalline phase was shown to depend weakly on the metal atom. As a result, a reliable set of enthalpies and entropies of the mentioned processes of fundamental importance was derived for ten metal complexes. Relationships between volatility and structure were established depending on the central metal. The suggested algorithm can be fairly easily transferred to the acetylacetonate or other β -diketonate isoligand complexes with metals of different valence.

Keywords: metal acetylacetonate; vapor pressure; enthalpy; entropy; sublimation; vaporization and fusion; structure–property relationships

1. Introduction

Metal acetylacetonates belong to the β -diketonate family and are considered classic precursors for metal-organic chemical vapor deposition (MOCVD) applied to obtain highquality film materials [1–6]. Admittedly, the success of film preparation, especially thin and multicomponent ones, is crucially dependent on the thermal properties of the precursors used, which have to provide the essential level of metal-containing vapors fed to the deposition zone, thereby causing the formation of a coating of the desired microstructure, thickness, and composition. These properties of special attention are the behavior in the condensed phase (mainly thermal stability and phase transitions) and the volatility quantified by saturated vapor pressures at various temperatures (p-T dependences) and thermodynamic functions (enthalpy and entropy) of the volatilization (sublimation or vaporization) processes. Despite the fact that metal acetylacetonates are the most usable and often irreplaceable MOCVD precursors in film material production, available data on their volatilization thermodynamics are in huge disarray [7–24]. This is illustrated by an example of the vapor pressure temperature dependencies for aluminum(III) acetylacetonate, Al(acac)₃ (Figure 1). Obviously, such scattering complicates the MOCVD optimization, and deposition experiments are unavoidably performed under empirical and ill-defined conditions. Validation of these thermodynamic data for metal tris-acetylacetonates is of



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interest of selecting the most efficient deposition conditions and reducing the number of "trial and failure" experiments or random screening experiments.

Figure 1. Literature data on temperature dependencies of vapor pressures for Al(acac)₃ obtained using dissimilar methods: K = Knudsen effusion method with weighing of the cell [9,11,23]; I = isotheniscope [10]; GC = gas chromatography [12,13,19]; SB = sublimation bulb [14]; S = static [14,16,17,21]; TE = torsion–effusion method [15]; K/MS = Knudsen effusion method with mass spectrometric registration of gas phase [18]; TGA = thermal gravimetric analysis [20,24]; CVM = method of calibrated volume [21], $p_{ref} = 1$ Pa.

Another source of interest in validated data on metal *tris*-acetylacetonates is their use in the diagnostic tool we developed for metal *tris*-complexes with β -diketonate ligands. The point is that, most often, the vapor pressure and enthalpy data on metal β -diketonates (not only acetylacetonates) accessible to the public are scattered and can vary many times over depending on the method used and the laboratory where the measurements were conducted [25–27]. This has forced us to develop a diagnostic check, resulting in reliable datasets for the standard molar enthalpies of sublimation, vaporization, and fusion. The tool was elaborated using the example of *tris*- β -diketonates of iron [26] and previously implemented on the series of *tris*- β -diketonates of iridium and scandium [25,27]. The main necessary condition for the application of the technique is reliable data on any substance which can be a basic molecule in the series of compounds under consideration. For β -diketonate complexes, such compounds are metal acelytacetonates. Therefore, to further apply the diagnostic model, it is necessary to refine the thermodynamic data on volatilization and fusion of these complexes.

There is also important outcome from validation of the thermodynamic data for metal *tris*-acetylacetonates. The diagnostic tool discussed above is grounded on the group additivity principles and structure–property relations, being within a series of the β -diketonates of the same metal or between the rows of two metals with the same set of β -diketonate ligands. In other words, the procedure focuses on changes in the organic residue of the complexes and developed in such a way that it avoids taking into account the contribution from the coordination center, thereby denying the central metal atom the "right

to vote". Obviously, the complexing agent should affect the thermodynamic properties of metal–organic compounds. The issue about the nature and level of this influence can be addressed using metal acetylacetonates. Revealing any correlations would open up the path for a diagnostic model that works not within a series of different β -diketonates of one metal, but within that of isoligand compounds of various metals.

This work focuses on *tris*-(acetylacetonato)metal (Al, Sc, Cr, Mn, Fe, Co, Ru, Rh, In, and Ir) complexes chosen as research objects (Figure 2). We collected data on vapor pressures, as well as sublimation, fusion, and vaporization enthalpies and entropies, accessible in the literary sources and appraised them using the help of our complementary measurements.



Figure 2. Structural formulas of *tris*-(acetylacetonato)metal complexes used throughout this article, M = Sc, Mn, Fe, Co, Ru, Rh, and Ir.

2. Materials and Methods

2.1. Materials

The samples of Al(acac)₃, Cr(acac)₃, and In(acac)₃ for investigation were prepared in a water–alcohol medium using a known procedure [16,21,28,29] starting with metal salts (AlCl₃·6H₂O, CrCl₃·10H₂O, and In(NO₃)₃·4.5H₂O) and the Hacac ligand neutralized with NaOH to shift the reaction toward chelate formation. The products were purified by double sublimation in a vacuum gradient furnace at residual pressure of 6.7 Pa and temperatures of 440 K (Al(acac)₃), 470 K (Cr(acac)₃), and 450 K (In(acac)₃). The melting points of the samples measured on a Kofler table were 470–472 K(Al(acac)₃), 488–490 K(Cr(acac)₃), and 460–462 (In(acac)₃), corresponding to the values reported in [28,30,31].

The purity of the samples was proven by elemental analysis and X-ray powder diffraction. Elemental analysis was carried out at the Nikolaev Institute of Inorganic Chemistry SB RAS (NIIC SB RAS) using a Vario Micro Cube analyzer. Elemental analyses for $C_{15}H_{21}O_6Al$ (mass %): calculated: C 55.6, H 6.5; found: C 55.4, H 6.6; for $C_{15}H_{21}O_6Cr$ (mass %): calculated: C 51.6, H 6.1; found: C 51.6, H 6.1; for $C_{15}H_{21}O_6In$ (mass %): calculated: C 43.7, H 5.1; found: C 43.7, H 5.1. The analysis of the purified compounds evidenced that the composition of C and H matched their chemical formulas within the measurement accuracy (0.2% for C and H). X-ray powder diffraction analysis was performed using a Shimadzu XRD-7000 (CuK α radiation, Ni filter, range 2 θ = 3°–40°, step of 0.03°, accumulation of 1 s, room temperature). Indication of X-ray diffraction patterns using the results for single crystals of Al(acac)₃ [32,33], Cr(acac)₃ [33], and In(acac)₃ [34] revealed that the synthesized compounds were single phases and corresponded to monoclinic (*P*2₁/*c*, Al(acac)₃ and Cr(acac)₃) and orthorhombic phases (*Pbca*, In(acac)₃).

2.2. Vapor Pressure Measurements (Transpiration Method)

The transpiration method was used to measure vapor pressures over the crystalline Al(acac)₃, Cr(acac)₃, and In(acac)₃ (Table S1). A complete description of the method and equipment can be found in [27]. The following equations exploiting the ideal gas law [35,36] were utilized to find the value of vapor pressure, p_i , at each temperature, T_i :

$$P_{i} = m_{i} \cdot R \cdot T_{a} / V \cdot M_{i} \text{ with } V = (n_{Ar} + n_{i}) \cdot R \cdot T_{a} / P_{a}, \tag{1}$$

where m_i and M_i are the mass and the molar mass of the compound transferred into the trap during the experiment, R is the molar gas constant, and V is the gas volume consisting of n_{Ar} and n_i moles of gas-carrier and compound, respectively; this volume is ascertained at the ambient temperature T_a and the atmospheric pressure P_a . The uncertainties in definition of vapor pressure, temperature, flow rate, and weighing of the transferred material were $\pm 5\%$, ± 0.5 K, $\pm 2\%$, and $\pm 5 \cdot 10^{-5}$ g, correspondently.

The experiments on Al(acac)₃ and Cr(acac)₃ were implemented independently at the Nikolaev Institute of Inorganic Chemistry of Siberian Branch of Russian Academy of Sciences, NIIC SB RAS, Novosibirsk, Russia (series 1, Table S1) and at the University of Rostock, Rostock, Germany (series 2, Table S1). The transpiration equipment at the University of Rostock acts on the same principles with the same accuracies described above using nitrogen as carrier gas; details can be found in [35–37].

2.3. Vapor Pressure Measurements (Knudsen Effusion Method)

The Knudsen effusion method with mass spectrometric registration of the gas phase composition was implied for an additional appraisal of vapor pressures over crystalline Al(acac)₃. The detailed procedure was previously described elsewhere [29,38,39]. The energy of electron impact was 35 eV. To calculate vapor pressure, the [Al(acac)₂]⁺ (m/z 225) peak was used. The dimensions of the internal volume of the Mo cylindrical effusion chamber were 7 mm in diameter and 8 mm in height. The effusion orifice diameter and the channel length were 0.3 mm and 0.4 mm, respectively. The vapor pressure, p_i , at a temperature, T_i , was calculated under isothermal conditions using the following equation:

$$v_{i} = \frac{2279.62mI_{i}T_{i}}{S_{eff}M^{1/2}\Sigma_{i}\int_{0}^{t}I_{i}T_{i}^{1/2}dt'}$$
(2)

where *m* is the mass of the sample of the molar mass *M* sublimated during the whole experiment time *t*, I_i is the intensity of ion current at the established temperature T_i , S_{eff} is the constant depending on the geometric dimensions of the effusion orifice, and I_i and T_i are current values of the intensity of ion current and temperature. The derivation of the equation is presented in [39]. The standard uncertainty of the temperature measurements was 1.0 K. The relative standard uncertainties of the intensity, mass, and vapor pressure measurements were 1%, 3%, and 10% respectively. The experimental results for Al(acac)₃ are tabulated in Table S2.

3. Results and Discussion

3.1. Vapor Pressure

We performed complementary vapor pressures measurements for crystalline $Al(acac)_3$, $Cr(acac)_3$, and $In(acac)_3$, using transpiration and effusion methods to resolve a conflict in the literature data (see Figure 1 and Section 3.2). In the case of $In(acac)_3$, there are no any correct data at all (see Section 3.2). The primary experimental data are listed in Tables S1 and S2. The experimental vapor pressures measured at different temperatures for the complexes (Figure 3) were approximated using the following equation:

$$R \cdot \ln(p/p_{\text{ref}}) = a + \frac{b}{T} + \Delta^g_{\text{cr}} C^o_{p,m} \cdot \ln(T/T_o),$$
(3)

where a and b are adjustable parameters, and $\Delta_{cr}^g C_{p,m}^o$ is the difference between the isobaric heat capacities of gaseous and crystalline ($C_{p,m}^o(cr)$) phases; T_o was chosen to be 298.15 K, with $p_{ref} = 1$ Pa. The standard molar sublimation enthalpies, $\Delta_{cr}^g H_m^o$, and entropies, $\Delta_{cr}^g S_m^o$, were calculated using the following equations:

$$\Delta_{\rm cr}^g H^{\rm o}_{\rm m}(T) = -\mathbf{b} + \Delta_{\rm cr}^g C^{\rm o}_{p,\rm m} \cdot T, \tag{4}$$

$$\Delta_{\rm cr}^{\rm g} S_{\rm m}^{\rm o}(T) = \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}(T) / T + R \cdot \ln(\frac{p_{\rm i}}{p^{\rm o}})$$
⁽⁵⁾

with $p^{\circ} = 0.1$ MPa and the parameter b from Equation (3). The derivation of Equations (3)–(5) was presented in detail in [35].



Figure 3. Dependencies of vapor pressures on reciprocal temperature for Al(acac)₃, Cr(acac)₃, and In(acac)₃ obtained using the transpiration methods (series 1 and 2) and Knudsen effusion method with mass spectrometric registration of the gas phase composition (series 3), $p_{ref} = 1$ Pa.

The $\Delta_{cr}^g C_{p,m}^o$ values used in Equations (3)–(5) were assessed with the help of the empirical equation offered by Chickos and Acree [40,41]:

$$-\Delta_{\rm cr}^{\rm g} C_{p,\rm m}^{\rm o} = 0.75 + 0.15 C_{p,\rm m}^{\rm o}({\rm cr}).$$
(6)

We previously tested this equation successfully for metal (Fe(II,III), Ir(III), and Sc(III)) complexes [25–27,42]. The experimental $C_{p,m}^{o}(cr)$ values of 429.6 ± 0.6 J·K⁻¹·mol⁻¹ for Al(acac)₃ and 430.3 ± 0.6 J·K⁻¹·mol⁻¹ for Cr(acac)₃ available in the literature [43] were exploited to appraise the $\Delta_{cr}^{g}C_{p,m}^{o}$ values via Equation (6) (Table S3). To get $C_{p,m}^{o}(cr)$ for In(acac)₃, on which there are no any data, we compiled all the heat capacity values derived from precise adiabatic and differential scanning calorimetry measurements for ten metal *tris*-acetylacetonate complexes [43–46] (Table S3). The $C_{p,m}^{o}(cr)$ values and the $\Delta_{cr}^{g}C_{p,m}^{o}$ values calculated from these data using Equation (6) turned out to be practically the same. Therefore, the $C_{p,m}^{o}(cr, 298.15 \text{ K})$ values were hardly dependent on metal type for *tris*-acetylacetonate complexes. Thus, by calculating the weighted average of 429 ± 8 J·K⁻¹·mol⁻¹ from these data using the experimental uncertainties as a weighting factor, we attributed this figure to In(acac)₃ and estimated the $\Delta_{cr}^{g}C_{p,m}^{o} = 65.1 \pm 1.2 J·K^{-1}·mol^{-1}$ for this complex (Table S3).

Using the available data on crystalline heat capacity, we could also estimate the value of $C_{v,m}^{o}(cr, 298.15 \text{ K})$ for other metal acetylacetonate complexes. Using $C_{v,m}^{o}(cr) = 191.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ previously obtained for ferrocene [42] and applying the group contribution method (contribution value for $[C_aH] = 17.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [41]), it was possible to calculate the increment value for iron: $[Fe] = 191.2 - 10[C_aH] = 16.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. After that, combining the value obtained with experimental $C_{p,m}^{o}(cr)$ value of iron(III) acetylacetonate [44], we could calculate the increment responsible for acetylacetonate: $[acac] = (429.9 - 16.2)/3 = 137.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. With reliable $C_{\nu,m}^{o}(cr)$ values for metal acetylacetonates, M(acac)₃, the metal increment could be assessed as follows (using the example of scandium): $[Sc] = 425.1 - 3[acac] = 11.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Having carried out similar calculations for other compounds, it can be seen the [M] values fluctuated in a very narrow range of $-4.6-28.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ with a weighted average value of 11.8 ± 8.2 J·K⁻¹·mol⁻¹, much lower than that for [acac]. This means that the heat capacities of the crystalline β -diketonate complexes affected by the organic component (the number of ligands and substituents in the ligand), but not by the central metal atom. Thus, assuming that the increment values of any metal [M] are nearly the same, we propose the following equation to evaluate $C_{n,m}^{o}(cr)$ value of metal acetylacetonate complexes:

$$C_{p,m}^{o}(cr, M(acac)_{n}), J \cdot K^{-1} \cdot mol^{-1} = n_{1} \cdot [M] + n_{2} \cdot [acac] = 11.8 \cdot n_{1} + 137.9 \cdot n_{2},$$
 (7)

where n_1 and n_2 are the numbers of metals and acetylacetonate ligands, respectively. In the absence of any experimental data, we can recommend this equation to assess the value of $C_{p,m}^{o}(cr)$ for acetylacetonates of other metals of different valency (not only 3+) within a relative standard uncertainty of no more than 2%. In principle, using the specific [M] values (see Table S3) or the averaged value ($11.8 \pm 8.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and an empirical procedure worked out in our recent study [26], such an approach can be transferred to the β -diketonate complexes with ligands other than acetylacetone, which we will demonstrate in our forthcoming articles.

The calculated $\Delta_{cr}^g C_{p,m}^o$ values (see Table S3) were applied to approximate via Equation (3) the experimental vapor pressures over crystalline compounds measured in this work with the help of transpiration and effusion methods, resulting in the following equations:

$$\ln\left(p/p_{\rm ref}\right) = \frac{401.0}{R} - \frac{145401.3}{RT} - \frac{65.2}{R} \ln\frac{T}{298.15} \text{ for Al}(\rm{acac})_{3}, \tag{8}$$

$$\ln\left(p/p_{\rm ref}\right) = \frac{393.1}{R} - \frac{147708.7}{RT} - \frac{65.3}{R} \ln\frac{T}{298.15} \text{ for } \operatorname{Cr}(\operatorname{acac})_3,\tag{9}$$

$$\ln\left(p/p_{\rm ref}\right) = \frac{411.1}{R} - \frac{153285.7}{RT} - \frac{65.1}{R} \ln \frac{T}{298.15} \text{ for } \ln(\rm{acac})_3, \tag{10}$$

Equations (8) and (9) represent a joint treatment of three sets of vapor pressure data on Al(acac)₃ and two sets on Cr(acac)₃ (see Figure 3, series 1, series 2, and series 3) obtained separately using transpiration setups and the effusion method (see Sections 2.2 and 2.3). Equations (8)–(10) describing the dependences of the sublimation vapor pressures of Al(acac)₃, Cr(acac)₃, and In(acac)₃ on temperature can be applied for the enhancement of the MOCVD and allied gas phase deposition process. The results are summarized in Table 1.

Table 1. Standard molar sublimation enthalpies, $\Delta_{cr}^g H_m^o(T_{av})$, and standard molar sublimation entropies, $\Delta_{cr}^g S_m^o(T_{av})$, at an average temperature (T_{av}) over the experimental range (ΔT) and at 298.15 K ^a.

Compound	$\Delta T (T_{av}),$ K	n ^b	$\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(T_{\mathrm{av}}),\ \mathrm{kJ}\cdot\mathrm{Mol}^{-1}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}}), J \cdot \mathrm{Mol}^{-1} \mathrm{K}^{-1}$	$\Delta^{g}_{cr}H^{o}_{m}$ (298.15 K), kJ·Mol ^{-1 c}	$\Delta_{cr}^{g} S_{m}^{o}$ (298.15 K), J·K ⁻¹ ·Mol ^{-1 c}
Al(acac) ₃ series 1	379–460 (419.0)	15	117.6 ± 0.8	217.0 ± 1.6	125.5 ± 1.4	239.3 ± 2.6
Al(acac) ₃ series 2	378–455 (416.6)	11	115.3 ± 1.1	211.1 ± 1.9	123.0 ± 1.6	232.9 ± 2.9
Al(acac) ₃ series 3	382–434 (408.0)	7	124.5 ± 4.2	232.0 ± 7.7	131.6 ± 5.2	252.5 ± 9.8
Cr(acac) ₃ series 1	395–477 (436.0)	11	118.6 ± 1.0	206.0 ± 1.7	127.6 ± 1.5	230.8 ± 2.6
Cr(acac) ₃ series 2	401–470 (435.5)	5	122.1 ± 2.0	213.0 ± 3.5	131.1 ± 2.5	237.7 ± 4.3
In(acac) ₃	384–436 (409.6)	10	126.7 ± 2.3	229.7 ± 4.2	134.0 ± 2.9	250.4 ± 5.2

^a The uncertainties of sublimation enthalpies and entropies $U(\Delta_{cr}^g H_m^o / \Delta_{cr}^g S_m^o)$ are the expanded ones (0.95 level of confidence, k = 2). ^b Number of experimental points. ^c Combined expanded uncertainties (0.95 level of confidence, k = 2) calculated according to the procedure described in [37].

3.2. Sublimation/Vaporization Enthalpies and Entopies of Metal(III) β -Diketonates and Their Temperature Adjustment to T = 298.15 K. Evaluation of the Thermodynamic Characteristics

To date, there have been quite an impressive number of published measurements of vapor pressures and sublimation enthalpies for Al(acac)₃, Cr(acac)₃, and In(acac)₃ [7–24,29,47–55]. We compiled the relevant literature data, supplemented by our own for evaluation (Table 2). Practically all the values responsible for the enthalpies, $\Delta_{cr,l}^g H_m^o(T)$, and entropies, $\Delta_{cr,l}^g S_m^o(T)$, of the crystal–gas and liquid–gas phase transitions were derived from *p*–*T* measurements performed with the help of varied methods (they are also indicated in Table 2), referring to significantly diverse temperatures, *T*, which makes any comparison meaningless. The only way to perceive these values is to attribute these thermodynamic characteristics to a common temperature, e.g., to the reference temperature *T* = 298.15 K. For this purpose, well-known equations describing the Kirchhoff law were applied:

$$\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}(298.15\,{\rm K}) = \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}(T) + \Delta_{\rm cr}^{\rm g} C_{p,{\rm m}}^{\rm o}(298.15\,{\rm K}-T), \tag{11}$$

$$\Delta_{l}^{g} H_{m}^{o}(298.15 \text{ K}) = \Delta_{l}^{g} H_{m}^{o}(T) + \Delta_{l}^{g} C_{p,m}^{o}(298.15 \text{ K} - T),$$
(12)

$$\Delta_{\rm cr}^{\rm g} S_{\rm m}^{\rm o}(298.15\,{\rm K}) = \Delta_{\rm cr}^{\rm g} S_{\rm m}^{\rm o}(T) + \Delta_{\rm cr}^{\rm g} C_{p,{\rm m}}^{\rm o} {\rm ln} \, \frac{298.15{\rm K}}{T}, \tag{13}$$

$$\Delta_{l}^{g} S_{m}^{o}(298.15 \text{ K}) = \Delta_{l}^{g} S_{m}^{o}(T) + \Delta_{l}^{g} C_{p,m}^{o} \ln \frac{298.15 \text{ K}}{T}.$$
(14)

Complex (State) CAS	Method ^b	T-Range (T), ^c K	$\Delta^{g}_{cr,l}H^{o}_{m}(T), d^{d}$ kJ·mol ⁻¹	$\Delta^{g}_{cr,l}S^{o}_{m}(T), d$ J·K ⁻¹ ·mol ⁻¹	$\Delta^{g}_{cr,l}H^{o}_{m}$ (298.15 K), ^e kJ·mol ⁻¹	$\Delta^{g}_{cr,l}S^{o}_{m}$ (298.15 K), ^e J·K ⁻¹ ·mol ⁻¹	Refs.
1	2	3	4	5	6	7	8
Al(acac) ₃ (cr) 13963-57-0	I K GC GC SB S TE S S TE S S K/MS GC TGA S CVM K TGA TGA T	$\begin{array}{c} 422-493 \ (458) \\ 374-414 \ (394) \\ 383-413 \ (398) \\ 353-368 \ (360.5) \\ 403-473 \ (438) \\ 323-458 \ (360.5) \\ 332-458 \ (391) \\ 388-404 \ (396) \\ 337-405 \ (371) \\ 426-471 \ (449) \\ 432-464 \ (448) \\ 310-380 \ (345) \\ 423-471 \ (447) \\ 413-443 \ (428) \\ 424-468 \ (446) \\ 376-467 \ (422) \\ 345-410 \ (378) \\ 433-463 \ (448) \\ 379-460 \ (419) \end{array}$	$\begin{array}{c} 19.14\\ 104.74\\ 66.0\\ 120.0\pm 3.0\\ 24.2\\ 19.2\\ 105\pm 2\\ 111\pm 4\\ 47.0\pm 0.5\\ 108.05\pm 0.36\\ 102.0\pm 3.3\\ 126.8\pm 1.0\\ 105.2\pm 3.6\\ 93\\ 108.2\pm 4.6\\ 106.0\pm 2.4\\ 117.31\pm 1.67\\ 107.1\\ 117.6\pm 0.4\\ \end{array}$	52.7 42.2 196.54 ± 0.86 182.7 ± 4.9 191.1 ± 2.7 220 197.7 ± 8.4 191.9 ± 4.3 $-$ 217.0 ± 0.8	$\begin{array}{c} (30\pm20)\\ 111.0\pm7\\ (74\pm20)\\ 128.4\pm5.2\\ (33\pm20)\\ (25\pm20)\\ 111.2\pm7\\ 117.6\pm3.3\\ (52\pm20)\\ 117.9\pm1.9\\ 111.9\pm3.6\\ 129.6\pm1.4\\ 115\pm10\\ (102\pm10)\\ 117.7\pm5.1\\ 113.8\pm2.8\\ 121.2\pm2.3\\ 114.0\pm5.3\\ 125.5\pm0.7 \end{array}$	$\begin{array}{c} 203.2 \pm 13 \\ (122 \pm 40) \\ 247.9 \pm 9.8 \\ (78 \pm 40) \\ (59 \pm 40) \\ 206 \pm 13 \\ 223.1 \pm 6.2 \\ (80 \pm 40) \\ 223.1 \pm 4.0 \\ 209.6 \pm 6.8 \\ 256.6 \pm 2.7 \\ 218 \pm 20 \\ (198 \pm 20) \\ 223.5 \pm 9.8 \\ 214.2 \pm 5.4 \\ 232.8 \pm 4.4 \\ 216.7 \pm 9.8 \\ 239.3 \pm 1.3 \end{array}$	[7,8] [9] [10] [11] [12] [13] [14] [14] [15] [16] [17] [18] [19] [20] [21] [21] [22] [21] [22] [24] This work
	Т	378-455 (417)	115.3 ± 0.5	211.1 ± 1.0	123.0 ± 0.8	232.9 ± 1.4	series 1 This work,
	K/MS	382–434 (408)	124.5 ± 2.1	232.0 ± 3.9	131.6 ± 2.6	252.5 ± 4.9	series 2 This work, Series 3
					123.9 \pm 0.9 $^{ m f}$	$236.4\pm1.6~^{\rm f}$	This work
Al(acac) ₃ (l) 13963-57-0	S S GC TGA	471–536 (504) 468–515 (492) 471–538 (505) 471–513 (492)	$77.54 \pm 0.33 \\ 78.7 \pm 1.1 \\ 78.5 \pm 3.6 \\ 80.2$	$\begin{array}{c} 131.59 \pm 0.71 \\ 133.6 \pm 1.1 \\ 133.8 \pm 2.7 \\ - \end{array}$	$104.3 \pm 1.1 \\ 104.0 \pm 1.2 \\ 105 \pm 10 \\ 104.2 \pm 4.4 \\ 104.2 \pm 1.6^{\text{ f}}$	$199.8 \pm 4.8 \\ 198.7 \pm 4.7 \\ 202 \pm 20 \\ 200.1 \pm 8.7 \\ 199.4 \pm 6.2^{\text{ f}}$	[16] [17] [19] [24] This
	IC				100.7 ± 1.9	$\textbf{192.0} \pm \textbf{3.7}$	This work
Cr(acac)3 (cr) 21679-31-2	I K T SB/SPM TGA I K GC GC S DSC K S S SC K/MS GC TGA K/MS K/MS CVM K TGA	$\begin{array}{c} 389-397\ (393)\\ 374-414\ (394)\\ 365-421\ (385)\\ 390-403\ (397)\\ 335-356\ (346)\\ 363-393\ (378)\\ 374-398\ (386)\\ 443-493\ (468)\\ 323-463\ (393)\\ 462-486\ (474)\\ 5511\\ 325-375\ (350)\\ 357-486\ (422)\\ 350-375\ (363)\\ 428-483\ (456)\\ 413-443\ (428)\\ 350-411\ (384)\\ 356-411\ (384)\\ 443-465\ (454)\\ \end{array}$	$\begin{array}{c} 27.76 \pm 2.9 \\ 91.46 \\ 112.1 \\ 110.8 \pm 0.8 \\ 85.9 \\ 39.7 \\ 123 \pm 3 \\ 28.8 \\ 28.8 \\ 28.8 \\ 127.40 \pm 0.80 \\ 141.5 \pm 5.6 \\ 126.8 \pm 2.1 \\ 113.0 \pm 2.4 \\ 126.8 \pm 2.1 \\ 126.4 \pm 3.6 \\ 91 \\ 118.7 \pm 2.5 \\ 127.4 \pm 0.6 \\ 127.4 \pm 0.5 \\ 128.20 \pm 1.60 \\ 120.8 \\ \end{array}$	$\begin{array}{c} -\\ 291.2\\ 185.2 \pm 1.6\\ -\\ -\\ 62.3\\ 62.3\\ 224.00 \pm 1.67\\ -\\ 194.8 \pm 5.1\\ -\\ 233.1 \pm 2.7\\ 216\\ 206.9 \pm 5.9\\ 231.5 \pm 1.1\\ 230.5 \pm 0.9\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\$	$\begin{array}{c} (31\pm20)\\ (97.5\pm7)\\ 118\pm8\\ 117\pm10\\ (89\pm10)\\ (45\pm20)\\ 129.5\pm4.4\\ (40\pm20)\\ (35\pm20)\\ 138.9\pm7.5\\ (158\pm20)\\ 130.1\pm2.4\\ 120.6\pm2.9\\ 131.0\pm3.4\\ 137\pm10\\ (99\pm10)\\ 124.0\pm1.7\\ 131.3\pm1.1\\ 135.8\pm1.3\\ 130.3\pm3.3\\ 124.2\pm8.9 \end{array}$	$(14 \pm 40) (154.0 \pm 13) 206 \pm 16 205 \pm 20 (60 \pm 40) 234.2 \pm 7.9 (76 \pm 40) (64 \pm 40) 254 \pm 13 265.0 \pm 5.0 217.2 \pm 5.3 242.2 \pm 6.2 261 \pm 20 (239 \pm 20) 223.1 \pm 3.2 242.6 \pm 2.2 254.1 \pm 2.9 239.4 \pm 6.0 223 \pm 16 $	[47] [9] [48] [49] [50] [10] [11] [12] [13] [16] [51] [18] [52] [53] [19] [20] [54] [29] [22,23] [24] This
	Т	395–477 (436)	118.6 ± 0.5	206.0 ± 0.9	127.6 ± 0.8	230.8 ± 1.3	work, series 1 This
	Т	401–470 (434)	122.1 ± 1.0	213.0 ± 1.8	131.1 ± 1.3	237.7 ± 2.2	work, series 2 This
		402 552 (510)	04.0 + 0.6	10(0 + 0 7	129.6 ± 0.9 °	236.2 ± 1.7 °	work
Cr(acac) ₃ (l) 21679-31-2	S TGA S	483-553 (518) 490-536 (513) 489-552 (521) 491-563 (527)	$84.2 \pm 3.6 \\ 82.2 \pm 2.0 \\ 89.9 \\ 81.84 \pm 0.27$	130.8 ± 2.7 131.8 ± 4.0 131.21 ± 0.53	$113 \pm 10 \\ 110.3 \pm 1.5 \\ 114.0 \pm 4.1 \\ 111.5 \pm 1.4 \\ 111.1 \pm 2.0^{\text{ f}}$	$209 \pm 20 \\ 204.4 \pm 5.2 \\ 212.0 \pm 8.3 \\ 205.3 \pm 5.4 \\ 206.1 \pm 6.7^{\text{ f}}$	[19] [52] [24] [16] This work
	IC				107.1 ± 2.4	197.1 ± 4.2	work
In(acac) ₃ (cr) 14405-45-9	GC T	423–478 (451) 384–436 (410)	95.7 ± 3.6 126.7 ± 1.2	$\begin{array}{c} 162.6 \pm 2.7 \\ 229.7 \pm 2.1 \end{array}$	(105 ± 10) 134.0 \pm 2.9	(190 ± 20) 250.4 \pm 5.2	[19] This work
In(acac) ₃ (l) 14405-45-9	S GC	435–490 (463) 478–533 (506)	$\begin{array}{c} 86.6 \pm 0.2 \\ 85.1 \pm 3.6 \end{array}$	$\begin{array}{c} 145.2 \pm 0.4 \\ 141.1 \pm 2.7 \end{array}$	$(107.9 \pm 1.1) \ (112 \pm 10)$	(202.2 ± 4.2) (210 ± 20)	[55] [19]

Table 2. Compilation of enthalpies and entropies of sublimation/vaporization, $\Delta_{cr,l}^g H_m^o$ and $\Delta_{cr,l}^g S_m^o$, for *tris*(β -diketonato)metal (aluminum(III), chromium(III), scandium(III), manganese(III), iron(III), cobalt(III), ruthenium(III), rhodium(III), indium(III), and iridium(III)) complexes available in the literature at different temperatures *T* and referred to 298.15 K^a.

 Table 2. Cont.

Complex (State) CAS	Method ^b	T-Range (T), ^c K	$\Delta^{g}_{\mathrm{cr},1}H^{\mathrm{o}}_{\mathrm{m}}(T), ^{\mathrm{d}}$ kJ·mol ⁻¹	$\Delta^{g}_{cr,l}S^{o}_{m}(T)$, ^d J·K ⁻¹ ·mol ⁻¹	Δ ^g _{cr,l} <i>H</i> ^o _m (298.15 K), ^e kJ·mol ⁻¹	$\begin{array}{c} \Delta^{g}_{\mathrm{cr,l}} S^{o}_{m}(298.15\ \mathrm{K}), ^{e}\\ \mathrm{J}{\cdot}\mathrm{K}^{-1}{\cdot}\mathrm{mol}^{-1} \end{array}$	Refs.
Sc(acac) ₃ (cr) 14284-94-7	SB/SPM TGA K/MS TGA K/MS K/MS S T T TGA	$\begin{array}{c} 380-398\ (389)\\ 413-443\ (428)\\ 330-390\ (360)\\ 420-450\ (424)\\ 345-391\ (386)\\ 330-390\ (360)\\ 422-460\ (441)\\ 385-458\ (422)\\ 394-456\ (425)\\ 403.2 \end{array}$	$\begin{array}{c} 99.6\pm 0.8\\ 95\\ 123.8\pm 2.1\\ 118\pm 4\\ 119.2\pm 2.1\\ 124.3\pm 4.4\\ 103.2\pm 2.7\\ 117.6\pm 0.7\\ 120.7\pm 0.8\\ 119.2\pm 0.8\\ \end{array}$	$\begin{array}{c} 167.4 \pm 1.7 \\ 224 \\ 228.0 \pm 5.8 \\ - \\ 230.7 \pm 8.1 \\ 179.9 \pm 4.7 \\ 212.7 \pm 1.2 \\ 217.9 \pm 1.5 \end{array}$	$\begin{array}{c} 105.5\pm10\\ (103.4\pm10)\\ 127.6\pm2.4\\ 126.3\pm6.7\\ 124.9\pm2.2\\ 128.3\pm4.5\\ 112.5\pm5.1\\ 125.6\pm0.9\\ 128.9\pm1.1\\ 126.1\pm1.1\\ \end{array}$	$184.6 \pm 20 \\ (247.3 \pm 20) \\ 240.2 \pm 4.4 \\ - \\ - \\ 242.9 \pm 8.4 \\ 205.5 \pm 8.9 \\ 233.4 \pm 2.1 \\ 240.7 \pm 2.0 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ $	[49] [20] [54] [56] [38] [38] [25] [25] [25] [25] [25],
	TCA	4(0, 500 (400)	05 + 4		$126.4 \pm 1.1^{+}$	236.7 ± 2.7 ¹	work
	S	463–490 (477)	83 ± 4 87.9 ± 1.7	146.4 ± 1.2	109.8 ± 3.3 111.7 ± 2.8	208.5 ± 4.3	[38]
Sc(acac) ₃ (l) 14284-94-7					111.3 \pm 5.0 $^{ m f}$	208.5 ± 8.6	this work
	IC				109.7 \pm 2.5	206.0 ± 5.0	this work
Fe(acac)3 (cr) 14024-18-1	SB/SPM T TGA K SB T C K/MS LT GC TE K TGA TGA K/MS T	$\begin{array}{c} 378-405\ (392)\\ 363-423\ (393)\\ 335-356\ (346)\\ 406-441\ (424)\\ 373-402\ (388)\\ 381-402\ (392)\\ 400-458\ (429)\\ 298\\ 309-360\ (335)\\ 338-355\ (347)\\ 453-488\ (471)\\ 369-388\ (378.5)\\ 369-388\ (379)\\ 430-450\ (440)\\ 413-443\ (428)\\ 340-405\ (373)\\ 400-458\ (429)\\ \end{array}$	$\begin{array}{c} 99.0\pm0.8\\ 114.2\\ 114.9\\ 117\pm16\\ 121\pm5\\ 112\pm6\\ 100\\ 138\pm5\\ 126.4\pm1.6\\ 114.2\pm1.5\\ 132.9\pm3.6\\ 124.6\pm1.3\\ 124.6\pm1.2\\ 118\\ 112\\ 130.5\pm2.5\\ 124.1\pm1.2 \end{array}$	$162.8 \pm 1.6 \\ 296.6 \\ - \\ 205 \pm 30 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ $	$\begin{array}{c} 105\pm10\\ 120\pm8\\ 118\pm10\\ 125\pm16\\ 128.2\pm7\\ 118\pm10\\ 109\pm20\\ 138\pm5\\ 130.8\pm2.0\\ 117\pm10\\ 144\pm10\\ 129.8\pm1.9\\ 129.7\pm1.8\\ 127\pm10\\ 120\pm10\\ 135.5\pm2.7\\ 132.2\pm2.0 \end{array}$	181 ± 20 215 ± 16 -228 ± 30 237.4 ± 13 246 ± 21 -245.4 ± 3.7 227 ± 20 262 ± 20 244.4 ± 3.6 240.1 ± 3.3 -283 ± 20 256.1 ± 5.2 246.4 ± 4.0	[45] [48] [50] [26] [14] [14] [26] [58] [53] [59] [19] [60] [60] [61] [20] [54] [54]
	TGA	452-535 (494)	82±1		$130.6 \pm 1.7^{\text{ f}}$ 108 ± 5	$244.4 \pm 3.3^{\text{ f}}$	[02] [26], this work [63]
	GC	488–548 (518)	93.3 ± 3.6	154.1 ± 2.7	122 ± 10	226 ± 20	[19] [26],
Fe (acac) ₃ (l) 14024-18-1	IC				$110.3 \pm 3.9^{+1}$ 109.1 ± 2.9^{-1}	203.0 ± 5.5	work [26], this work
Ir(acac) ₃ (cr) 15635-87-7					136.8 ± 1.4	234.3 ± 2.8	[27], this work
	Ι	383-391 (387)	77.8 ± 0.8	-	(83.5 ± 20)	(174.1 ± 40)	[47]
Mn(acac) ₃ (cr) 14284-89-0	T TGA K/MS K/MS	355-445 (385) 335-356 320-380 (350) 340-400 (370)	$113.0 \\ 117.3 \\ 124.7 \pm 1.9 \\ 132.2 \pm 2.5$	293.3 246.4 ± 9.6	$\begin{array}{c} 118.6\pm8\\ 120.4\pm10\\ 128.0\pm2.2\\ 137.0\pm2.4\\ \textbf{131.3}\pm\textbf{3.1}^{\mathrm{f}}\end{array}$	$\begin{array}{c} 309 \pm 16 \\ -\\ 238.1 \pm 4.0 \\ 259.4 \pm 4.4 \\ \textbf{249.6} \pm \textbf{5.8}^{\mathrm{f}} \end{array}$	[48] [50] [53] [54] This work
Mn(acac) ₃ (l) 14284-89-0	IC		19.7 ± 2.6	43.2 ± 5.7	111.6 ± 4.0	206.4 ± 8.1	This work
	Ι	378-393 (386)	74.9 ± 4.6	-	(81.8 ± 20)	(159.2 ± 40)	[47]
	Т	350-430 (390)	107.1	274.5	112.8 ± 8	291.2 ± 16	[48]
	TGA	335-361 (348) 453	86.3	-	(89.6 ± 10) (151.9 ± 20)	_	[45]
Co(acac) ₃ (cr) 21679-46-9	K/MS	455 318-382 (350)	142.0 ± 0.9 134.6 ± 2.1	_	(131.9 ± 20) 138.0 ± 2.4	255.6 ± 4.3	[53]
	TGA K/MS	433-463 (448) 350-415 (383)	$\begin{array}{c} 138\\ 120.1\pm3.8\end{array}$	$\begin{array}{c} 311\\ 207.1\pm9.6\end{array}$	$egin{array}{c} 147.3 \pm 10 \ 125.5 \pm 1.6 \ 129.2 \pm 2.6 \ ^{ m f} \end{array}$	(336.3 ± 20) 222.7 \pm 4.3 241.0 \pm 6.0 $^{\rm f}$	[20] [54] This work
Ru(acac)3 (cr) 14284-93-6	T K K K/MS	423-493 (458) 398-413 (406) 394-441 (418) 377-434 (406)	$\begin{array}{c} 127.0 \pm 0.5 \\ 139.7 \pm 2.5 \\ 148.81 \pm 1.68 \\ 129.1 \pm 1.0 \end{array}$	$212.5 \pm 1.0 \\ -210.0 \pm 2.5$	$\begin{array}{c} 137.1 \pm 0.9 \\ 150.0 \pm 6.7 \\ 158.1 \pm 6.7 \\ 136.2 \pm 1.8 \\ \textbf{137.4} \pm \textbf{1.6}^{\mathrm{f}} \end{array}$	$\begin{array}{c} 240.9\pm2.6\\ 270\pm12\\ 277\pm12\\ 229.4\pm3.2\\ \textbf{238.3}\pm\textbf{3.9}^{\mathrm{f}} \end{array}$	[65] [66] [67] [68] This work

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Complex (State) CAS	Method ^b	T-Range (T), ^c K	$\Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}(T), \mathrm{^{d}}$ kJ·mol ⁻¹	$\Delta^{g}_{cr,l}S^{o}_{m}(T), d$ J·K ⁻¹ ·mol ⁻¹	$\Delta^{g}_{cr,l}H^{o}_{m}$ (298.15 K), ^e kJ·mol ⁻¹	$\Delta^{g}_{cr,l}S^{o}_{m}$ (298.15 K), ^e J·K ⁻¹ ·mol ⁻¹	Refs.
Ru(acac) ₃ (l) 14284-93-6	IC		11.4 ± 4.1	15.0 ± 5.4	$\textbf{126.0} \pm \textbf{4.4}$	$\textbf{223.3} \pm \textbf{6.7}$	This work
Rh(acac) ₃ (cr) 14284-92-5	T K/MS S T S	412-483 (448) 348-414 (381) 473-498 (486) 398-463 (431) 458-521 (490)	$\begin{array}{c} 128.28 \pm 0.50 \\ 121.65 \pm 0.51 \\ 100.8 \pm 1.9 \\ 127.1 \pm 0.6 \\ 127.0 \pm 1.0 \end{array}$	$\begin{array}{c} 211.63 \pm 1.13 \\ 199.45 \pm 1.32 \\ 156.1 \pm 2.2 \\ 207.9 \pm 1.0 \\ 208.0 \pm 1.6 \end{array}$	$\begin{array}{c} 138.2 \pm 0.9 \\ 127.0 \pm 1.2 \\ (113 \pm 20) \\ 135.9 \pm 1.0 \\ 139.8 \pm 1.2 \end{array}$	$\begin{array}{c} 238.9 \pm 2.5 \\ 215.7 \pm 2.3 \\ (189 \pm 40) \\ 232.4 \pm 2.4 \\ 241.1 \pm 3.1 \end{array}$	[69] [69] [46] [46]
					135.7 \pm 1.1 $^{ m f}$	$230.5\pm2.5^{\rm\ f}$	This work

^a Values in bold are recommended for further thermodynamic calculations. The uncertainty of these sublimation/vaporization enthalpies $U(\Delta_{cr,l}^{g}H_{m}^{o})$ and entropies $U(\Delta_{cr,l}^{g}S_{m}^{o})$ is the expanded uncertainty (0.95 level of confidence, k = 2). ^b Methods: I = isoteniscope; K = Knudsen effusion method with weighing of the cell; GC = gas chromatography; SB = sublimation bulb; S = static; TE = torsion-effusion method; K/MS = Knudsen effusion method with mass spectrometric registration of gas phase; TGA = thermal gravimetric analysis; CVM = method of calibrated volume; T = transpiration (or gas-saturation method); SB/SPM = sublimation bulb combined with spectrophotometry; DSC = differential scanning calorimetry; C = calorimetry; LT = Langmuir technique; IC = indirect calculations performed according to the equations $\Delta_1^{g} H_m^o(298.15 \text{ K}) / \Delta_1^{g} S_m^o(298.15 \text{ K}) = 100 \text{ K}$ $\Delta_{cr}^{dr} H_{m}^{o}(298.15 \text{ K}) / \Delta_{cr}^{dr} S_{m}^{o}(298.15 \text{ K}) - \Delta_{cr}^{l} H_{m}^{o}(298.15 \text{ K}) / \Delta_{cr}^{l} S_{m}^{o}(298.15 \text{ K}) \text{ with } \Delta_{cr}^{l} H_{m}^{o}(298.15 \text{ K}) / \Delta_{cr}^{l} S_{m}^{o}(298.15 \text{ K}) + \Delta_{cr}^{l} H_{m}^{o}(298.15 \text{ K}) / \Delta_{cr}^{l} S_{m}^{o}(298.15 \text{ K}) + \Delta_{cr}^{l} H_{m}^{o}(298.15 \text{ K}) +$ values from Table S4 (see text). c Experimental temperature range and/or temperature given in literary source which sublimation/vaporization thermodynamic characteristics is referred to. $^{\rm d}$ Values of the sublimation/vaporization enthalpy and entropy (if available) and uncertainties (if available) are listed as given in the literary source. ^e The uncertainty of each sublimation/vaporization enthalpy $u(\Delta_{cr,l}^g H_m^o)$ and entropies $u(\Delta_{cr,l}^g S_m^o)$ at 298.15 K is the standard combined uncertainty (at a 0.68 level of confidence, k = 1) including uncertainties in the experimental vapor pressure or enthalpy measurement conditions and temperature adjustment to T = 298.15 K [37]. When there were no any experimental details, we estimated the uncertainty from our experience. [†] Weighted average value. We used the uncertainty as the weighing factor. Values in parentheses were excluded from the calculation of the mean.

We performed the first correct comparison of the available sublimation/vaporization enthalpies and entropies of the tris(acetylacetonato)metal(III) complexes (Table 2) with the heat capacity differences (from Table S3). If the primary data on experimental vapor pressures were available in literary sources [9–11,14,15,17,18,21–24,29,47–49,52–55], we treated them uniformly via Equations (3)-(5) (these equations are also applicable to vaporization data processing, provided that the difference between the isobaric heat capacities of gaseous and liquid phases, $\Delta_1^g C_{p,m}^o$, from Table S3 is used). In cases where only the $\Delta_{cr.l}^g H_m^o(T) / \Delta_{cr.l}^g S_m^o(T)$ values are reported, we applied Equations (11)-(14) to refer these values to the reference temperature. The argument in favor of processing the primary p-T data is that they allow calculating both thermodynamic phase transition characteristics—enthalpy and, no less important, entropy. Given the fact that, in most cases, the authors limited themselves to indicating only the enthalpy of sublimation or vaporization (see Table 2), the benefit of such a priority is obvious. The $\Delta_{cr,l}^g H_m^o(298.15 \text{ K}) / \Delta_{cr,l}^g S_m^o(298.15 \text{ K})$ values in Table 2 are accompanied by combined uncertainties associated with the experimental vapor pressure measurement conditions and temperature adjustment to T = 298.15 K (the procedure is described elsewhere [37]). When the necessary information about the measurements (mainly about the uncertainties in measuring the vapor pressure) was missing, we estimated the uncertainty from our experience. Such a unified processing of all the data, both available in the literature and obtained in this work, enabled a thorough analysis and evaluation of the sublimation/vaporization results.

As can be seen, the scatter of the resulting $\Delta_{cr,l}^g H_m^o(298.15 \text{ K})/\Delta_{cr,l}^g S_m^o(298.15 \text{ K})$ values for each substance was unacceptably large. This may be explained by examining the methods utilized and experimental details. A thorough analysis of the shortcomings of the experimental methods applied for the exploration of such specific objects as metal β -diketonate complexes and the quality of the resulting sublimation and vaporization enthalpies was provided in detail in our previous studies devoted to the diagnostic check of the thermodynamics of scandium(III), iron(III), and iridium(III) β -diketonates [25–27]. The data compiled within this work were obtained with the same set of methods and suffer from a similar methodological negligence. Following a similar critical analysis of the literature methods and experimental conditions allowed us to eliminate the doubtful data (bracketed in Table 2), while the remaining $\Delta_{cr,l}^g H_m^o(298.15 \text{ K})$ values, together with the $\Delta_{cr,l}^g S_m^o(298.15 \text{ K})$ values, were taken to count the appropriate weighted average for each compound using the experimental uncertainties as a weighting factor.

In our previous studies, we evaluated the sublimation/vaporization enthalpy for Sc(acac)₃ [25] and Fe(acac)₃ [26]. We also included in Table 2 those $\Delta_{cr,l}^{g}H_{m}^{o}(T)$ values which were recognized as correct in [25,26] and accompanied them by the corresponding $\Delta_{cr,l}^{g}S_{m}^{o}(T)$ values from literary sources (if available) and $\Delta_{cr,l}^{g}S_{m}^{o}(298.15 \text{ K})$ values adjusted using Equations (13) or (14) and averaged within this study. The averaged $\Delta_{cr}^{g}H_{m}^{o}(298.15 \text{ K})$ and $\Delta_{cr}^{g}S_{m}^{o}(298.15 \text{ K})$ values already verified by us for Ir(acac)₃ [27] are also provided in Table 2.

All average values (with expanded uncertainties of a 95% confidence level) for $Al(acac)_3$, $Cr(acac)_3$, $In(acac)_3$, $Sc(acac)_3$, $Fe(acac)_3$, and $Ir(acac)_3$ are presented in bold, and they were considered by us to be reliable and acceptable for further calculations (Table 2).

3.3. Structure–Property Relationships in Metal(III) Acetylacetonates. Influence of the Central Atom on the Sublimation/Vaporization Enthalpy and Entropy

In our recent studies [25–27], we developed several tools to validate the thermodynamic properties of metal(III) complexes with various β -diketones on the basis of structureproperty correlations. One such tool is the correlation between the enthalpies of vaporization, $\Delta_l^g H_m^o$ (298.15 K), of the pairs of molecules of the metal *tris*-complexes, M(L)₃, and the β -diketonate ligands, HL, which the complex consists of. In other words, these dependencies were considered through changes in the organic species. In the framework of this study, we aimed to determine whether there are correlations in a series of compounds which have the same organic component, but a different metal center. Does the metal have "voting rights"?

We expanded a number of compounds with *tris*-acetylacetonates of manganese, cobalt, ruthenium, and rhodium. For this, we compiled the thermodynamic sublimation data available in the literature [20,45–50,53,54,64–69] in Table 2 and evaluated them in a similar way as described above. Points on vapor pressure over crystalline Mn(acac)₃ and Co(acac)₃ not published in original literary sources [54] are tabulated in Table S5.

A critical analysis of the literature and our own complementary results on acetylacetonate complexes with different metal(III) resulted in a set of enthalpies and entropies of sublimation and vaporization (Table 2). We additionally supported the results on vaporization derived from experimental methods by calculating the $\Delta_1^g H_m^o(298.15 \text{ K})/\Delta_1^g S_m^o(298.15 \text{ K})$ values using the sublimation enthalpies/entropies and enthalpies/entropies of fusion, $\Delta_{cr}^l H_m^o/\Delta_{cr}^l S_m^o$, according to the fundamental relation between phase transition thermodynamic characteristics (denoted as IC in Table 2):

$$\Delta_{\rm l}^{\rm g} H_{\rm m}^{\rm o}(298.15\,{\rm K}) = \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}(298.15\,{\rm K}) - \Delta_{\rm cr}^{\rm l} H_{\rm m}^{\rm o}(298.15\,{\rm K}). \tag{15}$$

$$\Delta_{1}^{g} S_{m}^{o}(298.15 \text{ K}) = \Delta_{cr}^{g} S_{m}^{o}(298.15 \text{ K}) - \Delta_{cr}^{l} S_{m}^{o}(298.15 \text{ K}).$$
(16)

The fusion temperatures and enthalpies, $\Delta_{cr}^{l} H_m^o(T_{fus})$, and entropies, $\Delta_{cr}^{l} S_m^o(T_{fus})$, of fusion available for *tris*(acetylacetonato)metal(III) complexes [30,51,52,63,70–72] are compiled in Table S3 and adjusted to 298.15 K as described in [25,26,73]. The $\Delta_{cr}^{l} H_m^o(298.15 \text{ K}) / \Delta_{cr}^{l} S_m^o(298.15 \text{ K})$ values enabled the validation of the thermodynamic data on all three types of phase transitions (liquid–gas, crystal–gas, and crystal–liquid) for internal consistency. For example, the vaporization enthalpies/entropies of Al(acac)₃, Cr(acac)₃, Sc(acac)₃, and Fe(acac)₃ calculated according to Equations (15) and (16) coincided within the uncertainties with those obtained experimentally. Such consistency of data is an additional argument in favor of the values of sublimation enthalpies/entropies recommended for M(acac)₃ at 298.15 K. Another benefit of the relations (15) and (16) is the possibility to supplement the absent information by indirect derivation of the phase transition enthalpy. Thus, the missing vaporization enthalpies for Mn(acac)₃ and Ru(acac)₃ (denoted as IC in Table 2) were calculated according to Equations (15) and (16) and used for structure–properties correlations, as shown below.

The general linear relationships of thermochemical and thermodynamic properties (for example, gas-phase enthalpies of formation or enthalpies of vaporization) between chemical families are well known for organic compounds. For example, analysis of the "structure-property" relationship in the chemical families of R-substituted benzamides and R-substituted benzoic acids revealed a simple linear behavior [74]. These linear correlations are useful in establishing the internal consistency of the experimental results available for each chemical series. When considering a number of metal acetylacetonates, it would be reasonable to apply the "structure–property" analysis in pairs of metal β -diketonate– metallocene; however, data on the enthalpies of sublimation, vaporization, and fusion for the latter are extremely scarce. Therefore, to study the influence of the central atom, we used the simplest correlation from the molar mass, M, of tris-acetylacetonate complexes (see Table S6), starting with the values of the $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K})$ from Table 2. When constructing the dependence, a weighted least squares method was used; the value of the uncertainty was the decisive factor. It is well known that the enthalpy of sublimation is unique for each solid, since, according to the general thermochemical Equation (15), it includes two independent contributions: the additive contribution of the enthalpy of vaporization and the non-additive contribution of the enthalpy of fusion. The latter is especially important for metal-containing compounds (see Table S4). Thus, any "structure-property" correlations for the enthalpy of sublimation are usually limited to molecules of complexes of the same metal or metals of the same group, where the non-additive contributions of the enthalpy of fusion may not differ much. To our surprise, despite the fact that the metals of this study belonged to different groups of the periodic table, a linear correlation of sublimation enthalpy with the atomic number of the metal up to rhodium (102.91 g mol⁻¹) was observed with a satisfactory correlation coefficient (Figure 4a):



$$\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\rm o}({\rm M}({\rm acac})_3, 298.15 \,{\rm K}) {\rm kJ} \cdot {\rm mol}^{-1} = 0.19 \cdot M + 62.3 \,{\rm with} r^2 = 0.94. \tag{17}$$

Figure 4. Dependencies of sublimation, $\Delta_{cr}^g H_m^o$, (**a**) and vaporization, $\Delta_l^g H_m^o$, (**b**) enthalpies (in kJ mol⁻¹) at 298.15 K of *tris*(acetylacetonato)metal(III) complexes on their molar mass, *M* (in g mol⁻¹).

Beginning with the rhodium complex, the curve seemed to flatten out. This means that, in complexes containing metals with atomic masses up to values comparable with those for the β -diketonate ligand ($M(\text{acac}^-) = 99.11 \text{ g mol}^{-1}$), there was a uniform, albeit insignificant (about 5–18 kJ mol⁻¹), contribution of the metal to the sublimation enthalpy.

However, in complexes with "heavy" central atoms with a large number of electrons, the electron density was apparently redistributed in such a way that other parameters began to exert a critical influence on this thermodynamic parameter.

Unlike that of sublimation, the enthalpy of vaporization of molecules, as a rule, obeys the rules of additivity [26,75]. When studying the influence of the central atom on the vaporization of the *tris*-acetylacetonate complexes (Figure 4b), the analysis also included the data obtained using Equation (15) (denoted as IC in Table 2). The weighted mean of $\Delta_1^g H_m^o$ (298.15 K) values was taken for correlation (Table S6). Unfortunately, data on the enthalpies of vaporization and fusion for metal *tris*-acetylacetonates are very limited, and the uncertainties in the resulting $\Delta_1^g H_m^o$ (298.15 K) values are large, since metal acetylacetonates have a rather low thermal stability and often begin to decompose already upon melting (e.g., In(acac)₃, Rh(acac)₃, and Ir(acac)₃). Nevertheless, even better linear correlation with the corresponding vaporization enthalpies was observed (Figure 4b):

$$\Delta_1^g H_m^o(M(acac)_3, 298.15 \text{ K}) \text{kJ} \cdot \text{mol}^{-1} = 0.31 \cdot M + 3.20 \text{ with } r^2 = 0.98.$$
(18)

As is known, the volatility of precursors depends on two parameters—the enthalpy and the entropy of volatilization. However, the variation in the entropy values of sublimation and vaporization at 298.15 K of acetylacetonate complexes was small (Table S6). Taking into account the dimension of this thermodynamic parameter in J mol⁻¹ K⁻¹ and the uncertainties from experiment and processing, it is obvious that the main factor influencing the volatility of the complex was the enthalpy of its vaporization. Therefore, the average value of the entropy of sublimation, 238 ± 8 J mol⁻¹ K⁻¹ at 298.15 K, may successfully be used in assessing the compound's vapor pressure. As for the entropy of vaporization, despite the fact that the correlation of such a small changing parameter was always unstable, there was a tendency for the parameter to increase linearly with molecular weight (Figure 5), providing a possibility to assess the entropic contribution to the vapor pressure:

$$\Delta_1^g S_m^o(M(acac)_3, 298.15 \text{ K}) / J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 0.4 \cdot M + 62.5 \text{ with} r^2 = 0.94.$$
(19)



Figure 5. Dependence of vaporization entropy, $\Delta_1^g S_m^o$, (in J·mol⁻¹ K⁻¹) at 298.15 K of *tris*(acetylacetonato)metal(III) complexes on their molar mass, *M* (in g mol⁻¹).

Undoubtedly, all revealed correlations require additional confirmation by analyzing data on series of isoligand *tris*-complexes with other β -diketones (e.g., dipivaloylmethane),

for which there is also a sufficient amount of thermodynamic data. However, it is quite clear that the central atom affects the thermodynamics of the sublimation and especially vaporization of metal *tris*-acetylacetonates.

4. Conclusions

In this study, we analyzed a massive set of experimental data on the processes of sublimation, vaporization, and fusion of metal(III) (Al, Sc, Cr, Mn, Fe, Co, Ru, Rh, In, Ir) acetylacetonates available in the literature. A huge dissemination of the data was observed. Using the transpiration method and Knudsen effusion method with mass spectrometric registration of the gas phase composition, we performed complementary measurements of saturated vapor pressures over crystalline aluminum(III), chromium(III), and indium(III) acetylacetonates in order to resolve a conflict of literature data.

Thermodynamic data on the enthalpies and entropies of sublimation, vaporization, and fusion were adjusted to the reference temperature and properly evaluated. As a result, many anomalies reported in the literature were resolved, and a set of values for enthalpies and entropies of fundamental importance was obtained. First, they can be recommended for practical use in the precise control of precursor volatilization in MOCVD processes. Secondly, these values can be used for checking the quality of corresponding thermodynamic data of other β -diketonates of the studied metals. Thirdly, the use of these values made it possible for the first time to compare properly the thermodynamic characteristics depending on the molar mass of the complexes. The influence of the central metal atom on the enthalpy of sublimation, as well as the enthalpy and entropy of vaporization, was shown. These correlations, revealed for metal acetylacetonate compounds, can be refined by performing additional thermodynamic experiments and processing the available data on isoligand *tris*-complexes with other β -diketones. Further expansion is under development.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/coatings13081458/s1, Table S1: Saturated vapor pressures of Al(acac)₃, Cr(acac)₃, and In(acac)₃ obtained using the transpiration method: p_i —from the experimental data and $p_{calc.}$ —from the corresponding equation ($p_{ref} = 1$ Pa, standard uncertainty $u(p_i) = 0.05 \cdot p_i$); Table S2: The results of the vapor pressure measurements of the Al(acac)₃ using the Knudsen effusion method with mass spectrometric registration of the gas phase composition: p_i —from the experimental data and $p_{calc.}$ —from the corresponding equation ($p_{ref} = 1$ Pa); Table S3: Compilation of data on molar heat capacities $C_{p,m}^{o}$ and heat capacity differences for *tris*(acetylacetonato)metal(III) complexes at 298.15 K (in J.K⁻¹.mol⁻¹); Table S4: Compilation of available experimental fusion temperatures and standard molar enthalpies of fusion, $\Delta_{cr}^{l}H_{m}^{o}(T_{fus})$, along with, calculated from these data, entropies of fusion, $\Delta_{cr}^{I} S_{m}^{o}(T_{fus})$, for *tris*(acetylacetonato)metal(III) complexes; Table S5: The experimental vapor pressure points for Mn(acac)₃ and Co(acac)₃ obtained using the Knudsen effusion method with mass spectrometric registration of the gas phase composition, which were used for the estimation of volatility in [18] but not published in original literary sources; Table S6: Compilation of enthalpies, $\Delta_{cr1}^g H_m^o$, and entropies, $\Delta_{crl}^{g} S_{m}^{o}$, of phase transitions available for *tris*(acetylacetonato)metal(III) complexes at 298.15 K. References [25,26,38,40-46,51,52,54,63,70-73] are cited in the Supplementary Materials.

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