Article

Metal-Organic Chemical Vapor Deposition Precursors: Diagnostic Check for Volatilization Thermodynamics of Scandium(III) β-Diketonates

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Abstract: Scandium complexes with β-diketonate ligands are valuable precursors for the metal–organic chemical vapor deposition (MOCVD) of scandia based materials, but data on their volatilization thermodynamics crucial to MOCVD technology are in a huge disarray. We have addressed this issue with a diagnostic tool based on the principles of group additivity and structure–property relationships, which had been developed by us specifically for metal–organic objects. For this purpose, a mass of experimental data on the vapor pressures and enthalpies of sublimation, vaporization and fusion available in the literature for scandium(III) β-diketonates has been compiled and analyzed. Additionally, saturated vapor pressures and thermodynamic sublimation characteristics have been obtained for scandium(III) complexes with acetylacetone, hexafluoroacetylacetone, and 3-methyl-2,4-pentanedione by transpiration and thermogravimetric methods. New data have allowed us to arbitrate the conflict of literature data. As a result, a consistent set of enthalpies of the three discussed processes has been obtained for eight scandium complexes. Dispersion interactions and non-additive effects have been shown to be typical for metal *tris*-β-diketonates. They have been taken into account to improve the diagnostic check. It is now possible to quite easily assess the thermodynamics of *tris*-β-diketonate complexes with different metals which are in demand as precursors in gas-phase technology.

Keywords: metal β-diketonate; vapor pressure; enthalpy of vaporization; enthalpy of sublimation; enthalpy of fusion; group additivity; structure–property relationships

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1. Introduction

Chemical vapor deposition is actively involved in science and industry in order to obtain high-quality film materials [1,2]. The process has many varieties, differing in the types of chemical reactions and the conditions for their procedures. However, the application principle is general and is based on the delivery of vapors of a compound containing the necessary elements (precursor) to the object to be coated (substrate), where it is converted into the target material by decomposition, oxidation, or other chemical reactions [3]. The variant in which metal compounds with organic ligands act as precursors is called MOCVD (metal–organic chemical vapor deposition). In classical MOCVD, the required concentration of metal-containing precursor vapors supplied to the reaction zone is determined by the evaporator mode, which is set according to the thermal properties of the compound, mainly, volatility [4]. The quantitative expression for the volatility of MOCVD precursors is their saturated vapor pressures at different temperatures (p-T dependences) and thermodynamic characteristics of the volatilization (sublimation or vaporization) processes allowing precise concentration control [5].

Among the MOCVD precursors, metal β-diketonate complexes are undoubtedly the permanent leaders not only because of their relatively simple synthesis and stability in air, but also due to the structure of the ligand ion ([$R^1C(O)(R')C(O)CR^2$]-), in which multiple variations of substituents (R^1, R^2, R') makes it possible to obtain compounds with the required thermal properties—suitable vapor pressure and melting point. Most often, the vapor pressure data available in the literature for metal β-diketonates are scattered and can vary significantly depending on the method used. Figure 1, left illustrates the vapor pressure temperature dependencies for scandium(III) acetylacetonate, $Sc(acac)_3$, as an example. As a rule, the *p*-*T* data on metal complexes are approximated using linear regression and the thermodynamic characteristics (sublimation/vaporization enthalpies and entropies) are estimated using the Clausius–Clapeyron equation and the least squares method (see Figure 1, center). The thermodynamic characteristics of such processing are attributed to the average temperature of the experimental interval. As a result, the enthalpy of sublimation published in the literature for $Sc(acac)_3$ (Figure 1, right) varies between 49 and 124 kJ mol^{-1}, and the temperatures to which these values are referred to are 360–441 K [6–14]. It is hardly possible to compare these thermodynamic data on sublimation/vaporization and determine which result might be correct. Such a scatter of thermodynamic data is typical of metal β-diketonates for which multiple measurements exist (for example [15,16]). This confuses optimization of the MOCVD process, and the deposition experiments are inevitably conducted under ill-defined and empirically selected conditions.

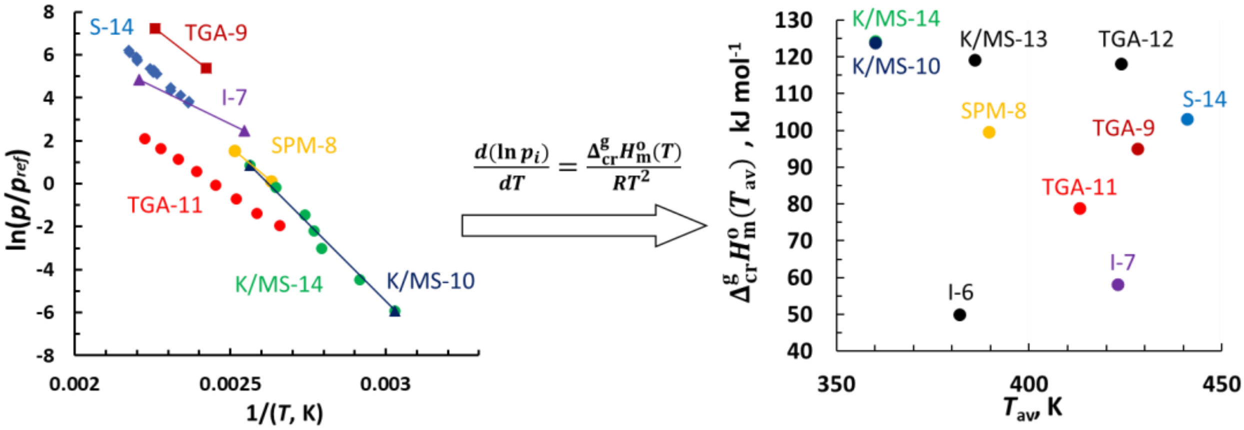
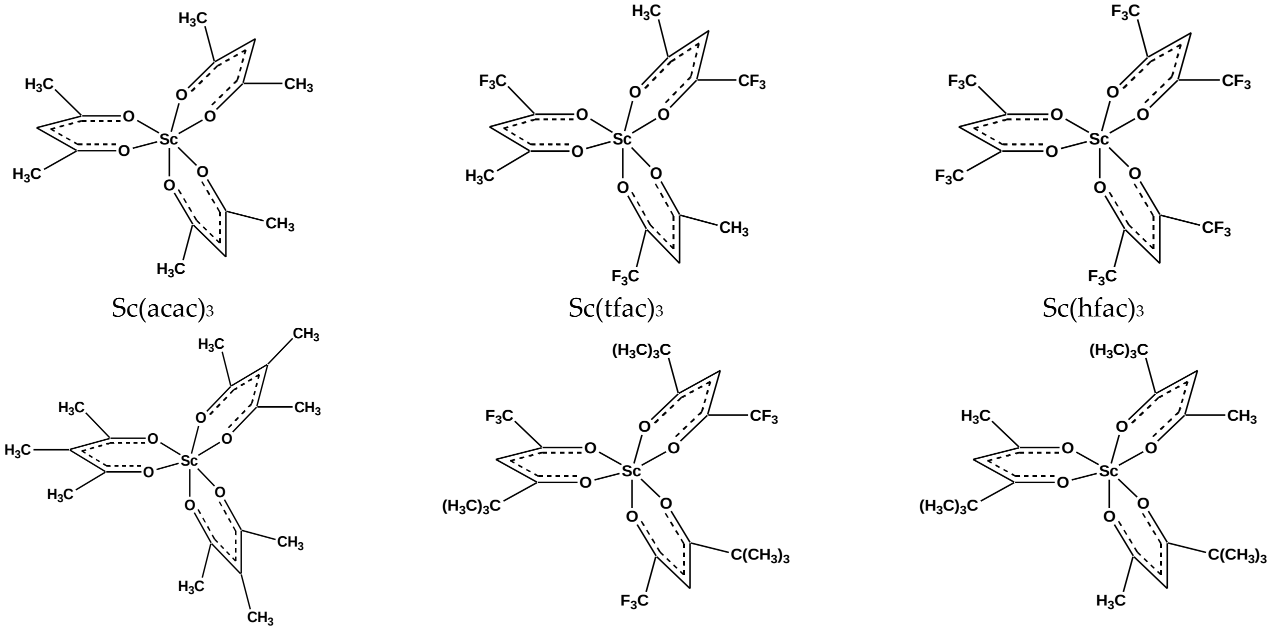


Figure 1. Literature data on vapor pressure temperature dependencies (**left**) and the enthalpy of sublimation, $\Delta_{cr}^{g}H_m^o$ (T_{av}), at the average temperature of the experimental interval, T_{av}, (**right**) estimated by the Clausius–Clapeyron equation (**center**) for $Sc(acac)_3$ obtained by using different methods: I = isotheniscope [6,7]; SPM = spectrophotometry [8]; TGA = thermogravimetric analysis [9,11,12]; K/MS–Knudsen effusion method with mass spectrometric registration of gas phase [10,13,14]; S = static [14], p_{ref} = 1 Pa.

Recently, we have started developing a diagnostic tool to check the consistency of thermodynamic data on metal–organic compounds using a series of iron *tris*-β-diketonates as a touchstone [15]. It is based on the principles of group additivity and structure–property relationships. The group additivity (GA) approach is extensively used in the world of organic compounds to quickly appraise a thermodynamic or thermophysical property (enthalpy of formation, enthalpy of vaporization, heat capacity) of a molecule of interest whose properties have not been measured yet. One of the most popular GA approaches has been developed by Sydney W. Benson [17]. In the GA methods, the molecule of interest is summed completely from well-defined groups. To date, numerous organic group contributions to the vaporization enthalpy have been defined and continue to be evaluated [18], but for metal-containing groups, these values are not available yet. Despite the fact that the GA method is mainly developed for organic substances, single attempts were made to apply it to metal-containing compounds as well. For example, Sevast'yanov et al. [19–21] calculated the enthalpies of vaporization of organometallic compounds of strontium, barium and titanium by the method of group contributions, but due to discrepancies between the experiment and the estimation up to 60 kJ mol^{-1}, these efforts could hardly be designated as successful. The most obvious reason for such failure is an insufficient experimental database, as well as difficulties in a proper definition of structural units required for the parametrization of the GA method. We have adopted the GA methods for the metal complexes to overcome these difficulties and parametrized a system of group contributions to the vaporization enthalpy, as well as to the necessary condensed phase heat capacities related to metal β-diketonates [15,22,23]. As a result, a diagnostic tool has been proposed [15].

This diagnostic tool can be used to thoroughly review the available thermodynamic data, discarding seemingly "sick" ones while tracking down data sets that exhibit certain unusual features and require explanations. For example, it has been discovered that iron complexes with branched substituents in β-diketonate ligands do not obey the additivity rule due to presence of strong dispersion–attraction forces among ligands [24]. However, is this diagnostic tool universal? To confirm or refute the versatility of the diagnostic tool, its application for *tris*-β-diketonates with metals other than iron is essential. This will have two important outcomes. Firstly, it will make it possible to verify the thermodynamic data on the sublimation and vaporization of another set of β-diketonate complexes valuable for MOCVD. Secondly, it will undoubtedly improve and extend our diagnostic tools.

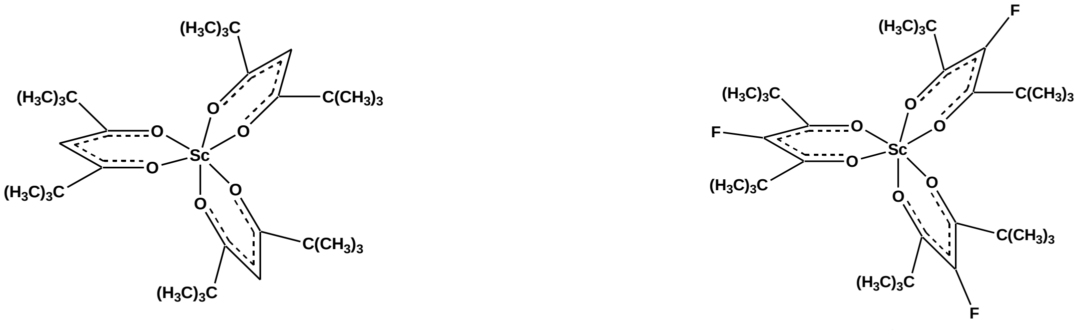
Tris-β-(diketonato)scandium complexes were chosen as research objects (Figure 2). There are several reasons for choosing scandium as the central atom. Firstly, the compounds with this metal are monomers in both condensed and gaseous phases. Secondly, complexes are stable in storage, which facilitates their investigation. Thirdly, these complexes are thermally stable, so it is likely to obtain data on three important phase transitions—sublimation, vaporization, and melting. From a practical point of view, reliable thermodynamic data on *tris*-β-(diketonato)scandium complexes are important for the MOCVD of Sc-containing films, which are in demand in various fields. In particular, it is well known that coatings containing scandium oxide are widely used in optics due to their wide bandwidth and high melting point [11,25–27] and are promising materials for microelectronics [28,29], SOFC [30] etc.



Sc(acac)$_3$ Sc(tfac)$_3$ Sc(hfac)$_3$

Sc(Meacac)$_3$ Sc(ptac)$_3$ Sc(pac)$_3$

Figure 2. *Cont.*



$Sc(thd)_3$

$Sc(tfhd)_3$

Figure 2. *Tris*-β-(diketonato)scandium complexes studied in this work: $Sc(acac)_3$–scandium(III) acetylacetonate, $Sc(tfac)_3$–scandium(III) trifluoroacetylacetonate, $Sc(hfac)_3$–scandium(III) hexafluoroacetylacetonate, $Sc(ptac)_3$–scandium(III) pivaloyltrifluoroacetonate, $Sc(thd)_3$–scandium(III) dipivaloylmethanate, $Sc(pac)_3$–scandium(III) pivaloylacetonate, $Sc(tfhd)_3$–scandium(III) 2,2,6,6–tetramethyl-4-fluoro-3,5-heptanedionate, $Sc(Meacac)_3$–scandium(III) 3-methyl-2,4-pentanedionate.

In this work, we collected data on vapor pressures, sublimation, vaporization and fusion enthalpies available in the literature and evaluated them using our own complementary measurements.

2. Materials and Methods

2.1. Materials

The samples of $Sc(acac)_3$, $Sc(Meacac)_3$, $Sc(hfac)_3$, $Sc(ptac)_3$, and $Sc(thd)_3$ prepared earlier were used for thermodynamic investigation. The synthesis and characterization (CHF-analysis, ^{1}H NMR spectroscopy, X-ray diffraction analysis, melting point etc.) of the complexes were described in detail in our previous articles [14,31,32]. Before the start of the experiment, the compounds were subjected to additional purification by sublimation in a vacuum gradient furnace at a residual pressure of 1.33 Pa and temperatures of 318–453 K. During the transpiration experiment, elemental analyses of complex collected in the trap were also carried out to confirm the purity of the compound and reveal the absence of decomposition.

2.2. Heat Capacity Measurements

The specific isobaric heat capacities of $Sc(ptac)_3$ in the temperature range from 188 K to 321 K, $Sc(thd)_3$ in the temperature range from 187 K to 321 K and $Sc(acac)_3$ in the temperature range from 231 K to 372 K were determined using PerkinElmer DSC Pyris 1 furnished with an intra-cooler. The temperature calibration was done using the melting transition of such metals as indium and zinc according to [33]. The heat flow calibration was implemented using a sapphire disc. Firstly, empty crucibles were used to establish a base line during the blank run. The heat capacity measurement was performed in two steps. Then, the sample of scandium complex was weighted with Sartorius microbalances (m = 6.863 mg) with a standard uncertainty of (5×10^{-6}) g, loaded in the sample crucible and clamped. The sample was first cooled at a rate of 10 K·min^{-1} from room temperature down to 173 K (223 K for $Sc(acac)_3$). At the lowest temperature, the calorimeter was kept at least for 10 min to achieve thermal equilibrium and signal stabilization and then the sample was heated up to 321 K at the rate of 10 K·min^{-1}. During heat capacity study of $Sc(acac)_3$ the whole temperature interval was split in 50 K steps. The sample was heated at 10 K·min^{-1} within these steps. Between steps the studied sample was kept in isothermal conditions for 2 min. Exactly the same temperature program was used for measuring the heat flow for the unloaded crucible. Finally, the base line was subtracted from the sample heat flow for specific heat capacity determination by using the Pyris software (version 7.0.0.0110). The standard relative uncertainty for heat capacity $u_r(C^{o}_{p,m}(cr))$ was 2% and standard uncertainty in temperature is at the level of 0.2 K. The whole set of heat capacity data was averaged with 1 K step. The detailed description of the heat capacity determination can be found in the recent study of heat capacity of lithium *bis*((trifluoromethyl)sulfonyl)amide [34].

2.3. Vapor Pressure Measurements

To measure vapor pressures over the solid Sc(acac)$_3$, Sc(Meacac)$_3$, and Sc(hfac)$_3$, the transpiration method was used (Table S1). There is a complete description of the method and equipment in [16]. The following equations were used to obtain values 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 is the mass and M_i is the molar mass of the compound transported during the experiment, R is the molar gas constant, V is the volume of the gas which is composed of n_{Ar} of gas-carrier and n_i moles of compound; this volume is determined at the ambient temperature T_a and the atmospheric pressure P_a. The total uncertainty in vapor pressure determination was not above ±5%. The temperature was maintained constant within ±0.5 K. The flow rate was kept constant within ±2%. The mass of the transported material was determined by weighing the cold trap $\pm 5 \cdot 10^{-5}$ g.

The transpiration experiments on Sc(acac)$_3$ were carried out independently at the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences, NIIC SB RAS (series 1, Table S1) and at the University of Rostock (series 2, Table S1). The transpiration setup at the University of Rostock operates on the same principles with the same accuracies described above, using nitrogen as carrier gas. Details on the setup can be found elsewhere [35–37].

2.4. Isothermal Thermogravimetric Analysis (TGA)

Isothermal TGA was used for an additional appraisal of the enthalpy of sublimation for Sc(acac)$_3$. The experiments were carried out with the Perkin Elmer Pyris 6 TGA setup. The detailed procedure has already been described elsewhere [38]. Approximately 13 mg of the sample was put in a plain platinum crucible and heated with a ramp of 10 K·min^{-1} under a dry nitrogen purge gas (dew point < 160 K) flow rate of 200 mL·min^{-1} to the maximal temperature of the study. Isothermal TGA curves were measured in the temperature range 375–423 K. Measurements of the mass loss rate dm·dt^{-1} in a typical experiment were performed in a few consequent series with the decreasing temperature steps. The mass loss rate determination in each series was performed in steps consisting of six to eight temperature points. The reproducibility of the results was confirmed by a sequence of several runs. The enthalpy of sublimation was derived from the temperature dependence of the mass loss rate (r = dm·dt^{-1}) multiplied with the square root of absolute temperature ($r\sqrt{T}$) according to the Clausius–Clapeyron equation. The experimental results of the temperature dependence of mass loss in TGA determination of the enthalpy of sublimation for Sc(acac)$_3$ are listed in Table S2.

3. Results and Discussion

3.1. Heat Capacity

The experimental values of the molar isobaric heat capacity, $C^{\text{o}}_{\text{p,m}}(\text{cr})$, of solid Sc(acac)$_3$, Sc(ptac)$_3$, and Sc(thd)$_3$ are given in Figure S1 (the values at the corresponding temperatures are listed in Table S3). The smoothed dependences of molar heat capacities in the crystalline phase over the whole temperature range can be described by the following equations:

$$C^{\text{o}}_{\text{p,m}}(T,\ \text{cr}) = 163.7 + 0.9609 \cdot T - 0.00015 \cdot T^2 \text{ with } r^2 = 0.9997 \text{ for Sc(acac)}_3, \tag{2}$$

$$C^{\text{o}}_{\text{p,m}}(T,\ \text{cr}) = 278.76 + 0.88 \cdot T + 0.0028 \cdot T^2 \text{ with } r^2 = 0.9996 \text{ for Sc(ptac)}_3, \tag{3}$$

$$C^{\text{o}}_{\text{p,m}}(T,\ \text{cr}) = 282.29 + 1.74 \cdot T + 0.0015 \cdot T^2 \text{ with } r^2 = 0.9996 \text{ for Sc(thd)}_3. \tag{4}$$

The root-mean-square deviations of the experimental heat capacity values from the smoothed $C^{o}_{p,m}(T, \mathrm{cr})$ curve did not exceed 1.5% over the studied temperature range. The values of $C^{o}_{p,m}$(298.15, cr) = 434 ± 9 J·K^{-1}·mol^{-1} for Sc(acac)$_3$, $C^{o}_{p,m}$(298.15, cr) = 790 ± 16 J·K^{-1}·mol^{-1} for Sc(ptac)$_3$ and $C^{o}_{p,m}$(298.15, cr) = 934 ± 19 J·K^{-1}·mol^{-1} for Sc(thd)$_3$ necessary for the vapor pressure processing (see Sections 3.2 and 3.3) have been derived using these equations.

The analysis of data sets has not revealed any thermal anomaly in the behaviors of the complexes within considered temperature ranges. Sc(acac)$_3$ has been already investigated by adiabatic calorimetry [39], but over the lower temperature interval of 5 to 305 K. A comparison of the results of DSC and adiabatic calorimetry has revealed that $C^{o}_{p,m}(\mathrm{cr})$-values obtained in our work are slightly higher than the literature in the intersecting temperature range 230–300 K (Figure S1). Although, the deviation doesn't exceed the combined uncertainty of both techniques ~2%, adiabatic calorimetry is well known to be a more reliable and precise method than DSC. This has convinced us to use the literature value of $C^{o}_{p,m}$(298.15, cr) = 425.1 ± 0.9 J·K^{-1}·mol^{-1} for further calculations [39]. Sc(ptac)$_3$ has been investigated for the first time. Sc(thd)$_3$ has been studied by Santos [40], but the measurements seem incorrect (see Table S4 and Figure S2 for details).

3.2. Vapor Pressure

We have performed additional vapor pressure measurements for crystalline Sc(acac)$_3$ and Sc(hfac)$_3$ using the transpiration method in order to resolve a conflict of literature data (see Figure 1 and Section 3.3). The vapor pressures of Sc(Meacac)$_3$ have been measured for the first time. The primary experimental data are given in Table S1. The experimental vapor pressures measured at different temperatures for Sc complexes (Figure 3a) are approximated using the following equation [41]:

$$R \cdot \ln(p/p_{ref}) = \mathrm{a} + \frac{\mathrm{b}}{T} + \Delta^{\mathrm{g}}_{\mathrm{cr,l}}C^{\mathrm{o}}_{\mathrm{p,m}} \cdot \ln(T/T_o), \tag{5}$$

where a and b are adjustable parameters, $\Delta^{\mathrm{g}}_{\mathrm{cr,l}}C^{o}_{\mathrm{p,m}}$ is the difference between isobaric heat capacities of gaseous and crystalline ($C^{o}_{p,m}$(cr)) or liquid ($C^{o}_{p,m}$(l)) phases, p_{ref} = 1 Pa, T_o was chosen to be 298.15 K. The derivation of Equation (5) is presented in detail in [41]. The standard molar sublimation/vaporization enthalpies, $\Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}$, and entropies, $\Delta^{\mathrm{g}}_{\mathrm{cr,l}}S^{\mathrm{o}}_{\mathrm{m}}$, have been calculated via the following equations:

$$\Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}(T) = -\mathrm{b} + \Delta^{\mathrm{g}}_{\mathrm{cr,l}}C^{\mathrm{o}}_{\mathrm{p,m}} \cdot T, \tag{6}$$

$$\Delta^{\mathrm{g}}_{\mathrm{cr,l}}S^{\mathrm{o}}_{\mathrm{m}}(T) = \Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}(T)/T + R \cdot \ln(\frac{p_i}{p^{\mathrm{o}}}) \tag{7}$$

with p^{o} = 0.1 MPa and the adjustable parameter b from Equation (5).

The $\Delta^{\mathrm{g}}_{\mathrm{cr,l}}C^{\mathrm{o}}_{\mathrm{p,m}}$ values used in Equations (5)–(7) have been calculated according to the empirical equations proposed by Chickos and Acree [42]:

$$-\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\mathrm{o}}_{\mathrm{p,m}} = 0.75 + 0.15C^{\mathrm{o}}_{\mathrm{p,m}}(\mathrm{cr}), \tag{8}$$

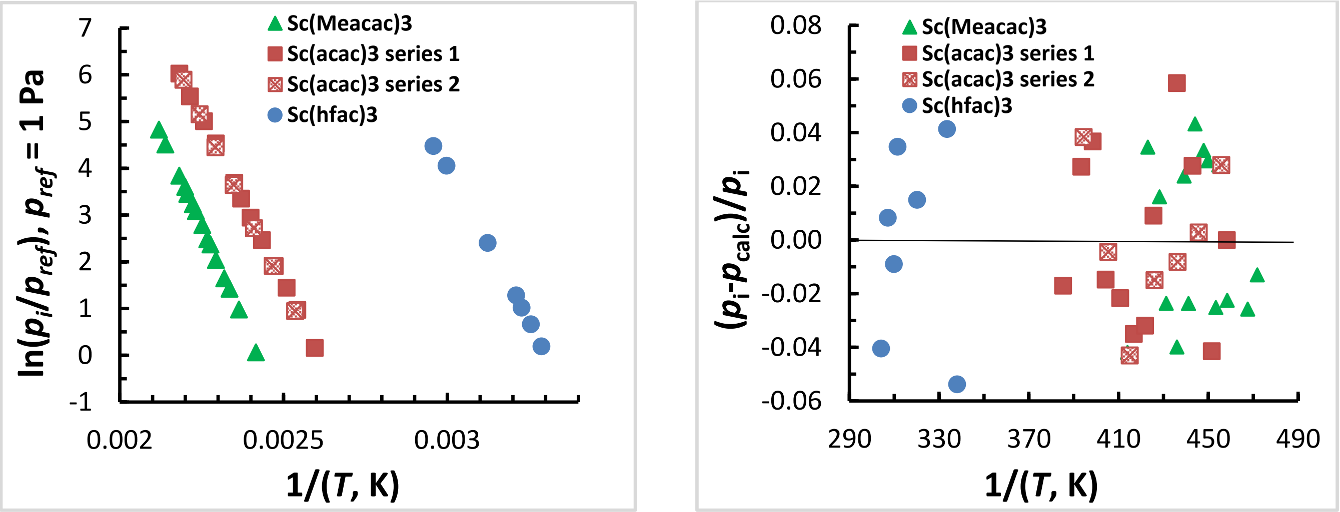
$$-\Delta^{\mathrm{g}}_{\mathrm{l}}C^{\mathrm{o}}_{\mathrm{p,m}} = 10.58 + 0.26 \cdot C^{\mathrm{o}}_{\mathrm{p,m}}(\mathrm{l}). \tag{9}$$

These equations work successfully for iron(II,III) and iridium(I,III) complexes, as shown in our previous works [15,22,23,43]. The experimental $C^{o}_{p,m}$(cr) value of 425.1 ± 0.9 J·K^{-1}·mol^{-1} for Sc(acac)$_3$ available in literature [39] as well as our DSC results for Sc(ptac)$_3$ and Sc(thd)$_3$ have been used to estimate the $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\mathrm{o}}_{\mathrm{p,m}}$ values according to Equation (8). The missing $C^{o}_{p,m}$(cr) values for other complexes (Sc(Meacac)$_3$, Sc(tfac)$_3$, Sc(hfac)$_3$, Sc(pac)$_3$, and Sc(thfd)$_3$) have been estimated using the experimental $C^{o}_{p,m}$(cr) value for Sc(acac)$_3$, the group contributions known for organic compounds [44], and an empirical procedure developed in our recent work [15] for the *tris*(β-diketonato)metal complexes (values in Table S4, given in bold). The calculated $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\mathrm{o}}_{\mathrm{p,m}}$ values are also given in Table S4 and they were used in Equation (5) to approximate the experimental vapor pressures over crystalline compounds measured in this work. The following equations have been obtained from our transpiration results:

$$\ln(p/p_{\mathrm{ref}}) = \frac{395.4}{\mathrm{R}} - \frac{145537.5}{\mathrm{R}T} - \frac{64.5}{\mathrm{R}} \ln \frac{T}{298.15} \text{ for Sc(acac)}_3, \tag{10}$$

$$\ln(p/p_{\mathrm{ref}}) = \frac{429.1}{\mathrm{R}} - \frac{166835.9}{\mathrm{R}T} - \frac{76.9}{\mathrm{R}} \ln \frac{T}{298.15} \text{ for Sc(Meacac)}_3, \tag{11}$$

$$\ln(p/p_{\mathrm{ref}}) = \frac{457.0}{\mathrm{R}} - \frac{137851.7}{\mathrm{R}T} - \frac{92.0}{\mathrm{R}} \ln \frac{T}{298.15} \text{ for Sc(hfac)}_3. \tag{12}$$



(**a**) (**b**)

Figure 3. Dependencies of vapor pressures on reciprocal temperature for Sc(acac)$_3$, Sc(Meacac)$_3$, Sc(hfac)$_3$ obtained by the transpiration method (**a**); deviations of the experimental pressure, p_i, values from those calculated with Equations (10)–(12), p_{calc}, (**b**); p_{ref} = 1 Pa.

Equation (10) represents a joint treatment of two sets of vapor pressure data (see Figure 3a, series 1 and series 2) on Sc(acac)$_3$ obtained independently with using different transpiration setups (see Section 2.3). Figure 3b illustrates the deviations in values of experimental pressures (Figure 3a) and those calculated via the Equations (10)–(12). These deviations do not exceed the standard uncertainties in pressure $u(p)$. Their random character is evidence of the absence of significant systematic errors in our experimental results as well as in their processing. Thus, these Equations (10)–(12) describing the temperature dependences of the sublimation vapor pressures of Sc(acac)$_3$, Sc(Meacac)$_3$, and Sc(hfac)$_3$ can be used for the optimization of the MOCVD and related gas phase deposition process. The results are summarized in Table 1.

We additionally have studied the sample of Sc(acac)$_3$ with the TGA method. Admittedly, the plotting of the mass loss rates $\mathrm{d}m\cdot\mathrm{d}t^{-1}$ against a reciprocal temperature yields only vapor pressure analogue values and not the absolute vapor pressures. However, the slope of the latter correlation provides the $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}})$ value given in Table 1 for comparison with the transpiration results. The mass loss rates $\mathrm{d}m\cdot\mathrm{d}t^{-1}$ for Sc(acac)$_3$ measured at different temperatures are given in Table S2.

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 average temperature (T_{av}) of the experimental temperature range (ΔT) and at the reference temperature 298.15 K [a].

Compound	ΔT (T_{av}), K	n [b]	$\Delta_{cr}^{g}H_{m}^{o}(Tav)$, kJ·mol^{-1}	$\Delta_{cr}^{g}S_{m}^{o}(Tav)$, J·mol^{-1} K^{-1}	$\Delta_{cr}^{g}H_{m}^{o}$(298.15), kJ·mol^{-1} [c]	$\Delta_{cr}^{g}S_{m}^{o}$(298.15), J·K^{-1}·mol^{-1} [c]
Sc(acac)$_3$ series 1	385–458 (421.8)	12	117.6 ± 1.3	212.7 ± 3.5	125.6 ± 1.8	233.4 ± 4.2
Sc(acac)$_3$ series 2	394–456 (425.1)	7	120.7 ± 1.7	217.9 ± 3.0	128.9 ± 2.2	240.7 ± 4.0
Sc(acac)$_3$ TGA	375–423 (403.2)	28	119.2 ± 1.6	-	126.1 ± 2.1	-
Sc(Meacac)$_3$	414–472 (443.0)	15	132.8 ± 1.7	226.1 ± 4.4	144.0 ± 2.8	256.5 ± 6.5
Sc(hfac)$_3$	304–338 (321)	7	108.5 ± 2.1	262.9 ± 7.6	110.6 ± 2.6	269.4 ± 8.5

[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].

3.3. Sublimation/Vaporization Enthalpies of Scandium(III) β-Diketonates and Their Temperature Adjustment to T = 298.15 K

To date, sublimation and vaporization enthalpies are available for seven scandium(III) β-diketonates [6–14,32,40,45–50]; the relevant literature data are compiled for evaluation together with the data obtained in this work (Table 2). Almost all crystal–gas and liquid–gas phase transition enthalpies have been derived from p-T measurements by using different methods also indicated in Table 2. As already mentioned in the introduction, the $\Delta_{cr,l}^{g}H_{m}^{o}(T)$ values found in the literature refer to different temperatures, T, which vary considerably, making any comparison meaningless. The only way to comprehend these values is to adjust the sublimation/vaporization enthalpies to a common temperature, e.g., to the reference temperature T = 298.15 K. This can be done according to Kirchhoff's law using the following equations:

$$\Delta_{cr}^{g}H_{m}^{o}(298.15\ \mathrm{K}) = \Delta_{cr}^{g}H_{m}^{o}(T) + \Delta_{cr}^{g}C_{p,m}^{o}(298.15\ \mathrm{K} - T), \tag{13}$$

$$\Delta_{l}^{g}H_{m}^{o}(298.15\ \mathrm{K}) = \Delta_{l}^{g}H_{m}^{o}(T) + \Delta_{l}^{g}C_{p,m}^{o}\ (298.15\ \mathrm{K} - T). \tag{14}$$

Table 2. Compilation of enthalpies of sublimation/vaporization, $\Delta_{cr,l}^{g}H_{m}^{o}$, for *tris*(β-diketonato)scandium(III) complexes available in the literature at different temperatures T and referred to 298.15 K [a].

Complex (State) CAS	Method [b]	*T*-Range (*T*), [c] K	$\Delta_{cr,l}^{g}H_{m}^{o}(T)$, [d] kJ·mol^{-1}	$\Delta_{cr,l}^{g}H_{m}^{o}$(298.15 K), [e] kJ·mol^{-1}	Ref.
1	2	3	4	5	6
acac (cr) 14284-94-7	I	376–388 (382)	49.8 ± 2.5	(55.2 ± 10)	[6]
	I	393–453 (423)	58.2 ± 0.8	(66.3 ± 25)	[7]
	SPM	380–398 (389)	99.6 ± 0.8	105.5 ± 5.0	[8]
	TGA	413–443 (428)	95	103.4 ± 5.6	[9]
	K/MS	330–390 (360)	123.8 ± 2.1	127.8 ± 1.6	[10]
	TGA	376–450 (413)	79 ± 1	(87.1 ± 2.2)	[11]
	TGA	420–450 (424)	118 ± 4	126.3 ± 6.7	[12]
	K/MS	345–391 (386)	119.2 ± 2.1	124.9 ± 2.2	[13]

Table 2. *Cont.*

Complex (State) CAS	**Method** [b]	***T*-Range (*T*),** [c] **K**	$\Delta^{g}_{cr,l}H^{o}_{m}(T)$, [d] **kJ·mol**$^{-1}$	$\Delta^{g}_{cr,l}H^{o}_{m}$**(298.15 K),** [e] **kJ·mol**$^{-1}$	**Ref.**
	K/MS	330–390 (360)	124.3 ± 4.4	128.3 ± 4.5	[14]
	S	422–460 (441)	103.2 ± 2.7	112.5 ± 5.1	[14]
	T	385–458 (422)	117.6 ± 0.7	125.6 ± 0.9	this work, series 1
	T	394–456 (425)	120.7 ± 0.8	128.9 ± 1.1	this work, series 2
	TGA	403.2	119.2 ± 0.8	126.1 ± 1.1	this work TGA
				126.2 ± 1.0 [f]	
acac (l) 14284-94-7	DSC	445–555 (550)	(169 ± 7)	(201.5 ± 7.5)	[45]
	TGA	460–520 (490)	85 ± 4	109.8 ± 5.3	[12]
	S	463–490 (477)	87.9 ± 3.3	111.7 ± 2.8	[14]
				111.3 ± 5.0 [f]	
	IC			**109.5 ± 2.5**	this work
Meacac (cr) 26758-81-6	T	414–472	132.8 ± 0.9	**144.0 ± 2.8**	this work
Meacac (liq) 26758-81-6	IC-WC			**126.8 ± 5.8**	this work
tfac (cr) 14634-68-5	I	343–366 (355)	28.5 ± 1.3	(30.9 ± 18)	[7]
	T	363–381 (372)	117.6 ± 1.7	**123.0 ± 5.1**	[46]
tfac (liq) 14634-68-5	I	366–413 (390)	53.1 ± 1.0	(67.3 ± 2.9)	[7]
	S	397–457 (427)	82.2 ± 0.8	102.0 ± 1.0	[47]
	T	381–433 (407)	80.8 ± 0.8	97.3 ± 1.2	[46]
	TGA	373–403 (388)	78	91.8 ± 6.8 [g]	[9]
	S	386–464 (425)	82.7 ± 0.3	101.9 ± 1.2	[14]
				100.5 ± 1.3 [f]	
	IC			**98.9 ± 5.5**	this work
hfac (cr) 18990-42-6	I	313–348 (316)	60.2 ± 1.3	(63.5 ± 7.9)	[7]
	TGA	333–363 (348)	55	(59.6 ± 3.5)	[9]
	K/MS	296–319 (316)	113.4 ± 3.8	115.1 ± 3.2	[13]
	S	327–365 (347)	109.8 ± 0.7	111.4 ± 1.9	[14]
	T	304–338 (321)	108.5 ± 1.1	110.6 ± 1.3	this work
				111.3 ± 2.0 [f]	
hfac (l) 18990-42-6	IC			**87.6 ± 2.8**	this work
ptac (liq) 20146-67-2	K/MS	317–354 (329)	105.4 ± 2.1	112.4 ± 3.0 [g]	[13]
	S	382–452 (417)	67.7 ± 0.8	95.2 ± 3.1	[32]
				104.1 ± 4.3 [f]	
thd (cr) 15492-49-6	TGA	413–443 (428)	90	(108.3 ± 8.4) [g]	[9]
	TGA	375–424 (400)	97 ± 1	119.5 ± 4.0	[48]
	TGA	356–414 (385)	98.2 ± 3	(110.4 ± 3.6) [h]	[12]
	S	387–425 (426)	103.5 ± 5.6	121.5 ± 3.1	[49]
				120.7 ± 4.8 [f]	

Table 2. *Cont.*

Complex (State) CAS	**Method** [b]	***T*-Range (*T*),** [c] **K**	$\Delta^{g}_{cr,l}H^{o}_{m}(T)$, [d] **kJ·mol^{-1}**	$\Delta^{g}_{cr,l}H^{o}_{m}$**(298.15 K),** [e] **kJ·mol^{-1}**	**Ref.**
thd (liq) 15492-49-6	S	458–558 (508)	76.1 ± 0.8	(131.2 ± 2.4)	[50]
	DSC	571	80.2 ± 2.3	(151.1 ± 3.3)	[40]
	TGA	434–465 (450)	77 ± 2	119.2 ± 3.1	[48]
	TGA	434–465 (450)	78.7 ± 3	(118.3 ± 6.2) [h]	[12]
	S	426–492 (426)	76.8 ± 5.8	110.2 ± 3.0	[49]
				114.6 ± 4.3 [f]	
	IC			**109.3 ± 6.6**	this work
pac (l) 1431616-60-2	K/MS	336–383 (353)	105.0 ± 4.6	**115.0 ± 5.6** [i]	[13]
tfhd (cr) 1818329-42-8	S	374–421 (423)	95.1 ± 2.1	**111.7 ± 5.1**	[32]
tfhd (liq) 1818329-42-8	S	427–512 (423)	73.5 ± 2.1	**104.4 ± 3.4**	[32]
	IC			**104.4 ± 6.8**	this work

[a] Values in bold are recommended for further thermodynamic calculations. Uncertainty of these sublimation/vaporization enthalpies $U(\Delta^{g}_{cr,l}H^{o}_{m})$ is the expanded uncertainty (0.95 level of confidence, k = 2). [b] Methods: I = isotheniscope; SPM = spectrophotometry; TGA = thermal gravimetric analysis; K/MS–Knudsen effusion method with mass spectrometric registration of gas phase; S = static; T = transpiration (or gas-saturation method); DSC = differential scanning calorimetry; IC, IC-WC = indirect calculations performed according to the equation $\Delta^{g}_{l}H^{o}_{m}$(298.15 K) = $\Delta^{g}_{cr}H^{o}_{m}$(298.15 K) − $\Delta^{l}_{cr}H^{o}_{m}$(298.15 K) with $\Delta^{l}_{cr}H^{o}_{m}$(298.15 K) values from Table 3 available in literature and estimated by involving Walden's constant (see text). [c] Experimental temperature range and/or temperature given in the literature source and which sublimation/vaporization enthalpy is referred to. [d] Values of the sublimation/vaporization enthalpy and uncertainties (if available) are listed as given in the literature source. [e] Uncertainty of each sublimation/vaporization enthalpy $u(\Delta^{g}_{cr,l}H^{o}_{m})$ at 298.15 K is the standard combined uncertainty (at 0.68 level of confidence, k = 1) including uncertainties associated with the experimental vapor pressure or enthalpy measurement conditions and temperature adjustment to T = 298.15 K, as described elsewhere [37]. In case of absence of any experimental details, we assessed the uncertainty based on our experience. [f] Weighted mean value. We used the uncertainty as the weighting factor. Values in parenthesis are excluded from the calculation of the mean. [g] Vapor pressures were studied in the temperature range that encompassed the melting temperature, which lead to a significant systematic error, uncertainty is additionally multiplied by one and a half. [h] Value of sublimation enthalpy is lower than value of vaporization enthalpy obtained within the same work by the same method. [i] The data were attributed to the vaporization process according to our visual measurements of T_{fus} = 332–334 K on a Kofler bench.

Since the required $\Delta^{g}_{cr,l}C^{o}_{p,m}$ values were absent in the past, the first correct comparison of the available sublimation/vaporization enthalpies of the *tris*(β-diketonato)scandium(III) complexes has been performed (see Table 2) using the heat capacity differences given in Table S4. If the primary experimental vapor pressure data are available in the literature [11,14,32,48], we have treated them uniformly by using Equations (5) and (6). In cases, where only the $\Delta^{g}_{cr,l}H^{o}_{m}(T)$ values are reported, we used Equations (13) or (14) to adjust these values to the reference temperature T = 298.15 K. The $\Delta^{g}_{cr,l}H^{o}_{m}$(298.15 K) values are provided by combined uncertainties including uncertainties associated with the experimental vapor pressure measurement conditions and temperature adjustment to T = 298.15 K as described elsewhere [37]. In case of absence of necessary measurement details (mostly, about uncertainties in the vapor pressure measurement), we assessed the uncertainty based on our experience. Such a uniform processing of all data available in the literature and obtained in this work has allowed a thorough analysis and evaluation of the available sublimation/vaporization results.

Despite the seemingly impressive number of vapor pressure and sublimation/vaporization enthalpy measurements published for $Sc(acac)_3$, $Sc(tfac)_3$, $Sc(hfac)_3$, and $Sc(thd)_3$, the scatter of the resulting $\Delta^{g}_{cr,l}H^{o}_{m}$(298.15 K) values for each compound are too large. This may be rationalized by examining the methods utilized for each compound, experimental details, and sample characterization.

Extremely low $\Delta^{\mathrm{g}}_{\mathrm{cr/l}}H^{\mathrm{o}}_{\mathrm{m}}$(298.15 K) values obtained with isoteniscope technique (Table 2, column 2, denoted as I) are the most evident [6,7]. The accuracy of this method and its applicability to the metal β-diketonate measurements has always been questioned due to a reaction of the mercury filling of the zero-gauge with complexes' vapors. This explanation makes it possible to completely disregard the isoteniscope results compiled in Table 2. The TGA method is quite often used to investigate the volatility of the MOCVD precursors [9,11,12,48]. However, the mass loss rate used as a measurable value in this method can be affected by the heating mode, sample size, temperature range, flow rate, etc. [38]. As a consequence, the sublimation/vaporization enthalpies derived from the temperature dependences of the mass loss rate may be occasionally correct, but very often these values are rather misleading. It means that the results of the TGA method should be considered as correct only with additional confirmation by alternative experimental or empirical methods. Some of the TGA data from refs [9,11,12,48] appear to be consistent with other entries in Table 2 and have been included in the averaging. To get sublimation and vaporization enthalpies from kinetic study of $\mathrm{Sc(acac)_3}$ and $\mathrm{Sc(tfac)_3}$ [12], we have added RT contribution [51] to the activation energy, E_a, reported in the reference (T is the temperature at which the kinetic parameter has been referenced). The DSC method used to determine the enthalpies of vaporization of $\mathrm{Sc(acac)_3}$ and $\mathrm{Sc(thd)_3}$) [40,45] also suffers from methodological ambiguities. The DSC curves obtained by heating a sample showed a sharp peak (melting) and a broad peak (attributed by the authors to vaporization). The latter peak was used to estimate the enthalpy of vaporization. However, the enthalpies of vaporization estimated for $\mathrm{Sc(acac)_3}$ and $\mathrm{Sc(thd)_3}$ are significantly higher than their enthalpies of sublimation (see Table 2). This apparent inconsistency is evidence that the second broad DSC peak belongs to vaporization and simultaneous decomposition. Another methodological inconsistency has been found in the studies of Fahlman and Barron [9] and Belova et al. [13] on $\mathrm{Sc(tfac)_3}$, $\mathrm{Sc(ptac)_3}$, and $\mathrm{Sc(thd)_3}$: vapor pressures has been studied in the temperature range encompassing melting. This leads to a significant systematic error and substantially reduces the reliability of the results [9,13]. Without knowledge of the melting point, Belova et al. [13] have erroneously attributed their mass-spectrometric experiments on $\mathrm{Sc(pac)_3}$ to the sublimation process. We have conducted visual measurements on the Kofler bench which have given T_{fus} = 332–334 K for this complex. For this reason, the result of Belova et al. [13] is now correctly assigned to the vaporization process.

A critical analysis of the literature data methods and experimental conditions allowed us to exclude dubious data (they are given in brackets in Table 2), the rest of the $\Delta^{\mathrm{g}}_{\mathrm{cr,l}}H^{\mathrm{o}}_{\mathrm{m}}$(298.15 K) values have been used to calculate the weighted average for each compound using the experimental uncertainties as a weighting factor. These average values (with the expanded uncertainties of a 95% confidence level) are highlighted in bold and are considered by us as reliable and acceptable for further calculations.

3.4. Fusion Enthalpies of Scandium(III) β-Diketonates

Information about fusion is important for several reasons. Firstly, from a technological point of view since the temperature dependencies of vapor pressure over crystalline and liquid compounds are different. This should be taken into account when setting deposition parameters. Secondly, the enthalpy of fusion, $\Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}$, is one of the contributions to the fundamental relation between phase transition enthalpies:

$$\Delta^{\mathrm{g}}_{\mathrm{l}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K}) = \Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K}) - \Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K}). \tag{15}$$

The fusion temperatures and enthalpies, $\Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(T_{\mathrm{fus}})$, available for *tris*(β-diketonato) scandium(III) complexes are given in Table 3. The $\Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(T_{\mathrm{fus}})$ values have been adjusted to 298.15 K with Equation (16) [44]:

$$\{\Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(T_{\mathrm{fus}}/\mathrm{K}) - \Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(298.15\ \mathrm{K})\}/(\mathrm{J{\cdot}mol^{-1}}) = \Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\mathrm{o}}_{\mathrm{p,m}}\ [(T_{\mathrm{fus}}/\mathrm{K}) - 298.15] - \Delta^{\mathrm{g}}_{\mathrm{l}}C^{\mathrm{o}}_{\mathrm{p,m}}\ [(T_{\mathrm{fus}}/\mathrm{K}) - 298.15], \tag{16}$$

where $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\mathrm{o}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\mathrm{o}}$ have been taken from Table S4. Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature are estimated to account for 30 % of the total adjustment [52]. The resulted $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values are listed in Table 3.

Since there are not any data on fusion of Sc(Meacac)$_3$, we have taken advantage of Walden's rule [53]:

$$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})/T_{\mathrm{fus}} = \mathrm{Walden's\ constant}, \tag{17}$$

which is used for a quick appraisal of $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ of the organic molecules with Walden's constant (WC) value of 56.5 J.K^{-1}.mol^{-1}. We have already tested the rule on *tris*-β-diketonates of iron [15] and iridium [16] getting WCs of 69 ± 2 J.K^{-1}.mol^{-1} and 69 ± 10 J.K^{-1}.mol^{-1} for these two sets of compounds, respectively. The very similar Walden's constant = 64 ± 1 J.K^{-1}.mol^{-1} has been derived from experimental fusion data on scandium(III) β-diketonates (Table S5). These WC numbers are somewhat higher than the classical value, which, apparently, is specific for metal–organic complexes. However, such close agreement of Walden´s constants for these three rows of different metal *tris*-β-diketonates makes us confident in their applicability to the $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ estimation. In this study, the value of T_{fus} = 485 ± 1 K has been determined visually using a Kofler bench and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ = 31.0 ± 3.0 kJ/mol has been estimated using the Walden´s constant of 64 ± 1 J.K^{-1}.mol^{-1} and adjusted to T =298.15 K for Sc(Meacac)$_3$ (Table 3).

The $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values enable 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, vaporization enthalpies of Sc(acac)$_3$, Sc(tfac)$_3$, Sc(thd)$_3$, Sc(tfhd)$_3$ have been calculated according to Equation (15) using their sublimation and fusion enthalpies and applied to support results derived from other methods (see Table 2, denoted as IC). Another opportunity of the relation (15) is an ability to fill in the absent information by deriving the enthalpy of phase transition indirectly. Thus, the missing vaporization enthalpies for Sc(Meacac)$_3$ and Sc(hfac)$_3$ (Table 2) have been calculated according to Equation (15) and used for structure–properties correlations as shown below.

Table 3. Compilation of available experimental fusion temperatures and standard molar fusion enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$ (T_{fus}), for *tris*(β-diketonato)scandium(III) complexes [a].

Complex	T_{fus}/K	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$, kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), [b] kJ·mol^{-1}	Ref.
Sc(acac)$_3$	460	28.8 ± 1.0	18.3 ± 3.3	[39]
	461.2 ± 0.3	25.6 ± 0.5	15.1 ± 3.3	[14]
		26.2 ± 0.4 [c]	16.7 ± 2.3 [c]	
Sc(Meacac)$_3$	485 ± 1 [d]	31.0 ± 3.0 [e]	17.2 ± 5.1	WC [e]
Sc(tfac)$_3$	378.7 ± 0.5	30.1 ± 0.8	24.1 ± 2.0	[14]
Sc(hfac)$_3$	369.2 ± 0.4	29.7 ± 0.6	23.7 ± 1.9	[14]
Sc(ptac)$_3$	331.6 ± 0.5	25.2 ± 0.7	21.7 ± 1.3	[32]
Sc(thd)$_3$	425.6 ± 0.5	26.7 ± 0.2	11.4 ± 4.6	[49]
	(454 ± 1)	(32.5 ± 1.0)	(13.8 ± 5.7)	[40]
Sc(tfhd)$_3$	423.0 ± 0.3	21.6 ± 1.3	7.3 ± 4.5	[32]

[a] Uncertainties in this table are expressed as expanded uncertainties at a level of confidence of 0.95 (k = 2). Values in parenthesis were excluded from the consideration as doubtful. [b] The enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$ at T_{fus} were adjusted to 298.15 K (see Equation (16)). Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature are estimated to account for 30 % of the total adjustment [52]. [c] Weighted mean value. We used the experimental uncertainty as the weighting factor. [d] According to visual measurements on a Kofler bench. [e] Calculated by the multiplication of the fusion temperature with Walden's constant (WC) of 64 ± 1 kJ·mol^{-1} (see Table S5) with uncertainty accessed to be ±3 kJ·mol^{-1}.

3.5. Structure-Property Relationships in Scandium(III) β-Diketonates

As a result of a critical analysis of the literature and our own complementary results on scandium(III) complexes with different β-diketonate ligands, a set of enthalpies of sublimation, vaporization (Table 2), and fusion (Table 3) at a reference temperature has been obtained. The extensive discussion on the shortcomings of the experimental methods and the quality of the resulting sublimation and vaporization enthalpies has prompted a search for additional validation of the thermodynamic properties recommended in Tables 2 and 3. For this purpose, we use structure–property correlations between series of structurally similar compounds, metal *tris*-complexes, $M(L)_3$, and corresponding β-diketones, HL. As the most appropriate property for such correlations, we consider the enthalpies of vaporization, $\Delta_l^g H_m^o$(298.15 K), compared in the pairs of molecules of the $M(L)_3$ complex and the HL ligands which the complex consists of.

The correlation of vaporization enthalpies of $Sc(L)_3$ and HL is shown in Figure 4a (the $\Delta_l^g H_m^o$(298.15 K) values used are collected in Table S6 [54–58]). The vaporization enthalpies of scandium complexes with β-diketones having methyl- and trifluoromethyl groups demonstrate a good linear correlation with the corresponding vaporization enthalpies of their ligands (Figure 4a):

$$\Delta_l^g H_m^o(\mathrm{Sc(L)_3},\ 298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = 2.20{\cdot}\Delta_l^g H_m^o(\mathrm{HL},\ 298.15\ \mathrm{K}) + 19.2 \text{ with } r^2 = 0.9953, \tag{18}$$

making us confident in the high quality of the data on $Sc(acac)_3$, $Sc(Meacac)_3$, $Sc(tfac)_3$, and $Sc(hfac)_3$. At the same time, a significant deviation from a straight line is observed for the other four complexes ($Sc(ptac)_3$, $Sc(thd)_3$, $Sc(pac)_3$, $Sc(tfhd)_3$) where the *tert*-butyl substituents are in the ligand. However, such a strong deviation can hardly be associated with the poor-quality experimental data we have selected, and the procedure provided for this selection to be carried out since it tends to be reproducible for *tris*-complexes. To get more insight, we have correlated the vaporization enthalpies, $\Delta_l^g H_m^o$(298.15 K), of *tris*-β-diketonates of iron and iridium with the corresponding β-diketones. We have recently evaluated the $\Delta_l^g H_m^o$(298.15 K) data for these complexes [15,16] and they are listed in Table 4. The same trends observed for the $Sc(L)_3$ have turned out to be also found for the $Fe(L)_3$ (see Figure 4b) and $Ir(L)_3$ (Figure 4c) complexes. The linear correlations between $\Delta_l^g H_m^o$(298.15 K) for $M(acac)_3$, $M(Meacac)_3$, $M(tfac)_3$, and $M(hfac)_3$ (M = Fe or Ir) and their corresponding HL are as follows:

$$\Delta_l^g H_m^o(\mathrm{Fe(L)_3},\ 298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = 3.16{\cdot}\Delta_l^g H_m^o(\mathrm{HL},\ 298.15\ \mathrm{K}) + 19.2 \text{ with } r^2 = 0.9955, \tag{19}$$

$$\Delta_l^g H_m^o(\mathrm{Ir(L)_3},\ 298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = 3.2{\cdot}\Delta_l^g H_m^o(\mathrm{HL},\ 298.15\ \mathrm{K}) + 20.3 \text{ with } r^2 = 0.9936. \tag{20}$$

Table 4. Experimental, $\Delta_l^g H_{m\ \mathrm{exp}}^o$, assessed with GA method, $\Delta_l^g H_{m\ \mathrm{GA}}^o$, vaporization enthalpies of *tris*-β-diketonate complexes $M(L)_3$ (M = Sc, Fe, Ir) at 298.15 K, calculations of the dispersion interactions (Δ), in kJ mol^{-1} [a].

Complex	**Sc**			**Fe**			**Ir**		
	$\Delta_l^g H_{m\ \mathrm{exp}}^o$ [b]	$\Delta_l^g H_{m\ \mathrm{GA}}^o$ [c]	Δ [d]	$\Delta_l^g H_{m\ \mathrm{exp}}^o$ [15]	$\Delta_l^g H_{m\ \mathrm{GA}}^o$ [b]	Δ [d]	$\Delta_l^g H_{m\ \mathrm{exp}}^o$ [16]	$\Delta_l^g H_{m\ \mathrm{GA}}^o$ [b]	Δ [d]
$M(acac)_3$	109.9 ± 2.2 [e]	-	-	110.8 ± 3.3	-	-	115.1 ± 7.4	-	-
$M(tfac)_3$	100.4 ± 1.3 [e]	104.4	−4.0 ± 1.3	100.3 ± 1.9	105.3	−5.0 ± 1.9	97.6 ± 3.2	-	-
$M(hfac)_3$	87.6 ± 2.8	98.8	−11.2 ± 2.8	77.6 ± 1.8	99.7	−22.1 ± 1.8	78.3 ± 2.8	97.2	−18.9 ± 2.8
$M(Meacac)_3$	126.8 ± 5.8	122.2	4.6 ± 5.8	134.8 ± 6.9 [f]	123.1	11.7 ± 6.9	-	-	-
$M(thd)_3$	113.0 ± 3.6 [e]	157.6	−44.6 ± 3.6	121.8 ± 3.1	158.5	−36.7 ± 3.1	114.6 ± 4.2	156.0	−41.4 ± 4.2
$M(ptac)_3$	104.1 ± 4.3	128.2	−24.1 ± 4.3	-	-	-	103.4 ± 3.2	132.1	−28.7 ± 3.2
$M(pac)_3$	115.0 ± 5.6	133.8	−18.8 ± 5.6	-	-	-	-	-	-
$M(tfhd)_3$	104.4 ± 3.0 [e]	159.9	−55.5 ± 3.0	-	-	-	-	-	-

[a] Uncertainties in this table are expressed as expanded uncertainties at a level of confidence of 0.95 (k = 2). [b] From Table 2, column 5, in bold. [c] Calculated by using the GA method (see text). [d] Differences between $\Delta_l^g H_{m\ \mathrm{exp}}^o$ and $\Delta_l^g H_{m\ \mathrm{GA}}^o$. [e] Vaporization enthalpy values are calculated as average weighted value of both figures in bold in Table 2. [f] The $\Delta_l^g H_m^o$(298.15 K) value for $Fe(Meacac)_3$ was re-calculated with involving data on the formation enthalpy in crystal and gas phases (see Table S7) [55,59].

Thus, regardless of the central atom, the vaporization enthalpy values of the compounds with methyl- and trifluoromethyl-groups arrange in a straight line while those for molecules with branched substituents deviate significantly from it (see Figure 4).

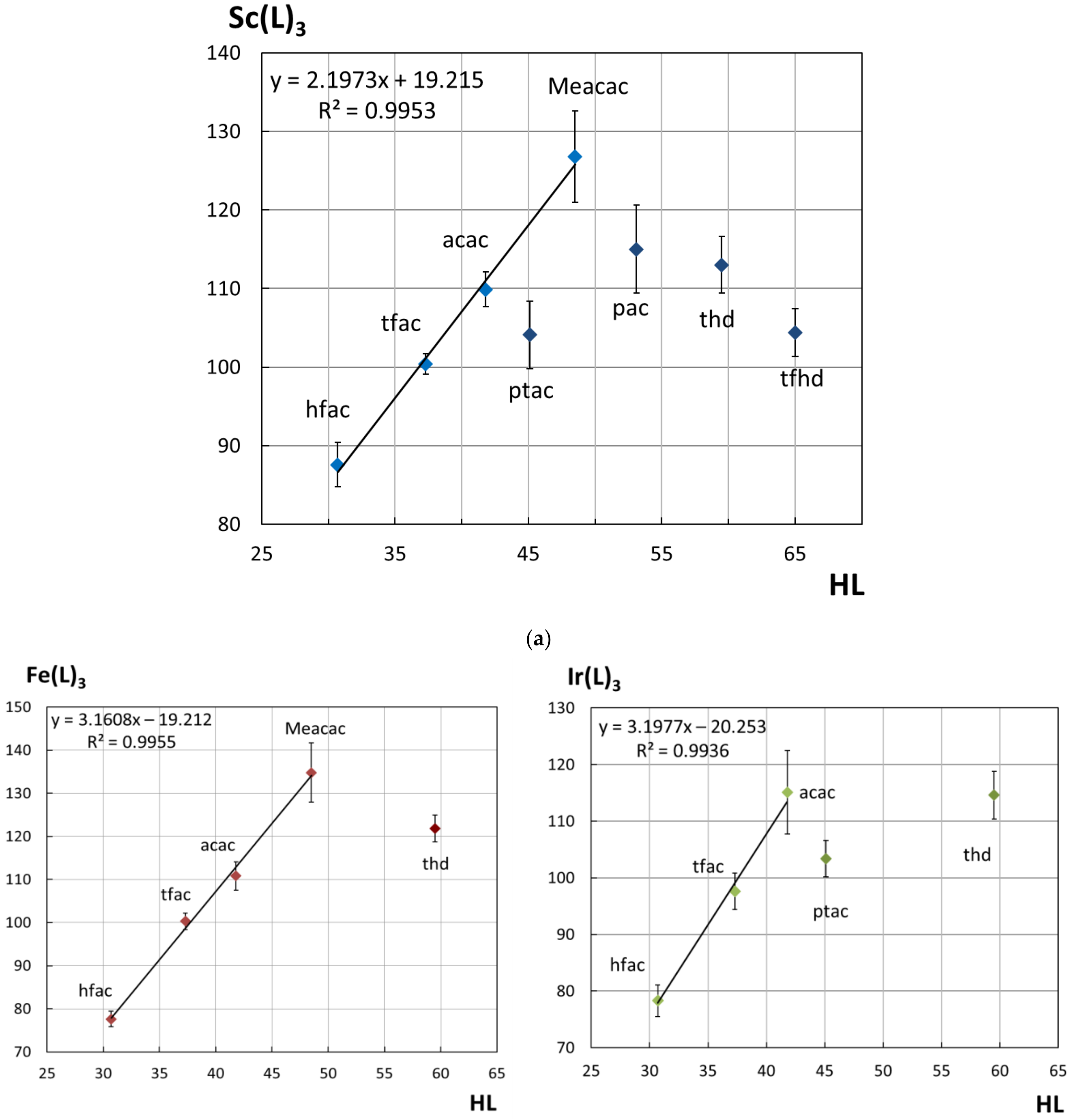
The reason for such deviation is associated with the structure of the complexes in which dispersion interactions are most pronounced, leading to an additional decrease in the enthalpy of vaporization (or sublimation) [24]. Obviously, the phenomenon needs to be taken into account when validating the thermodynamic data on Sc(L)$_3$ or other metal complexes. To this, we have appealed to the centerpiece approach supported by group additivity principles.

The centerpiece approach is essentially the same as we have developed to assess the heat capacity of metal β-diketonates [15]: there is a core molecule with well-studied thermodynamic properties, in which various substituents at different positions are replaced to mimic the structure of the molecule of interest. The crucial advantage of the centerpiece approach in comparison with the conventional Benson´s GA method [17] is a possibility to take into account the numerous “non-additive“ contributions, such as many interactions between nearest and non-nearest neighbor groups, between substituents, and between fragments of the molecule, which are not parameterized at all [60]. This centerpiece group contribution approach has already demonstrated their indispensability for organic compound classes with strong intramolecular interactions inherent, for example, to the aminoethanols [61,62], oxygen-containing group functionalized benzenes [63,64], pyridine and quinoline derivatives [65] etc. In our case, this approach can help us to avoid the necessity of defining the contribution related to the metal coordination center. Thus, combining the Sc(acac)$_3$-increment with a value of 109.9 ± 2.2 kJ mol^{-1} with organic group additivity values (GAVs) (see Table S8) [15,56], we have assessed the vaporization enthalpies, $\Delta_l^g H_m^o$ (298.15 K) $_{GA}$, of Sc complexes (Table 4). The same procedure has been applied to the series of Fe(L)$_3$ and Ir(L)$_3$. Since the data on Ir(acac)$_3$ have a large uncertainty, we have selected Ir(tfac)$_3$ as the core molecule when estimating the enthalpies of vaporization of iridium complexes by the GA method. The obtained values have been compared with the experimental enthalpies of vaporization, $\Delta_l^g H_m^o$ $_{exp}$, evaluated in this work and published by us earlier [15,16] and the differences (Δ) in the vaporization enthalpies which are responsible for contributions from specific interactions have been calculated (Table 4). A comparison of the Δ-values for all three series has revealed that the values for metal complexes with the same β-diketonate ligand are rather close. This means that not only contributions from organic groups, but also from dispersive interactions can be taken into account by mutual correlation of series of compounds with similarly shaped structures. The only condition is a well-defined dataset of *tris*-β-diketonate complexes of at least one metal. In this work, this is vaporization enthalpies of iron β-diketonates (see Equation (19)) [15]. We have correlated enthalpies of vaporization of Sc(L)$_3$ and Fe(L)$_3$ (Figure 5). A good linear relationship between the experimental values of these two series:

$$\Delta_l^g H_m^o(\mathrm{Sc(L)_3},\ 298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = 0.66{\cdot}\Delta_l^g H_m^o(\mathrm{Fe(L)_3},\ 298.15\ \mathrm{K}) + 36.1 \text{ with } r^2 = 0.9835, \quad (21)$$

has pointed to the high quality of data on scandium compounds. Together with data on Fe(L)$_3$, they generate the basis for a linear correlation between rows of metal *tris*-β-diketonates which can be an excellent quality assurance tool of the thermodynamic properties of metal-containing complexes with organic ligands valuable as precursors for MOCVD.

The possibilities of such a fairly quick and simple appraisal for evaluating the thermodynamics of *tris*-β-diketonate complexes with metals other than iron and scandium are demonstrated using iridium *tris*-complexes as an example. The experimental enthalpies of vaporization of iridium(III) *tris*-β-diketonates [16] have been correlated with the corresponding values for scandium (Figure 6a) and iron (Figure 6b) complexes. After confirming satisfactory quality (R^2 = 0.98 for Sc(L)$_3$ and R^2 = 0.93 for Fe(L)$_3$), they can be added to the database of *tris*-complexes for further exploration.



(**a**)

(**b**) (**c**)

Figure 4. Dependencies of vaporization enthalpies at 298.15 K, $\Delta_l^g H_m^o(298.15)$, of *tris*(β-diketonato)scandium(III) Sc(L)$_3$ (**a**), iron(III) Fe(L)$_3$ [15] (**b**), and iridium(III) Ir(L)$_3$ [16] (**c**) complexes vs. vaporization enthalpies at 298.15 K, $\Delta_l^g H_m^o(298.15)$, of corresponding ligand molecules, HL.

Using three series of compounds (Fe(L)$_3$, Sc(L)$_3$, and Ir(L)$_3$), we have tried to estimate the specific interactions occurring in β-diketonate complexes quantitatively. For this, we have averaged differences (Δ) in the enthalpies of vaporization ($\Delta_l^g H_m^o(298.15\text{ K})_{\text{GA}}$ and $\Delta_l^g H_{m\ \text{exp}}^o$ from Table 4, thus assessing the estimates responsible for dispersion interactions, $\Delta H(H\rightarrow R)_{\text{disp}}$ (Table S9). Now, having a precisely determined enthalpy of vaporization of the core molecule and combining its value with the GAVs for organic groups (Table S8) and $\Delta H(H\rightarrow R)_{\text{disp}}$ estimates responsible for dispersion interactions (Table S9), it is possible to assess roughly the vaporization enthalpy of metal *tris*-β-diketonate complexes, which are relevant for practical applications, when experimental thermodynamic data are lacking. The assessed enthalpy of vaporization together with enthalpy of fusion estimated with Walden's constant (see Section 3.4) can be used to calculate the enthalpy of sublimation for optimization of MOCVD conditions.

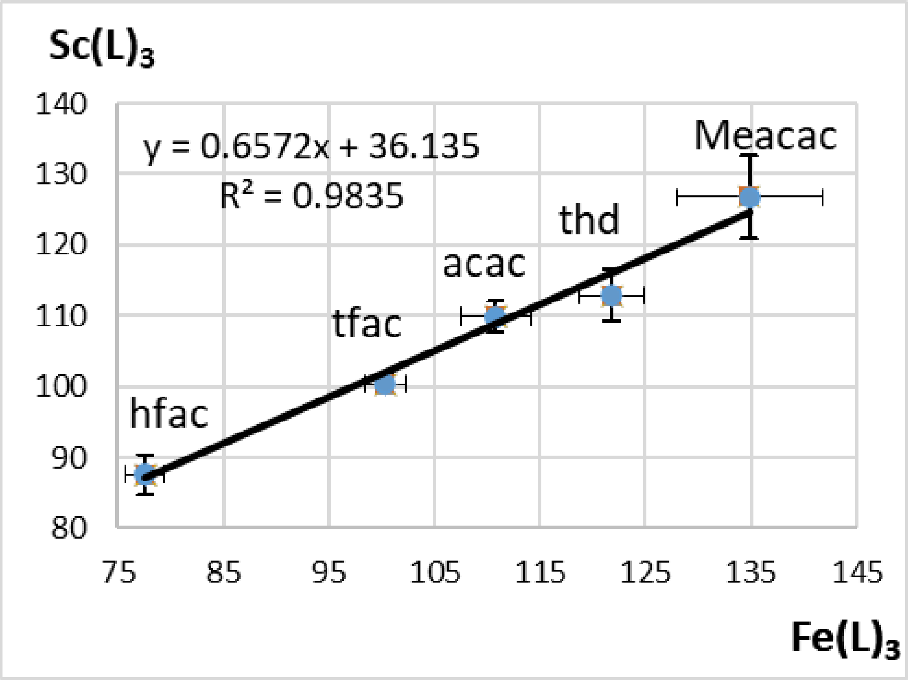
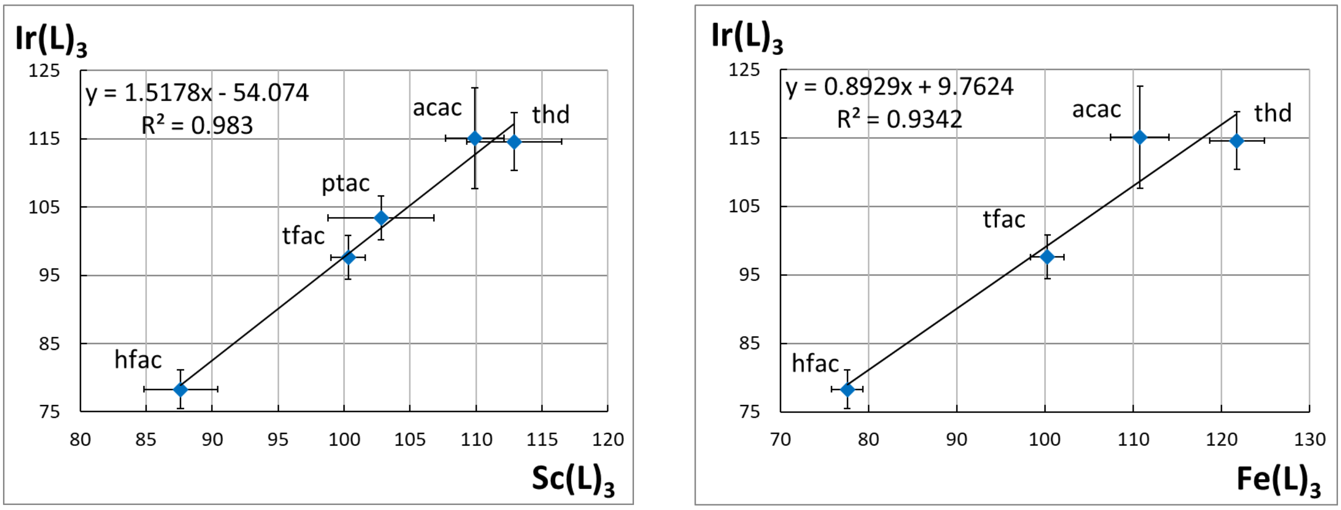


Figure 5. Dependence of vaporization enthalpies at 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15)$, of *tris*(β-diketonato)scandium(III) complexes Sc(L)$_3$ on vaporization enthalpies at 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15)$, of *tris*(β-diketonato)iron(III) complexes Fe(L)$_3$.



(**a**) (**b**)

Figure 6. Dependence of vaporization enthalpies at 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15)$ of *tris*(β-diketonato)iridium(III) complexes Ir(L)$_3$ on vaporization enthalpies at 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15)$ of *tris*(β-diketonato)scandium(III) Sc(L)$_3$ (**a**) and iron(III) complexes Fe(L)$_3$ (**b**).

4. Conclusions

In this work, we have analyzed a mas of experimental data on processes of sublimation, vaporization and fusion of scandium(III) β-diketonates available in the literature. A huge dissemination of the data has been observed. Using TGA and transpiration methods, we performed complementary measurements of saturated vapor pressures over crystalline scandium(III) acetylacetonate, scandium(III) hexafluoroacetylacetonate, and scandium(III) 3-methyl-2,4-pentanedionate and sublimation enthalpy in order to resolve a conflict in the literature data. The equations describing the vapor pressure temperature dependencies have been obtained for these three compounds and now can be used in the MOCVD experiments to calculate precisely vapor pressures of the precursors over wide temperature ranges. The study of scandium(III) 3-methyl-2,4-pentanedionate has been carried out for the first time. Applying our diagnostic tool, we also arbitrated and verified the whole array of data on scandium(III) β-diketonates discarding "sick" ones and isolating the data that can be trusted and that can be used to optimize settling conditions in MOCVD. As a result of diagnostics, a consistent set of values of enthalpy for sublimation, vaporization and fusion processes for a series of eight scandium(III) β-diketonates has been obtained.

Thanks to the as-obtained reliable data on scandium complexes, our diagnostic tool for assessment of the thermodynamic properties of metal-containing complexes with organic ligands has been upgraded and amplified. First of all, dispersion interactions and non-additive effects have been proved and seem to be typical for metal *tris*-β-diketonate. The estimates responsible for dispersion interactions have been assessed. Secondly, two verified sets of data on vaporization enthalpy—new ones for scandium(III) β-diketonates and those evaluated by us earlier for iron(III) β-diketonates—have been used to establish a linear structure–property correlation between series of metal *tris*-β-diketonates. The general transferability of the contributions (from both the ligand organic groups and specific interactions) to the enthalpy of vaporization from one set of metal β-diketonates to the other has been established.

In this context, our diagnostic tool could now serve not only for checking the available experimental data, but also for assessing at least the level of the vaporization enthalpy for the metal *tris*-β-diketonate involved in the experimental study. Moreover, by combining it with the enthalpy of fusion estimated with Walden's constant as we have proposed in this work, the enthalpy of sublimation can also be calculated. Taking into account that the vigorously developing MOCVD technology has been constantly requiring new precursors with specifically defined thermal properties, the algorithm seems to be promising for a fairly simple appraisal of the thermodynamics of metal complexes of an arbitrary structure. This algorithm proposed for the first time for metal-containing compounds could be refined by performing additional thermodynamic experiments on scandium complexes (including newly obtained ones) and processing the available data on *tris*-complexes of other metals. The future expansion of this work is underway.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13030535/s1, Figure S1: Experimental molar heat capacity vs. temperature for crystalline Sc(acac)$_3$ (molar mass M = 342.28 g·mol^{-1}, red circles), Sc(ptac)$_3$ (molar mass M = 630.43 g·mol^{-1}, light blue circles) and Sc(thd)$_3$ (molar mass M = 594.76 g·mol^{-1}, blue circles) obtained by using PerkinElmer DSC Pyris 1 over the ranges of T = (231 K to 372) K, T = (188 K to 321) K, and (187 K to 321) K, respectively; the literature data on adiabatic calorimetry over the range of T = (21 K to 300) on Sc(acac)$_3$ are plotted for comparison (white circles) [1]; Figure S2: Physical principles of changing heat capacity of a compound in crystal, liquid, and gas phases; Table S1: Saturated vapor pressures of Sc(acac)$_3$, Sc(Meacac)$_3$, and Sc(hfac)$_3$ obtained by the transpiration method: p_i obtained from the experimental data and p_{calc}. obtained from the corresponding equation (p_{ref} = 1 Pa); Table S2: The results of the temperature dependence of mass loss in TGA determination of the enthalpy of sublimation for Sc(acac)$_3$; Table S3: Experimental values of heat capacities, $C^{\mathrm{o}}_{\mathrm{p,m}}$(cr), (in J.K^{-1}.mol^{-1}) for crystalline Sc(acac)$_3$ (molar mass M = 342.28 g·mol^{-1}), Sc(ptac)$_3$ (molar mass M = 630.43 g·mol^{-1}), and Sc(thd)$_3$ (molar mass M = 594.76 g·mol^{-1}) at atmospheric pressure obtained by using PerkinElmer DSC Pyris 1; Table S4: Compilation of data on molar heat capacities $C^{\mathrm{o}}_{\mathrm{p,m}}$ and heat capacity differences for tris(β-diketonato)scandium(III) complexes at 298.15 K (in J.K^{-1}.mol^{-1}); Table S5: Assessment of the *Walden's Constant* for calculation of fusion enthalpies $\Delta^{\mathrm{l}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(T_{\mathrm{fus}})$ of *tris*(β-diketonato)scandium(III) complexes; Table S6: Vaporization enthalpies of ligand molecules and *tris*(β-diketonato)scandium(III) complexes at 298.15 K taken for structure–property correlation (in kJ·mol^{-1}); Table S7: Vaporization enthalpy of Fe(Meacac)$_3$ taken for structure–property correlation at 298.15 K (in kJ·mol^{-1}); Table S8: Group-additivity values (GAVs) for calculations of vaporization enthalpy of metal β-diketonates at 298.15 K (in kJ·mol^{-1}); Table S9: Estimates for dispersion interactions $\Delta H(H{\rightarrow}R)_{\mathrm{disp}}$ (in kJ·mol^{-1}). References [15,22,39,40,42,44,54–59] are cited in the Supplementary Materials.

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Sample Availability: Samples of the compounds are available from the authors.

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