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Thermal Stability, Vapor Pressures, and Diffusion Coefficients of Some Metal 2,2,6,6-Tetramethyl-3,5-heptandionate [M(tmhd)$_n$] Compounds

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Many metal 2,2,6,6-tetramethyl-3,5-heptandionate [M(tmhd)$_n$] compounds are volatile enough to be useful as precursors of the metals in vapor-phase deposition processes, for example, metal organic chemical vapor deposition (MOCVD). The thermal stability, vapor pressures, and gaseous diffusion coefficients of these compounds are, therefore, of fundamental importance for achieving reproducible and effective depositions. The present communication reports the thermal stability, vapor pressures, enthalpies of sublimation, and diffusion coefficients (in nitrogen and/or helium) for some metal 2,2,6,6-tetramethyl-3,5-heptandionate compounds [M(tmhd)$_n$], namely, [Al(tmhd)$_3$], [Cr(tmhd)$_3$], [Cu(tmhd)$_2$], [Fe(tmhd)$_3$], [Mn(tmhd)$_3$], and [Ni(tmhd)$_2$] at temperatures between (341 and 412) K at ambient pressure. All of these are found to be stable under the investigated experimental conditions and thus are suitable precursors for CVD.

1. Introduction

Various metal-organic (or organometallic) compounds are frequently used as a precursor for depositing thin and high-quality films with a well-defined chemical composition and structural uniformity. The metal 2,2,6,6-tetramethyl-3,5-heptandionate [M(tmhd)$_n$] compounds are volatile at relatively low temperatures compared to most metals and their compounds. Thus, the desired coating can be produced after evaporation at low temperatures. To engineer such a process, the knowledge of the vapor pressures and their temperature dependence is essential because they determine the maximum theoretical growth rate and the composition. The knowledge of the precursor vapor pressure allows one to assess its maximum permissible vapor density for optimal deposition rates. The binary gaseous diffusion coefficients (D_{AB}) are needed for the calculation of the Sherwood ($\mathrm{Sh} = (h_M L)/(D_{AB})$) and Lewis ($\mathrm{Le} = \alpha/(D_{AB})$) numbers used to describe mass transfer processes (e.g., to calculate the buffer gas saturation in evaporators). Here h_M signifies the convection mass transfer coefficient, L a characteristic length, and α the thermal conductivity.

We have started a program to study the long-term thermal stability, vapor pressures, and diffusion coefficients of organometallic compounds over a range of temperatures. Recently, the thermal stability, vapor pressures, and diffusion coefficients of several diketonates were reported.[1,2] In the present communication we report the long-term thermal stability, vapor pressure, and the gaseous diffusion coefficient for aluminum 2,2,6,6-tetramethyl-3,5-heptandionate [Al(tmhd)$_3$], chromium 2,2,6,6-tetramethyl-3,5-heptandionate [Cr(tmhd)$_3$], copper 2,2,6,6-tetramethyl-3,5-heptandionate [Cu(tmhd)$_2$], iron 2,2,6,6-tetramethyl-3,5-heptandionate [Fe(tmhd)$_3$], manganese 2,2,6,6-tetramethyl-3,5-heptandionate [Mn(tmhd)$_3$], and nickel 2,2,6,6-tetramethyl-3,5-heptandionate [Ni(tmhd)$_2$] at different temperatures. The thermal stability was studied using thermogravimetry (TG), and the vapor pressures were measured using a Knudsen effusion method. The gaseous diffusion coefficients were determined by combining the accurate thermogravimetric measurements with the experimental vapor pressure data.

2. Experimental Section

[Al(tmhd)$_3$] (Strem, 99 %), [Cr(tmhd)$_3$] (Strem, 99 %), [Cu(tmhd)$_2$] (Strem, 99 %), [Fe(tmhd)$_3$] (ABCR, 99 %), [Mn(tmhd)$_3$] (ABCR, 99 %), and [Ni(tmhd)$_2$] (ABCR, 98 %) were used as received. N_2 (99.98 %) or He (99.998 %) were used as carrier gases in the differential thermal analysis/thermogravimetry (DTA/TG) experiments.

As some of the metal 2,2,6,6-tetramethyl-3,5-heptandionates were sensitive to moisture and/or oxygen, these were handled appropriately. These substances were stored in a glovebox and filled into the Knudsen cell also in the glovebox. A home-built stainless steel Knudsen cell was used for vapor pressure measurements. The experimental setup has been described in a previous publication[3] and was modified slightly for these air-sensitive substances.[1] The setup includes a Knudsen cell, two Pt-100 thermometers, a stainless steel thermostatted vessel (vacuum chamber), a cooling trap, a diffusion pump, a prevacuum pump, a pressure sensor with a display, and an operating unit and arrangement for flushing inert gas (e.g., nitrogen). The Knudsen cell is situated in a vacuum chamber, with good thermal contact around the cell. The temperature of the stainless steel chamber was controlled with a proportional integral differential (PID) temperature controller. The temperature was measured at two different places inside the chamber and did not differ more than 0.1 K.

A well-defined amount of the substance (depending upon the temperature of the measurement and the substance) was weighed (accuracy: 0.03 mg) into the cell. The filling and weighing was done under an inert gas atmosphere in a glovebox. The cell was then tightened and put into the vacuum chamber. The thickness of the aluminum foil used was 70 μm. The temperature of the chamber was maintained constant to better than ± 0.2 K, that is, the maximum uncertainty in temperature is ± 0.2 K. Prior to evacuation, enough time (at least 60 min) was allowed for the attainment of a constant temperature which was recorded with the help of a calibrated Pt-100 thermometer. During this time a nitrogen atmosphere was maintained in the chamber. It

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was ensured that the mass of evaporated substance prior to evacuation of the cell was less than the accuracy of mass measurement. The evacuation of the chamber was then started, and the time interval was measured between the time when the vacuum reached a pressure of around 10^{-3} mbar and the time when the high vacuum pump was turned off and the pressure was above 10^{-3} mbar. Typical times were (1 to 10) h [in this time the weight losses were between (3 and 50) mg depending on the hole size (ranging from (0.5 to 0.9) mm), the temperature, and the substance]. The cell was then brought to room temperature in a desiccator and weighed again. The uncertainties in the evaporation time and in the mass loss are estimated to be 0.5 min and 0.05 mg, respectively. The uncertainties in the diameter of the orifice and the thickness of the foil are estimated to be (0.005 and 0.002) mm, respectively. In the evaluation of the data, no additional calibration was performed. The maximum overall standard uncertainty in vapor pressure measurements was estimated to be (± 0.02 to ± 0.4) Pa in the pressure range (0.4 to 20) Pa, (± 0.01 to ± 0.02) Pa in the pressure range (0.1 to 0.4) Pa, and (± 0.005 to ± 0.01) Pa in the pressure range (0.02 to 0.1) Pa depending upon the system and the measured vapor pressure. This overall uncertainty was calculated assuming that all of the uncertainties are independent and random.

A commercial TGA/DTA (Bähr STA 503) analyzer was used to perform the thermogravimetric experiments. The atmosphere was well-defined, using either He or N_2. The flow rate of 100 $cm^3 \cdot min^{-1}$ was controlled by a calibrated mass flow controller. This flow rate was found to be sufficient to ensure that the concentration of substance at the top of the crucible remains nearly zero throughout the measurement as proved experimentally: a change in flow rate did not change the mass loss rate measurably. The pressure was atmospheric throughout. Open alumina crucibles were used in all experiments: the inner diameter being 5.35 mm and the inner height 7.2 mm. The samples were filled inside the crucible, so that the initial height of the sample inside the crucible was between (3.0 and 5.0) mm. From the initial height, which was measured at the beginning of each experiment with an estimated precision of ± 0.2 mm, the volume of the sample was calculated. Using the initial mass, the apparent density of the sample was derived. The temperature was typically reached within 30 min, and then the temperature was held constant, in some experiments until all of the sample was evaporated; in other experiments the temperature was changed after 2 h to the next temperature, so that several temperatures could be investigated within one run. The temperature sensor was calibrated by measuring the melting points of reference substances (4-nitrotoluene, naphthalene, indium, and potassium perchlorate) which cover the whole temperature range of the measurements. The overall uncertainty in mass loss rate was estimated to be ± 1 % and for the diffusion coefficient (± 0.005 to ± 0.015) $cm^2 \cdot s^{-1}$ arising mainly from the uncertainties in the initial distance between the sample surface and the top of the crucible.

3. Results and Discussion

Thermal Stability. The thermal stability of the compounds was investigated by isothermal TGA using a commercial DTA/TG (Bähr STA 503). The mass loss and the DTA signal were studied at a given temperature. When necessary a temperature program was used to study the thermal stability as a function of temperature. A compound can be considered to be a suitable precursor if in isothermal TGA a nearly linear mass loss as a function of time is found and no residual is left at the end. Some typical results of TGA for several compounds all held at (428 or 447) K are summarized in Figure 1. For all of these compounds the mass loss versus time curve was found according to the theory,[3,4] and the substances evaporate completely without leaving any measurable residue indicating an exclusive evaporation process taking place. The isothermal temperature for [Fe(tmhd)$_3$] and [Ni(tmhd)$_2$] was 428 K and for [Mn(tmhd)$_3$], [Al(tmhd)$_3$], [Cr(tmhd)$_3$], and [Cu(tmhd)$_2$] was 447 K. Metal 2,2,6,6-tetramethyl-3,5-heptandionates show in general a better thermal stability than the corresponding metal acetylacetonates.[1,2] These are also less susceptible to hydration and polymerization[5,6] possibly due to the steric hindrance generated by bulky substituent groups.

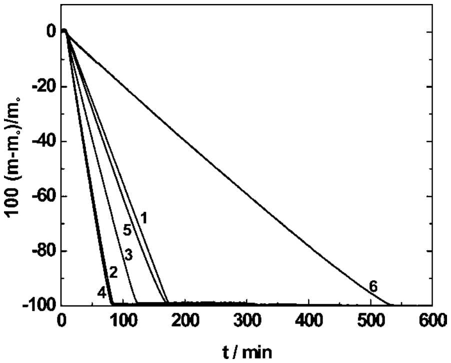

Figure 1. TG curve in isothermal mode; m_0, initial mass of the substance; m, mass of the substance after time t; 1, [Mn(tmhd)$_3$]; 2, [Al(tmhd)$_3$]; 3, [Cu(tmhd)$_2$]; and 4, [Cr(tmhd)$_3$] at 447 K. 5, [Fe(tmhd)$_3$]; and 6, [Ni(tmhd)$_2$] at 428 K.

Vapor Pressure. For the precursors [Al(tmhd)$_3$], [Cr(tmhd)$_3$], [Cu(tmhd)$_2$], [Fe(tmhd)$_3$], [Mn(tmhd)$_3$], and [Ni(tmhd)$_2$], which were found to be thermally stable, the vapor pressures p were determined from the measurement of the mass of the substance Δm evaporated in a definite time Δt in the Knudsen cell from the equation:[1]

$$p = \frac{\Delta m}{KA\Delta t}\sqrt{\frac{2\pi RT}{M}} \qquad (1)$$

where M is the molar mass of the substance; A, the area of the orifice; R, the universal gas constant; T, the temperature in Kelvin. The Clausing factor K of the orifice was calculated using the relation:[1]

$$K = 1 - \left(\frac{l}{d}\right) + 0.8\left(\frac{l}{d}\right)^2 \qquad (2)$$

where l is the thickness of the foil and d is the diameter of the orifice. The details of experimental parameters and the measured vapor pressures are given in Table 1.

The vapor pressure results as a function of temperature were fitted to an equation

$$\log_{10}(p/\mathrm{kPa}) = A_i - B_i/(T/\mathrm{K}) \qquad (3)$$

and the coefficients A and B were determined for the best fitting. These are given in Table 2. The enthalpy of sublimation for each compound was derived from these vapor pressure values [from the slopes of the $\log_{10}(p)$ versus $1/(T/\mathrm{K})$ plots] and is also reported in Table 2.

The vapor pressure of [Fe(tmhd)$_3$] measured in the temperature range of (341 to 408) K is shown in Figure 2 as a function of $1/T$. The enthalpy of sublimation derived from the temperature dependence of vapor pressures is 131.93 $kJ \cdot mol^{-1}$ [in the temperature range (341 to 408) K]. The vapor pressure values of Brunner and Curtis[7] are also shown in Figure 2. They differ from our values. In the low temperature region (up to 373 K)

Table 1. Details of Knudsen Cell Measurements at 10^{-5} Pa

T	Δt	d		Δm	p	T	Δt	d		Δm	p
K	s	mm	K	mg	Pa	K	s	mm	K	mg	Pa
$[\mathrm{Fe(tmhd)_3}]$											
395.93	4890	0.715	0.9098	31.91	3.32	360.45	56376			9.71	0.088
391.23	5868			27.72	2.19	351.05	65340			2.14	0.016
386.53	5850			16.23	1.38	369.05	11250			3.53	0.16
381.83	9108			13.92	0.75	379.55	5760			5.74	0.51
367.72	24696			6.65	0.131	398.55	3168	0.513	0.8784	13.56	4.35
405.34	4536			87.39	9.81	389.05	4140			6.88	1.67
372.42	13140			6.48	0.241	355.68	75960	0.719	0.9102	5.41	0.034
384.23	5760	0.696	0.9075	10.31	0.94	341.45	188820			3.28	0.008
389.05	4086			12.81	1.66						
$[\mathrm{Mn(tmhd)_3}]$											
395.93	4824	0.715	0.9098	28.23	2.95	388.98	7770			17.94	1.15
386.23	6868			14.54	1.06	398.55	4050			28.93	3.62
377.13	11556			8.73	0.37	403.27	3600			43.10	6.12
391.23	6330			24.2	1.92	379.48	17064			15.84	0.45
367.72	19908			5.18	0.126	360.44	73368	0.719	0.9102	7.43	0.048
381.23	8496			10.86	0.63	350.92	177228			6.31	0.016
400.64	5130			49.02	4.86	365.2	83520			13.77	0.079
405.34	4320			68.34	8.1	355.68	166248			9.36	0.026
372.42	13284			5.38	0.198	408.03	3720	0.513	0.8784	36.80	10.23
369.95	22968			7.18	0.152						
$[\mathrm{Ni(tmhd)_2}]$											
377.13	21276	0.715	0.9098	5.56	0.15	360.43	152748			5.77	0.021
391.23	12570			16.99	0.8	365.19	139788			10.19	0.041
386.53	14400			10	0.41	384.23	14040			8.5	0.358
398.15	3760			10.1	1.63	369.95	58680			8.66	0.084
391.23	5832			8.69	0.89	379.47	21024			6.83	0.189
400.64	5940			18.57	1.88	398.15	3780	0.513	0.8784	5.75	1.85
374.72	57168	0.719	0.9102	12.34	0.12	403.27	3888			8.49	2.66
374.72	62568			15.14	0.14	408.03	3780			12.74	4.15
$[\mathrm{Al(tmhd)_3}]$											
379.47	7416	0.715	0.9098	14.06	0.95	388.96	4248			18.17	2.16
369.95	8820			6.28	0.356	360.43	61930			15.2	0.12
384.23	4050			12.1	1.52	365.19	53220			18.9	0.175
350.92	90144			5.8	0.031	403.26	5796	0.509	0.8776	37.79	6.94
346.16	143316			7.45	0.025	408.22	3528			39.08	11.88
341.40	234684			6.06	0.012	412.78	3809			51.4	14.6
355.68	57024			6.76	0.058	403.26	4400			30.85	7.5
398.05	4860	0.719	0.9102	45.75	4.83						
$[\mathrm{Cr(tmhd)_3}]$											
355.56	50508	0.715	0.9098	5.36	0.051	360.43	71532			13.75	0.093
388.98	5976			21.49	1.8	365.19	60516			19.24	0.154
379.47	5184			8.64	0.827	369.95	23255			18.3	0.385
384.23	6696			22.2	1.65	346.16	166320			7.6	0.022
374.71	7020			9.57	0.67	398.5	3600	0.509	0.8776	23.85	6.90
350.92	70200			4.36	0.029	386.53	5055	0.719	0.9102	19.38	1.90
393.74	37476			29.22	3.94	365.19	50519			20.35	0.194
$[\mathrm{Cu(tmhd)_2}]$											
398.5	4500	0.703	0.9083	32.04	4.41	374.71	27972			23.18	0.501
408.2	3780			74.71	12.4	388.98	5004			17.47	2.15
403.64	6320			79.8	7.84	379.47	11700			12.09	0.629
365.19	61272			15.36	0.149	365.19	50360	0.715	0.9098	14.00	0.16
369.95	21384			11.74	0.329	379.47	26360			34.1	0.76
384.23	16164			34.55	1.31	393.74	4640			22.5	2.90

the vapor pressure values observed by them is higher by a factor of 3, and at higher temperature (408 K) the difference reduces to a factor of 1.3. The difference in vapor pressure is unclear. For the present study validation experiments with substances of well-established vapor pressures, namely, ferrocene, phenanthrene, and anthracene, were also performed. The results agreed with the literature values within the experimental uncertainty.

The measured values for the vapor pressure of $[\mathrm{Cu(tmhd)_2}]$ are shown in Figure 3 as a function of $1/T$. The vapor pressure of this substance has been reported in literature by several workers.[8−11] Our vapor pressure values for $[\mathrm{Cu(tmhd)_2}]$ agree within the experimental error with those of Tobaly and Lanchec[8] but are lower than the values reported by Yuhya et al.[9] The

Table 2. Constants for Equation 3 and the Molar Enthalpy of Sublimation ΔH_{sub}

			ΔH_{sub}(exp)	temp. range
substance	A_i	B_i	$\mathrm{kJ \cdot mol^{-1}}$	K
$[\mathrm{Fe(tmhd)_3}]$	14.93 ± 0.36	6891 ± 135	131.93 ± 2.59^{a}	341 to 408
			106.69^{b}	313 to 523
$[\mathrm{Cu(tmhd)_2}]$	14.25 ± 0.42	6600 ± 162	126.36 ± 3.10^{a}	365 to 408
			124.65^{c}	350 to 450
			105.09^{d}	365 to 550
			111.85^{e}	365 to 550
$[\mathrm{Al(tmhd)_3}]$	13.31 ± 0.43	6222 ± 163	119.12 ± 3.12^{a}	341 to 412
$[\mathrm{Cr(tmhd)_3}]$	14.54 ± 0.43	6670 ± 160	127.45 ± 3.06^{a}	350 to 398
$[\mathrm{Mn(tmhd)_3}]$	15.76 ± 0.24	7238 ± 81	138.95 ± 1.60^{a}	350 to 408
$[\mathrm{Ni(tmhd)_2}]$	15.30 ± 0.32	7200 ± 121	137.84 ± 2.32^{a}	360 to 408

[a] This work. [b] Ref 7. [c] Ref 8. [d] Ref 9. [e] Ref 10.

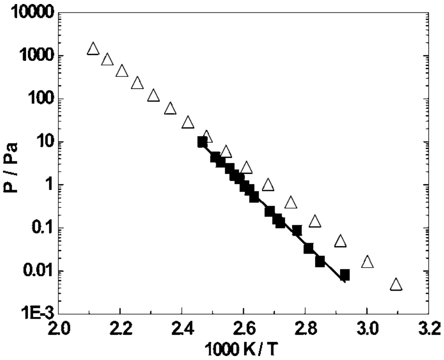

Figure 2. Vapor pressure of [Fe(tmhd)$_3$]; ■, this work; —, eq 3; △, ref 7.

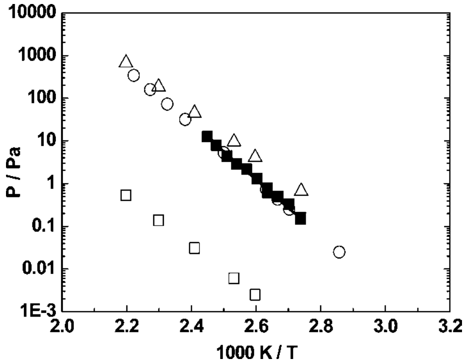

Figure 3. Vapor pressure of [Cu(tmhd)$_2$]; ■, this work; —, eq 3; △, ref 9; □, ref 10; ○, ref 8.

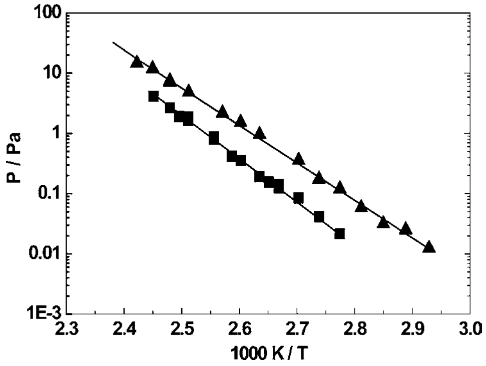

Figure 4. Vapor pressure of ■, [Ni(tmhd)$_2$]; ▲, [Al(tmhd)$_2$]; —, eq 3.

vapor pressure values of Igunov et al.[10] (cited in ref 9) are much lower. Yuhya et al.[9] used the transpiration method. Waffenschmidt et al.[11] reported the vapor pressure of [Cu(tmhd)$_2$] at higher temperatures where it decomposed. Therefore, the data provided by them does not represent the vapor pressure of the pure compound. The derived enthalpy of sublimation from the present vapor pressure data is 126.36 kJ·mol^{-1} at (365 to 408) K.

The measured vapor pressures for [Al(tmhd)$_3$] and [Ni(tmhd)$_2$] and [Cr(tmhd)$_3$] and [Mn(tmhd)$_3$] are shown in Figures 4 and 5 as a function of 1/T. No other vapor pressure data for these compounds are available in the literature. The enthalpy of sublimation values derived from these data are 119.12 kJ·mol^{-1} at (341 to 412) K, 137.84 kJ·mol^{-1} at (360 to 408) K, 127.45 kJ·mol^{-1} at (350 to 398) K, and 138.95 kJ·mol^{-1} at (350 to 408) K, respectively. The enthalpies of sublimation for these compounds are also not available in the literature.

Diffusion Coefficient. No data for the gaseous diffusion coefficients D_{AB} for these compounds are available in the literature. The binary diffusion coefficients of [Al(tmhd)$_3$], [Cu(tmhd)$_2$], [Fe(tmhd)$_3$], and [Mn(tmhd)$_3$] were measured in both helium and nitrogen atmosphere using thermogravimetric experiments. The product of vapor pressure and the binary diffusion coefficient of the substances in carrier gas was calculated from the experimental mass loss (Δm) for the time t using the equation:[3]

$$p_A^{vap}D_{AB} = [(h+H)^2 - H^2]\frac{RT\rho_A}{2Mt} = \left[\left(\frac{\Delta m}{S\rho_A}+H\right)^2 - H^2\right]\frac{RT\rho_A}{2Mt} \qquad (4)$$

Here T is the temperature, R the universal gas constant, and ρ_A the apparent density of the evaporating substance of molecular mass M. H is the initial distance between the surface (of surface area S) of the material and the top of the crucible which increases to ($h + H$) after time t in thermogravimetric experiments. The experimental vapor pressure determined from the Knudsen effusion method was used to derive the diffusion coefficient from eq 4.

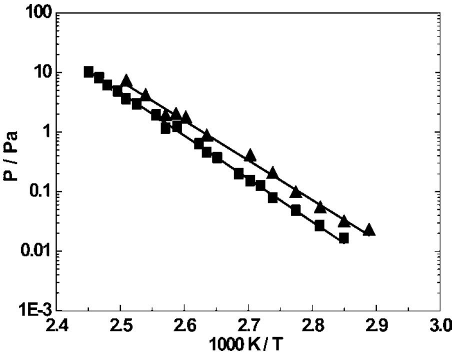

Figure 5. Vapor pressure of ■, [Mn(tmhd)$_2$]; ▲, [Cr(tmhd)$_2$]; —, eq 3.

The average, maximum, and minimum values of D_{AB} for at least three runs are reported in Table 3. The D_{AB} for A ≡ Fe(tmhd)$_3$ or Mn(tmhd)$_3$ in helium [B] are shown in Figure 6. From simple gas kinetic theory a T^n dependence with $n = 1.75$ to 2 is expected.[12] A curve with $n = 2$ is also included in the diagram.

Figure 7 shows D_{AB} for A ≡ Al(tmhd)$_3$, Cr(tmhd)$_3$, Cu(tmhd)$_2$, or Ni(tmhd)$_2$ in helium [B].

Figure 8 shows D_{AB} for A ≡ Al(tmhd)$_3$, Cu(tmhd)$_2$, Fe(tmhd)$_3$, or Mn(tmhd)$_3$ in nitrogen [B]. For [Cr(tmhd)$_3$] and [Ni(tmhd)$_2$], the mass loss in nitrogen was very small at the temperature of study, and hence it was not thought reasonable to use these values for the determination of gaseous diffusion coefficients. As expected the binary diffusion coefficients for [M(tmhd)$_n$ in helium are throughout higher than in nitrogen. No correlations are yet available for the estimation of the binary diffusion coefficients of metal organic compounds; hence, these could not be estimated.

A correlation of diffusion coefficients with $(M_{AB})^{1/2}$ was tried but was not successful. The temperature dependence of the measured diffusion coefficients can be represented within experimental uncertainty by the following equation:

$$D_{AB}/(\mathrm{cm}^2\cdot\mathrm{s}^{-1}) = A(T/\mathrm{K})^2 \qquad (5)$$

The constants A for eq 5, the root-mean-square deviation σ defined as $\sigma = \{[D_{AB}(\exp) - D_{AB}(\mathrm{cal})]^2/(n-1)\}^{1/2}$ with n as the number of temperatures studied, and the maximum deviation $\delta_{\max}$ are given in Table 4.

Table 3. Experimental Diffusion Coefficient for [M(tmhd)$_n$]: Minimum (Min), Maximum (Max), and Average (Ave) Values

system	T K	$D_{AB}^{(Min)}$ $cm^2 \cdot s^{-1}$	$D_{AB}^{(Max)}$ $cm^2 \cdot s^{-1}$	$D_{AB}^{(Ave)}$ $cm^2 \cdot s^{-1}$
[Fe(tmhd)$_3$]-N$_2$	378.42	0.0919	0.0959	0.0931
	387.39	0.0950	0.0988	0.0967
	396.43	0.1010	0.1024	0.1017
	405.50	0.1047	0.1089	0.1076
	414.66	0.1111	0.1122	0.1117
[Fe(tmhd)$_3$]-He	378.87	0.1871	0.2129	0.1948
	388.61	0.1990	0.2294	0.2107
	398.35	0.2074	0.2411	0.2207
	408.10	0.2168	0.2577	0.2313
[Mn(tmhd)$_3$]-N$_2$	387.18	0.0688	0.0741	0.0706
	396.20	0.0714	0.0780	0.0736
	405.26	0.0717	0.0794	0.0744
	414.43	0.0720	0.0799	0.0747
[Mn(tmhd)$_3$]-He	378.81	0.1578	0.1862	0.1646
	388.51	0.1608	0.1947	0.1700
	398.26	0.1639	0.1970	0.1738
	408.21	0.1677	0.1795	0.1713
[Cr(tmhd)$_3$]-He	368.24	0.1026	0.1151	0.1094
	383.42	0.1232	0.1527	0.1356
	387.88	0.1331	0.1457	0.1396
	393.14	0.1492	0.1509	0.1500
[Ni(tmhd)$_2$]-He	378.69	0.1583	0.2210	0.1932
	388.47	0.2003	0.2368	0.2116
	398.23	0.2099	0.2477	0.2215
	407.96	0.2206	0.2618	0.2329
[Al(tmhd)$_3$]-N$_2$	360.69	0.0565	0.0691	0.0638
	378.60	0.0753	0.0888	0.0811
	396.80	0.0834	0.0921	0.0874
[Al(tmhd)$_3$]-He	368.32	0.1516	0.1516	0.1516
	387.67	0.1525	0.1591	0.1552
	407.08	0.1668	0.1773	0.1724
[Cu(tmhd)$_2$]-He	370.24	0.1514	0.1657	0.1607
	389.95	0.1725	0.1838	0.1781
	409.64	0.1767	0.1905	0.1844
[Cu(tmhd)$_2$]-N$_2$	382.65	0.0500	0.0532	0.0511
	401.41	0.0588	0.0614	0.0602
	420.40	0.0618	0.0644	0.0629

4. Conclusions

Some metal 2,2,6,6-tetramethyl-3,5-heptandionate ([M(tmhd)$_n$] compounds which are volatile enough to be useful as chemical vapor deposition (CVD) precursors of the metals in vapor-phase deposition process were investigated. The metal 2,2,6,6-tetramethyl-3,5-heptandionates, namely, [Al(tmhd)$_3$], [Cr(tmhd)$_3$], [Cu(tmhd)$_2$], [Fe(tmhd)$_3$], [Mn(tmhd)$_3$], and [Ni(tmhd)$_2$], are stable, and hence their vapor pressures were measured at various temperatures. The vapor pressures of the other compounds vary from (0.09 to 0.45) Pa at 373 K. From these [Ni(tmhd)$_2$] is the least volatile, whereas [Al(tmhd)$_3$] and [Cr(tmhd)$_3$] are the most volatile. For [Cr(tmhd)$_3$], [Al(tmhd)$_3$], [Cu(tmhd)$_2$], [Fe(tmhd)$_3$], [Mn(tmhd)$_3$], and [Ni(tmhd)$_2$] a pressure of 1 Pa is reached at (380.3, 381.5, 382.6, 384.3, and 385.8) K, respectively. Regarding the volatility, these all are suitable precursors for CVD. The enthalpies of sublimation for these compounds determined from the temperature dependence of the vapor pressure do not differ much from one another and vary from (119 to 139) kJ·mol^{-1} in the respective temperature range. The gaseous diffusion coefficients D_{AB} of these compounds in helium vary from (0.11 to 0.24) $cm^2 \cdot s^{-1}$ in the temperature range of (342 to 413) K. The gaseous diffusion coefficients in nitrogen are lower and vary from (0.05 to 0.11) $cm^2 \cdot s^{-1}$ in the same temperature range.

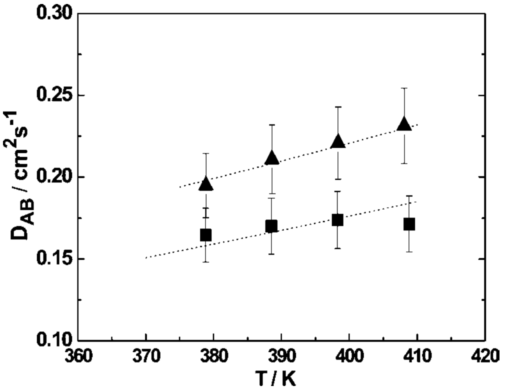

Figure 6. Gaseous D_{AB} in helium: ▲, [Fe(tmhd)$_3$]; ■, [Mn(tmhd)$_3$]; ········, eq 5.

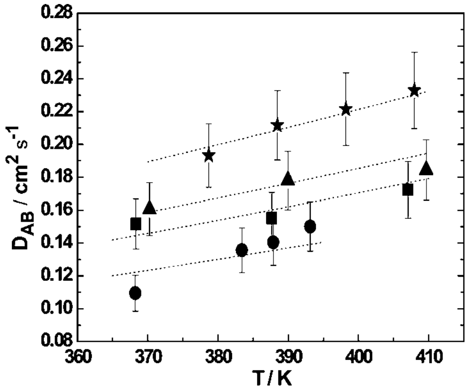

Figure 7. Gaseous D_{AB} in helium: ■, [Al(tmhd)$_3$]; ●, [Cr(tmhd)$_3$]; ▲, [Cu(tmhd)$_2$]; ★, [Ni(tmhd)$_2$]; ········, eq 5.

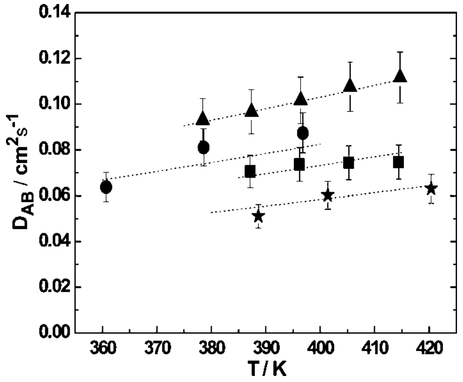

Figure 8. Gaseous D_{AB} in nitrogen: ●, [Al(tmhd)$_3$]; ★, [Cu(tmhd)$_2$]; ▲, [Fe(tmhd)$_3$]; ■, [Mn(tmhd)$_3$]; ········, eq 5.

Table 4. Constants for Equation 5 with the Root-Mean-Square Deviation σ and Maximum Deviation δ_{max}

system	A	σ $cm^2 \cdot s^{-1}$	δ_{max} $cm^2 \cdot s^{-1}$
[Fe(tmhd)$_3$]-N$_2$	$6.4396 \cdot 10^{-7}$	0.0011	0.0017
[Fe(tmhd)$_3$]-He	$1.3786 \cdot 10^{-6}$	0.0027	0.0030
[Mn(tmhd)$_3$]-N$_2$	$4.5770 \cdot 10^{-7}$	0.0027	0.0038
[Mn(tmhd)$_3$]-He	$1.1015 \cdot 10^{-6}$	0.0082	0.0120
[Al(tmhd)$_3$]-N$_2$	$5.1551 \cdot 10^{-7}$	0.0071	0.0072
[Al(tmhd)$_3$]-He	$1.0652 \cdot 10^{-6}$	0.0067	0.0071
[Cr(tmhd)$_3$]-He	$9.0087 \cdot 10^{-7}$	0.0100	0.0126
[Cu(tmhd)$_2$]-He	$1.5856 \cdot 10^{-6}$	0.0073	0.0099
[Cu(tmhd)$_2$]-N$_2$	$3.6465 \cdot 10^{-7}$	0.0021	0.0022
[Ni(tmhd)$_2$]-He	$1.3827 \cdot 10^{-6}$	0.0044	0.0050

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