

Thermal properties of volatile ruthenium(III) complexes

Kseniya V. Zherikova · Ludmila N. Zelenina ·
Natalia B. Morozova · Tamara P. Chusova

Received: 8 April 2011 / Accepted: 18 October 2011 / Published online: 16 November 2011
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract Complexes of ruthenium(III) with the following beta-diketone derivatives: 2,4-pentanedione ($\text{Ru}(\text{acac})_3$), 1,1,1,6,6,6-hexafluoro-2,4-pentanedione ($\text{Ru}(\text{hfac})_3$), and 2-methoxy-2,6-dimethyl-3,5-heptanedione ($\text{Ru}(\text{mdhd})_3$) were synthesized, purified, and identified by chemical analysis and melting points. By difference-scanning calorimetry (DSC) in vacuum the thermodynamic characteristics of melting processes were defined. Using the static method with quartz membrane zero-manometer, the temperature dependencies of saturated and unsaturated vapor pressure were obtained for $\text{Ru}(\text{hfac})_3$. The standard thermodynamic characteristics of vaporization processes enthalpy ΔH_{T^*} and entropy $\Delta S_{T^*}^\circ$ were determined.

Keywords Ruthenium(III) · β -Diketonates derivatives · DSC · Vapor pressure · Thermodynamic characteristics

Introduction

Metal and oxide films on the basis of ruthenium are of great importance in different spheres of electronics, radio, and electrical engineering, chemical industry as well as jeweler's art. Ruthenium-containing coatings deposited on different materials change significantly the properties and quality of products, raise their chemical stability and mechanical resistance, steady them corrosion-proof, improve sharply electrical properties etc [1]. Due to properties mentioned above the films are intensively used for the production of electrodes and

corrosion-proof diffusion barrier layers for further deposition of tantalum oxide (Ta_2O_5) and barium strontium titanate [(Ba, Sr) TiO_3] in gigabit-scale random access memories [2–5], resistor pastes in thin- and thick-film hybrid microcircuits [6], high capacity computer hard disk drives [7, 8], electrochemical supercapacitors of electricity [9].

For fabricating Ru-containing films and coatings with assigned structure and functional properties the method of metal–organic chemical vapor deposition (MOCVD) is widely used [1, 10, 11]. Key role in MOCVD processes plays both using different precursors and variation of deposition parameters (work temperatures, pressures etc.) that allow to obtain various metal, oxide, and composite layers. Besides for choice of deposition conditions the information about thermal properties of used precursor is necessary first of all. For this purpose the series of investigations are carried out by complex of methods (thermogravimetry, calorimetry, tensiometric methods, in situ high-temperature mass spectrometry etc.) [12].

Among numerous classes (carbonyls, cyclopentadienyl derivatives, allyl derivatives, heteroligand complexes, etc. [1, 10, 11, 13]), one of the most attractive ones of the volatile ruthenium compounds is the beta-diketonate derivatives because of their high volatility and thermal stability [14–17]. Investigation of vaporization of these compounds, determination of the fundamental quantitative thermodynamic data is the relevant problems for further efficient development of technological deposition processes. To this moment, vapor pressure data obtained for vaporization of the row of ruthenium beta-diketonates: 2,4-pentanedione ($\text{Ru}(\text{acac})_3$), 1,1,1-trifluoro-2,4-pentanedione ($\text{Ru}(\text{tfac})_3$), 2,2,6,6-tetramethyl-3,5-heptanedione ($\text{Ru}(\text{thd})_3$), 2,2,6,6-tetramethyl-4-fluoro-3,5-heptanedione ($\text{Ru}(\text{tfhd})_3$), and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione ($\text{Ru}(\text{ptac})_3$)—were published by us [4, 17–19].

K. V. Zherikova (✉) · L. N. Zelenina ·
N. B. Morozova · T. P. Chusova
Nikolaev Institute of Inorganic Chemistry SB RAS,
Lavrentiev av., 3, 630090 Novosibirsk, Russia
e-mail: ksenia@niic.nsc.ru

To continue the systematic investigation we studied the vaporization processes for ruthenium(III) 1,1,1,6,6,6-hexafluoro-2,4-pentanedionate ($\text{Ru}(\text{hfac})_3$) and the thermal behavior of $\text{Ru}(\text{hfac})_3$, $\text{Ru}(\text{acac})_3$, and ruthenium(III) 2-methoxy-2,6-dimethyl-3,5-heptanedionate ($\text{Ru}(\text{mdhd})_3$) in condensed phase.

Experimental

Synthesis and identification of Ru compounds

The synthesis of ruthenium(III) beta-diketonate derivatives was carried out according to a general method for obtaining beta-diketonates of platinum metals *via* the aqua complexes [20]. The compounds were purified by zone sublimation in a vacuum gradient furnace at $p = 7$ Pa and temperature range 323–453 K depending on nature of ligand. The complexes were identified *via* methods of chemical analysis for C, H, and F (Calculated/Found, %: C 24.94/24.74, H 0.42/0.38, F 47.35/47.55) and the melting points. All compounds are red crystalline substances.

Calorimetric investigation

Calorimetric measurements were performed using a Setaram DSC 111 (heating rate 0.5–1.0 K min^{-1} ; sample weight 13–25 mg) for definition of thermodynamic characteristics of melting process (m.p., $\Delta_{\text{melt}}H^\circ_{\text{m.p.}}$). The errors in the heat effect measurements estimated from calibration experiments ($\text{C}_6\text{H}_5\text{COOH}$, In) were less than 1.5 per cent. Four–five calorimetric experiments were performed for each investigated compounds. The samples exhibited only one phase transition (melting) over the temperature range studied (300–473 K). During the measurements the investigated substance was contained in evacuated glass ampoule.

Vapor pressure

The vapor pressure of $\text{Ru}(\text{hfac})_3$ was measured by the static method using a quartz membrane zero-manometer [21]. The error of the pressure measurement was 40 Pa. The error of the temperature measurement estimated from calibration against mercury, naphthalene, and argon did not exceed 0.5 K. The scheme and the main characteristics of the experimental unit are described in detail in [22]. The investigated compound was loaded into the membrane zero-manometer and after evacuation it was sealed. Pressure measurements were recorded after reaching the equilibrium at a given temperature. The pressures measured from low to high temperatures and backwards were identical at the same temperature. This procedure guaranteed

the achievement of equilibrium. The time of equilibrium establishment was 15–20 min. Two series of measurements were performed with sample weights 0.1664 and 0.0245 g (the volume of membrane vessel was 18.33 mL). Experimental data are shown in Fig. 1. Data analysis on saturated vapor pressure shows that under the examined conditions the pressure does not depend on initial concentrations, thus, at vaporization processes of these compounds the equilibria are monovariant.

Results and discussion

DSC investigation of Ru compounds

By differential-scanning calorimetry (DSC) melting points and the thermodynamic characteristics of melting were determined for $\text{Ru}(\text{acac})_3$, $\text{Ru}(\text{hfac})_3$, and $\text{Ru}(\text{mdhd})_3$. Results are listed in Table 1. The data calculated from static method experiments for $\text{Ru}(\text{hfac})_3$ are also listed in Table 1. The uncertainties quoted in this study refer to a 95 per cent confidence limit. The value of melting point for $\text{Ru}(\text{acac})_3$ conform to ones presented in [16] by using the same method (DSC)—505 K.

Vapor pressure

The measurements of saturated and unsaturated vapor pressure were carried out for $\text{Ru}(\text{hfac})_3$ by static method in the temperature interval 326–494 K.

The unsaturated vapor pressure was measured in series 2 of our experiments (Fig. 1) within temperature range 419–494 K. The average molecular weight of gas was

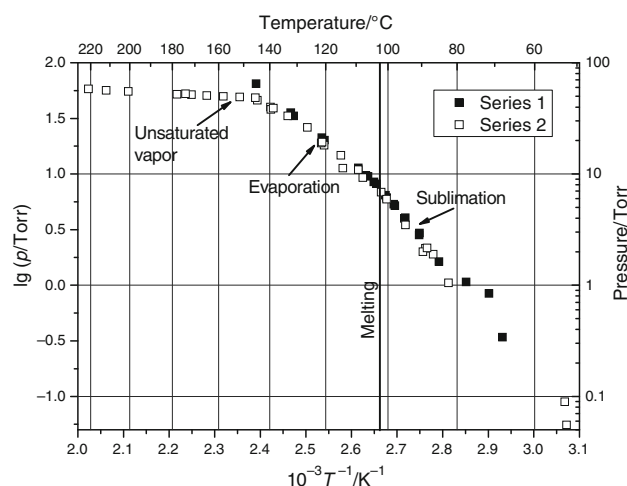


Fig. 1 Experimental data for two series of measurements with sample weights 0.1664 (series 1) and 0.0245 (series 2) g

Table 1 Melting points (m.p.), enthalpies ($\Delta_{\text{melt}}H_{\text{m.p.}}^{\circ}$), and entropy ($\Delta_{\text{melt}}S_{\text{m.p.}}^{\circ}$) for Ru(acac)₃, Ru(hfac)₃, and Ru(mdhd)₃

Compound	Method		Static method			
	Calorimetry					
	m.p./K	$\Delta_{\text{melt}}H_{\text{m.p.}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta_{\text{melt}}S_{\text{m.p.}}^{\circ}/\text{kJ mol}^{-1} \text{K}^{-1}$	m.p./K	$\Delta_{\text{melt}}H_{\text{m.p.}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta_{\text{melt}}S_{\text{m.p.}}^{\circ}/\text{kJ mol}^{-1} \text{K}^{-1}$
Ru(acac) ₃	503.9 ± 1.0	25.0 ± 0.6	49.6 ± 1.2			
Ru(hfac) ₃	374.1 ± 0.5	30.7 ± 0.4	82.1 ± 0.6	375 ± 2	29 ± 1.5	78 ± 3.5
Ru(mdhd) ₃	332.4 ± 0.5	47.5 ± 0.4	93.7 ± 0.6			

Table 2 Temperature dependencies of the saturated vapor pressure, enthalpy (ΔH_{T^*}), and entropy ($\Delta S_{T^*}^{\circ}$) of sublimation and evaporation for Ru(hfac)₃, normalized to the mean temperature (T^*) in the examined interval (ΔT)

Process	$\Delta T/\text{K}$	n^a	$\ln(p/p_0^b) \pm 2\sigma = A - B/T$ $f(T)$ σ^2	$\Delta H_{T^*}/\text{kJ mol}^{-1}$	$\Delta S_{T^*}^{\circ}/\text{J mol}^{-1} \text{K}^{-1}$
Subl.	341–374	21	26.38 – 11665.1/T 26.81 10 ⁴ /T ² – 1461.3/T + 1.992	97.0 ± 1.0	219.3 ± 2.8
Evap.	377–418	17	17.00 – 8145.2/T 10.96 10 ⁴ /T ² – 556.33/T + 0.707	67.7 ± 0.7	141.3 ± 1.7

^a n number of points

^b $p_0 = 1 \text{ atm} = 760 \text{ Torr} = 101.325 \text{ kPa}$

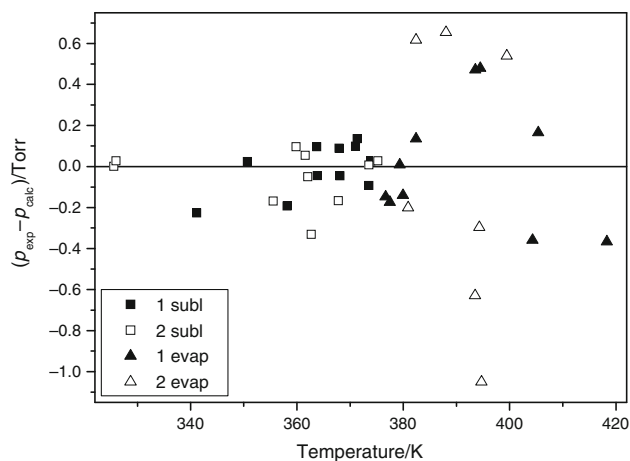
calculated from these experimental data using ideal gas law:

$$M_{\text{calc}} = \frac{m \cdot T \cdot R}{p \cdot V}, \quad (1)$$

where m is sample weight, T is experimental temperature, R is the gas constant, p is pressure measured, V is volume of the membrane zero-manometer.

Values obtained ($M_{\text{calc}} = 720 \pm 2 \text{ g mol}^{-1}$) were close to the molecular weight of monomer ($M = 722 \text{ g mol}^{-1}$), that was evidence of the absence of other molecular forms in the gas phase to within the accuracy specified above. Calculated molecular weight doesn't practically change up to 473 K. At higher temperatures it decreases owing to decomposition of Ru(hfac)₃.

Experimental data processing was performed by the method of least squares using the objective function described in [22]. The sought values were the enthalpies and entropies of vaporization at the mean temperature, because of lack the heat capacity data on the substances under consideration. The temperature dependences of pressure for sublimation and evaporation are summarized in Table 2. The deviations of the experimental pressures (p_{exp}) from those calculated (p_{calc}) by the equations given in Table 2 don't exceed maximum permissible values calculated from errors of temperature and pressure measurements and have a random character (see Fig. 2). It is evidence of the absence of significant systematic errors in our results. The thermodynamic characteristics of sublimation and evaporation are also presented in Table 2.

**Fig. 2** Difference between the experimental pressures (p_{exp}) and calculated ones (p_{calc}) for vaporization processes of Ru(hfac)₃ in two series of experiments

Based on the data for evaporation and sublimation processes for Ru(hfac)₃, the thermodynamic characteristics of melting for the examined compound were calculated (see Table 1). The results of calculation are in good agreement with calorimetric investigation.

Earlier the standard characteristics for sublimation of Ru(hfac)₃ have been presented in [23]: $\Delta H_{T^*} = 114.5 \pm 1.0 \text{ kJ mol}^{-1}$; $\Delta S_{T^*}^{\circ} = 271 \pm 6 \text{ J mol}^{-1} \text{K}^{-1}$, that have been obtained by Knudsen mass-loss effusion technique. The difference between data described in literature [23] and obtained by us can be explained by too narrow

Table 3 Temperature dependences of the saturated vapor pressure, enthalpy (ΔH_{T^*}), and entropy ($\Delta S^{\circ}_{T^*}$) of Ru(acac)₃ sublimation, normalized to the mean temperature (T^*) in the examined interval (ΔT)

Method	n^a	$\Delta T/K$	$\ln(p/p_0^b) = A - B/T$		$\Delta H_{T^*}/\text{kJ mol}^{-1}$	$\Delta S^{\circ}_{T^*}/\text{J mol}^{-1} \text{K}^{-1}$	Ref.
			A	B			
K	4	377–434	25.26	15528	129.1 ± 2.0	210 ± 5	18
F	7	423–493	25.56	15228	127.2 ± 1.0	212.5 ± 2.0	17
K + F	11	377–493	26.08	15537	129.2 ± 1.1	216.8 ± 2.5	This work

^a n number of points^b $p_0 = 1 \text{ atm} = 760 \text{ Torr} = 101.325 \text{ kPa}$

temperature interval within which the measurements of vapor pressure were carried out [23] (299.15–313.14 K). This can be a reason of mistake appearance during data treatment [23]. Taking into account our wide temperature interval (341–418 K) and also a good agreement between thermodynamic characteristics of melting obtained by static method and DSC our data should be preferred.

Previously, we published the data on the temperature dependence of vapor pressure for series of ruthenium(III) beta-diketonates measured by using the effusion Knudsen method with mass spectrometric registration of gas phase composition (K) and the flow method (F): Ru(acac)₃, measured using method K and F [17, 18], *trans*-Ru(tfac)₃, measured using method F [19], Ru(ptac)₃, Ru(tfhd)₃, Ru(thd)₃, measured using method K [18]. Now it is possible to obtain the thermodynamic characteristics of Ru(acac)₃ evaporation by combining the data obtaining by K [18] and F [17] methods with data on Ru(acac)₃ melting. First, we performed the joint treatment of experimental data on sublimation process. The results of this treatment and our previous investigations are presented in Table 3.

Data obtained by joint treatment were used to calculate the enthalpies and entropies and the temperature dependences of pressure for Ru(acac)₃ evaporation process:

$$\Delta_{\text{evap}} H = 104.2 \pm 2.0 \text{ kJ mol}^{-1}, \Delta_{\text{evap}} S^{\circ} = 167.2 \pm 3.0 \text{ J mol}^{-1} \text{K}^{-1} \quad (2)$$

$$\ln(p/p_0) = 20.11 - 12533/T \quad (3)$$

All data (published earlier [17–19], calculated from literature and our data on sublimation and melting processes and measured during this study) on $p - T$ are shown in Fig. 3. As can see from this figure the fluorinated complexes are more volatile than the non-fluorinated ones. In addition, the higher the fluorination (i.e., hfac vs. tfac vs. acac), the greater the volatility of compounds is. This trend is in agreement with the qualitative volatility rows of ruthenium(III) beta-diketonates arranged on the basis of the TG data published by us previously [20].

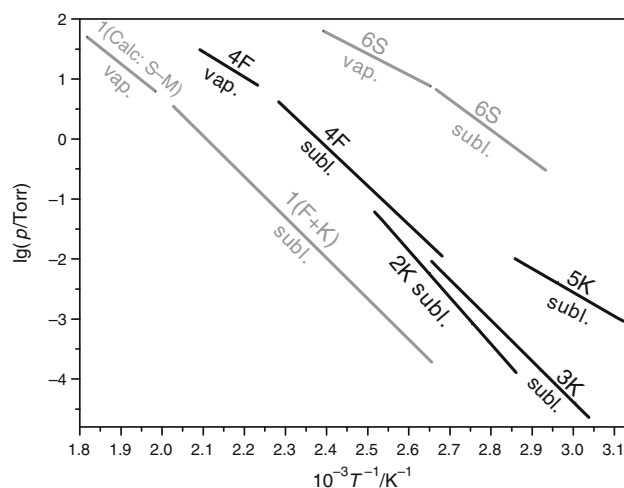


Fig. 3 Dependencies of logarithm of saturated vapor pressure on reciprocal temperature for the complexes Ru(acac)₃—1, Ru(thd)₃—2, Ru(tfhd)₃—3, *trans*-Ru(tfac)₃—4, Ru(ptac)₃—5, Ru(hfac)₃—6 obtained by using effusion method (K), flow method (F), static method (S), calculated from the sublimation and melting data (Calc: S-M); this study data are marked out gray

Conclusions

Thus, thermal behavior of ruthenium beta-diketonate derivatives (Ru(acac)₃, Ru(hfac)₃, and Ru(mdhd)₃) was investigated by DSC and the thermodynamic characteristics of melting process (m.p., $\Delta_{\text{melt}} H^{\circ}_{\text{m.p.}}$ and $\Delta_{\text{melt}} S^{\circ}_{\text{m.p.}}$) were obtained for the first time. Using static method with quartz membrane zero-manometer the temperature dependencies of vapor pressure were measured for Ru(hfac)₃ and the thermodynamic characteristics of vaporization processes (ΔH_T and ΔS°_T) of this complex were calculated. Thermodynamic values of melting process for Ru(hfac)₃ found by two independent methods (calorimetrically and by vapor pressure measurement) closely agreed with each other.

Acknowledgements The study was supported by Integral Interdisciplinary Project of the Siberian Branch of the Russian Academy of

Sciences N97 “The fundamentals of processes of chemical deposition of films and structures for nanoelectronics.”

References

1. Shibutami T, Kawano K, Oshima N, Yokoyama Sh, Funakubo H. Ruthenium film with high nuclear density deposited by MOCVD using a novel liquid precursor. *Electrochem Solid-State Lett.* 2003;6:C117–9.
2. Kim HW, Ju B-S, Kang C-J. Patterning of Ru electrode in O₂/Cl₂ gasus in reactive ion etcher. *Vacuum.* 2008;71:481–6.
3. Joo J-H, Seon J-M, Jeon Y-C, Oh K-Y, Roh J-S, Kim J-J, Choi J-T. Investigation of ruthenium electrodes for (Ba, Sr)TiO₃ thin films. *Jpn J Appl Phys.* 1998;37:3396–401.
4. Morozova NB, Zharkova GI, Semyannikov PP, Sysoev SV, Igumenov IK, Fedotova NE, Gelfond NV. MO CVD obtaining composite coating from metal of platinum group on titanium electrodes. *J Phys.* 2001;11(Pr3):609–16.
5. Cheng AHB, Daniels M, Luttmner JD. Etching Byproducts of Ruthenium Wafers Using Various Etching Chemistries. In: Simpson SR, Mendicino L, Rajeshwar K, Fenton JM, editors. *Environmental issues in the electronics/semiconductor industries and Electrochemical/photochemical methods for pollution.* Pennington: The Electrochemical Society; 1998. pp. 10–4.
6. Lemon TH. Thick-film ruthenium resistor pastes. New compositions for screen-printed circuits. *Platinum Metals Rev.* 1973;17:14–20.
7. *Metal Bulletin Monthly.* 2007;October:44–5.
8. Hendrix BC, Welch JJ, Roeder JF, Wang Z, Xu Ch, Stawasz M, Baum Th. Ultra-thin ruthenium films by pulsed chemical vapor deposition. In: Kar S, De Gendt S, Haussa M, Landheer D, MisraD, Iwai H, editors. *Physics and technology of high-k gate dielectrics 5.* Pennington: The Electrochemical Society; 2007. pp. 569–74.
9. Belyakov AI. Electrochemical supercapacitors: their state-of-the-art and design problems. *Electrochem Energy.* 2006;6:146–9.
10. Kim BS, Kang SY, Seo HS, ChS Hwang, Kim HJ. Improved nucleation behavior of Ru thin films prepared by MOCVD on TiCl₄ pretreated substrates. *Electrochem Solid State Lett.* 2007;10:D113–5.
11. Lai Y-H, Chou T-Y, Song Y-H, Liu Ch-Sh, Chi Y, Carty AJ, Peng Sh M, Lee G-H. Synthesis and characterization of ruthenium complexes with two fluorinated amino alkoxide chelates. The quest to design suitable MOCVD source reagents. *J Chem Mater.* 2003;15:2454–62.
12. Igumenov IK, Semyannikov PP, Trubin SV, Morozova NB, Gelfond NV, Mischenko AV, Norman JA. Approach to control deposition of ultra thin films from metal organic precursors: Ru deposition. *Surf Coat Technol.* 2007;201:9003–8.
13. Lee F-J, Chi Y, Liu Ch-Sh, Hsu P-F, Chou T-Y, Peng Sh-M, Lee G-H. Organometallic ruthenium source reagents for CVD. *Chem Vapor Depos.* 2001;7:99–101.
14. Aaltonen T, Ritala M, Arstila K, Keinonen J, Leskelä M. Atomic layer deposition of ruthenium thin films from Ru(thd)₃ and oxygen. *Chem Vapor Depos.* 2004;10:215–9.
15. Lashdaf M, Hatanpää T, Krause AOI, Lahtinen J, Lindblad M, Tiitta M. Deposition of palladium and ruthenium β -diketonates on alumina and silica supports in gas and liquid phase. *J Appl Catal A.* 2003;241:51–63.
16. Lashdaf M, Hatanpää T, Tiitta M. Volatile β -diketonato complexes of ruthenium, palladium and platinum. Preparation and thermal characterization. *J Therm Anal Calorim.* 2001;64:1171–82.
17. Bykov AF, Morozova NB, Igumenov IK, Sysoev SV. Investigation of thermal properties of ruthenium(III) beta-diketonate precursors for preparation of RuO₂ films by CVD. *J Therm Anal.* 1996;46:1551–65.
18. Morozova NB, Zherikova KV, Semyannikov PP, Trubin SV, Igumenov IK. Thermal properties of ruthenium(III) β -diketonates. *J Therm Anal Calorim.* 2009;98:395–9.
19. Sysoev SV, Cheremisina TN, Zelenina LN, Tkachev SV, Zherikova KV, Morozova NB, Kuratieva NV. Thermodynamic characteristics of phase conversion of structural isomers for volatile complex of ruthenium (III) trifluoroacetylacetonate. *J Therm Anal Calorim.* 2010;101:41–4.
20. Morozova NB, Mit'kin VN, Igumenov IK, Zemskov SV, Potapova OG. Ruthenium β -diketonates. *Koord Khim.* 1989;15:67–72.
21. Suvorov AV. *Thermodynamic Chemistry of the Vapor State.* Leningrad: Nauka; 1970.
22. Zelenina LN, Titov VA, Chusova TP, Stenin YuG, Titov AA. On the thermodynamic properties of germanium-iodide compounds. *J Chem Thermodyn.* 2003;35:1601–12.
23. Ribeiro da Silva MAV, Monte MJS, Giera E. Thermodynamic study of the sublimation of crystalline tris(1,1,1-trifluoro-2,4-pentanedionate)ruthenium(III) and tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)ruthenium(III). *J Chem Thermodyn.* 2001;33:369–76.