Substituent Effects on the Volatility of Metal *β*-diketonates

Bradley D. Fahlman[1] and Andrew R. Barron[1,2*]

[1] Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, USA

[2] Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, USA
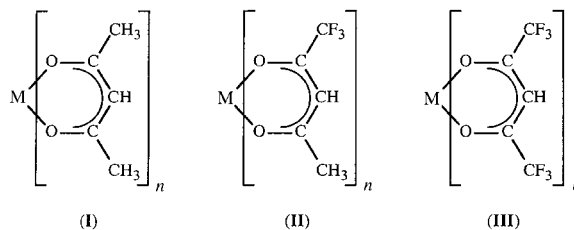
Volatile trends are established for a series of M(*β*-diketonate)$_n$ complexes, where M = Cu (n = 2); Al, Sc, Cr, Fe, Co, Ga (n = 3); Zr (n = 4) and *β*-diketonate = acetylacetonate (acac), trifluoroacetylacetonate (tfac), hexafluoroacetylacetonate (hfac) and 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd). Sublimation enthalpies (ΔH_{sub}) were calculated from thermogravimetric analysis (TGA) data, which show that the dependence of ΔH_{sub} on the number and type of intermolecular interactions appears to be more substantial than molecular mass effects. Irrespective of the metal, the ΔH_{sub} values for the M(tmhd)$_3$ derivative have a ΔH_{sub} value of between 93 and 99% of that of the M(acac)$_3$ derivative. In contrast, the M(tfac)$_3$ and M(hfac)$_3$ derivatives have ΔH_{sub} values of *ca.* 82% and 54% of the values for the corresponding M(acac)$_3$. Similar trends are observed for M(*β*-diketonate)$_2$ and M(*β*-diketonate)$_4$ derivatives. The relationship between the ΔH_{sub} and (T_{sub}) of the substituted *β*-diketonate derivatives as compared with the values for parent M(acac)$_n$ may be used to predict either quantity for a range of M(*β*-diketonate)$_n$ complexes where the values for M(acac)$_n$ are known. Using the TGA sublimation data, vapour pressures have been calculated for each of the M(*β*-diketonate)$_n$ complexes. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS *β*-diketonate; CVD precursor; enthalpy of sublimation; thermogravimetric analysis; vapour pressure

INTRODUCTION

Metal *β*-diketonate chelate compounds are invaluable precursors for the chemical vapour deposition (CVD) of metal and non-metal thin films.[1,2] In general, these compounds are favoured since they are relatively volatile, non-toxic and in the case of the parent acetylacetonate complexes (**I**), inexpensive.[3] Furthermore, replacing the substituent methyl groups of the parent derivative with other moieties has been demonstrated to influence the

volatility of these complexes. A common method used to enhance precursor volatility and corresponding efficacy for CVD applications is to incorporate partially (**II**) or fully (**III**) fluorinated ligands.[4]

(I)   (II)   (III)

The observed enhancement in volatility may be rationalized either by an increased amount of intermolecular repulsion due to the additional lone pairs

*Correspondence to: A. R. Barron, Department of Chemistry, Rice University, 6100 Main Street, Houston, TX 77005, USA. e-mail: arb@rice.edu

or that the reduced polarizability of fluorine (relative to hydrogen) causes fluorinated ligands to have less intermolecular attractive interactions.[5] Caulton and co-workers[3] have determined that, for a series of fluorinated zirconium fluoroalkoxides, the degree of volatility enhancement is a function of the degree of ligand fluorination. For example, $[Na(OR_f)]_4$ species showed a significant increase in volatility as the fluorine content was increased. Although the monomeric $Zr(OR_f)_4$ complexes displayed an analogous behaviour, it was to a much smaller extent. Similarly, in determining the thermodynamic properties for various complexes, $Ni(salen)Ln(hfa)_3$ (Ln = Y, Gd), Gleizes *et al.*[6] showed that solids possessing similar molecular and solid-state structures may have different volatilities depending on the nature of the ligand and the dimerization propensity of the complex.

A prediction of the volatility of a metal–organic compound as a function of its ligands and molecular structure would be desirable in order to determine the suitability of such a compound as a CVD precursor. In a study dealing with a range of inorganic and organic compounds[7] it was determined that a rough proportionality exists between a compound's melting point and its sublimation enthalpy. However, the largest deviations from the reported correlations were found for the inorganic compounds that were investigated. Hence, this reported correlation appears to be an oversimplification that may be best limited to simple organic solids, not inorganic or organometallic complexes. In this regard, we have undertaken a determination of sublimation enthalpies for a range of metal β-diketonate complexes in an attempt to correlate volatility with solid-state and/or molecular structures.

Enthalpies of sublimation for metal β-diketonate chelates have been previously determined through a variety of methods, most commonly from vapour pressure measurements using complex experimental systems such as Knudsen effusion,[8] temperature drop microcalorimetry[9] and, more recently, differential scanning calorimetry (DSC).[10,11] However, the measured values are highly dependent on the experimental procedure utilized. For example, the reported sublimation enthalpy of Al(acac)$_3$ (**I**, where M = Al, n = 3) varies from 47.3 to 126 kJ mol^{-1}.[12] While other thermal techniques, such as thermogravimetric analysis (TGA), have been utilized in molecular decomposition studies,[13,14] the few reports using such an approach to determine sublimation

enthalpies have provided relatively accurate and precise values.[15,16] It is this method that we have employed to examine the thermochemical properties for selected metal β-diketonates.

RESULTS AND DISCUSSION

A series of metal β-diketonate complexes were obtained from commercial sources or prepared according to literature methods. Each compounds was purified by recrystallization or sublimation and used as a polycrystalline solid for thermogravimetric/differential thermal analyses (TG/DTA), see Experimental. The non-fluorinated (**I**, acetylacetonate, acac), *tris*-fluorinated (**II**, trifluoroacetylacetonate, tfac) and *hexakis*-fluorinated (**III**, hexafluoroacetylacetylacetonate, hfac) series of ligands were chosen to provide a measure of the effect on volatility with fluorine substitution. In addition, the *tert*-butyl substituted ligand (**IV**, 2,2,6,6-tetramethyl-3,5-heptanedionate, tmhd) was used to determine the effect of added steric bulk on volatility.
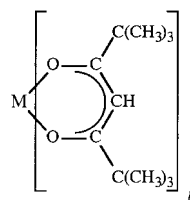
(**IV**)

Prior to a detailed analysis of volatility, it was important to first assess the volatility of each β-diketonate complex over a wide temperature range to ensure that each compound could be sublimed intact without decomposition, i.e., equation (1).

$$[M(\beta\text{-diketonate})_n]_{(solid)} \rightarrow [M(\beta\text{-diketonate})_n]_{(vapour)}$$

(1)
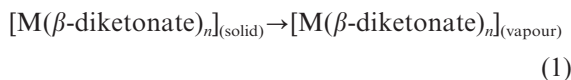
A simultaneous TG/DTA instrument was used to monitor the sample mass losses and energetic events as a function of temperature. The uniform mass loss of $M(\beta\text{-diketonate})_n$ is accompanied by a broad endothermic event characteristic of sublimation.[17] In some compounds this thermal event is quite broad or is shifted near the end of the sublimation process, while in other cases melting occurs as evi-

Table 1. Thermodynamic results on metal β-diketonate compounds*

Compound	M_w (g mol^{-1})	mp (°C)	Measured range (°C)	ΔH_{sub} (kJ mol^{-1})[†]	ΔS_{sub} (J K^{-1} mol^{-1})	T_{sub} calculated (°C)	T_{20} (°C)	Vapour pressure at at 150 °C (Torr)
Al(acac)$_3$	324	192	140–170	93 (119)[‡]	220	150	171	3.261
Al(tfac)$_3$	486	124	100–130	74 (101)[‡]	192	111	132	9.715
Al(hfac)$_3$	648	72	60–90	52 (72)[‡]	152	70	91	29.120
Al(tmhd)$_3$	577	256	140–170	88	213	140	161	3.378
Sc(acac)$_3$	342	205	140–170	95	224	151	172	3.218
Sc(tfac)$_3$	504	182	100–130	78	203	112	132	9.592
Sc(hfac)$_3$	666	90	60–90	55	159	73	94	28.890
Sc(tmhd)$_3$	595	151	140–170	90	218	142	162	3.331
Cr(acac)$_3$	349	214	140–170	91 (123)[21]	216	148	167	3.328
Cr(tfac)$_3$	511	185	100–130	71 (117)[21]	186	109	128	9.910
Cr(hfac)$_3$	673	84	60–90	46 (112)[21]	134	69	89	29.511
Cr(tmhd)$_3$	602	231	140–170	85	207	137	156	3.432
Fe(acac)$_3$	353	184	140–170	112 (113)[20]	259	161	182	2.781
Fe(tfac)$_3$	515	111	100–130	96	243	121	143	8.340
Fe(hfac)$_3$	677	97	60–90	60	169	81	101	25.021
Fe(tmhd)$_3$	606	164	140–170	111	263	150	177	2.910
Co(acac)$_2$	257	170	160–190	149	328	181	200	0.825
Co(tmhd)$_2$	426	254	160–190	143	322	171	192	0.898
Co(acac)$_3$	356	211	160–190	138 (118)[21]	311	170	190	1.059
Co(tfac)$_3$	518	155	100–130	119 (114)[21]	295	131	153	3.319
Co(hfac)$_3$	680	94	60–90	73	200	90	112	9.132
Co(tmhd)$_3$	609	143	160–190	132	305	161	179	1.211
Cu(acac)$_2$	262	284	140–170	120 (116)[39]	276	163	199	1.813
Cu(tfac)$_2$	369	195	100–130	112 (112)[21]	282	124	149	2.992
Cu(hfac)$_2$§	478	85	60–90	97 (108)[21]	287	81	89	4.045
Cu(tmhd)$_2$	430	198	140–170	114	273	155	189	1.994
Ga(acac)$_3$	367	193	140–170	90	214	147	168	3.339
Ga(tfac)$_3$	529	140	100–130	75	199	108	127	10.031
Ga(hfac)$_3$	691	83	60–90	53	157	68	88	30.115
Ga(tmhd)$_3$	619	220	140–170	87	213	138	157	3.459
Zr(acac)$_4$	488	172	140–170	126	289	162	185	1.719
Zr(tfac)$_4$	704	126	100–130	94	243	116	140	9.710
Zr(hfac)$_4$	919	42	60–90	59	166	83	105	24.890
Zr(tmhd)$_4$	824	319	140–170	120	278	159	180	1.872

* Melting points are from Strem Chemicals, Inc.
[†] Literature values given in parentheses.
[‡] Corresponds to the enthalpy of vaporization.[12]
§ Cu(hfac)$_2$.xH$_2$O ($\Delta H_{sub} = 102.0$ (kJ mol^{-1}), mp = 98 (°C).

denced by a sharp endotherm. Therefore, the position of this thermal event was not a good indicator of relative volatilities. In order to allow a simple and direct comparison of the relative volatility of the various compounds, a sublimation temperature was defined as the point when 20% mass loss had occurred (i.e., T_{20}) and T_{20} values were determined for each compound under flowing inert gas (argon): these values are listed in Table 1.

Determination of Sublimation Enthalpies (ΔH_{sub}) of Metal β-diketonates

The enthalpy of sublimation is a quantitative measure of the volatility of a particular solid. This information is useful when considering the feasibility of a particular precursor for CVD applications. An ideal sublimation process involves no compound decomposition and only results in a solid–gas phase
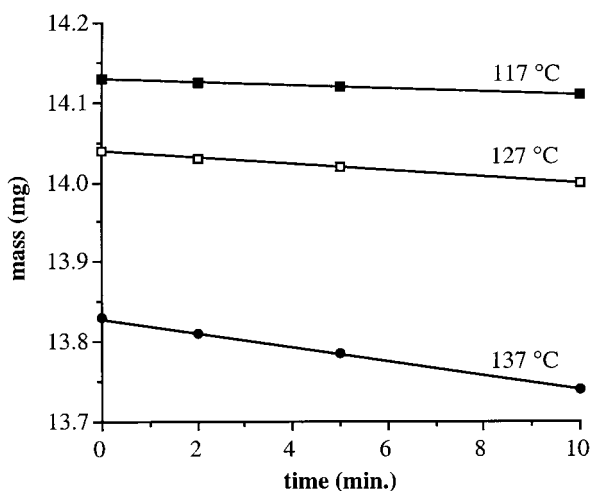
Fig. 1. Plot of TGA results for Cr(acac)$_3$ performed at different isothermal regions

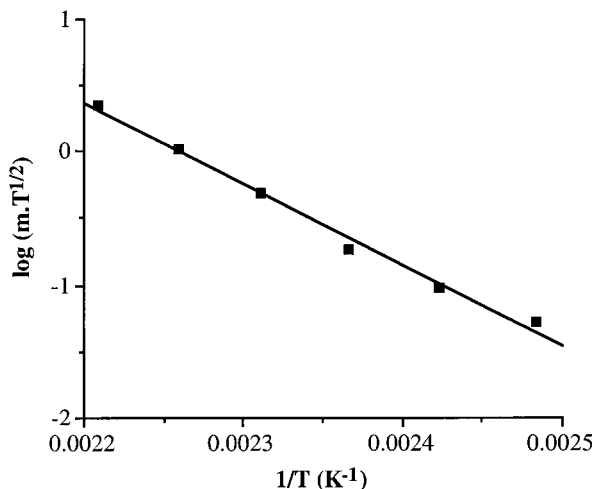Fig. 2. Plot of $\log(m_{sub}\sqrt{T})$ versus $1/T$ and the determination of the ΔH_{sub} (112.6 kJ mol^{-1}) for Fe(acac)$_3$ ($R^2 = 0.9989$)

change (i.e., equation (1)). Since phase changes are thermodynamic processes following zero-order kinetics, the evaporation rate or rate of mass loss by sublimation (m_{sub}), at a constant temperature (T), is constant at a given temperature (equation (2)).

$$m_{sub} = \frac{\Delta[\text{metal}\beta\text{-diketonate}]}{\Delta t} \qquad (2)$$

Therefore, the m_{sub} values may be directly determined from the linear mass loss of the TGA data in isothermal regions. As an illustrative example, Fig. 1 displays the data for the mass loss of Cr(acac)$_3$ at three isothermal regions under a constant argon flow. Each isothermal data set exhibits a linear relation ($R^2 > 0.99$). As expected for an endothermal phase change, the linear slope, equal to m_{sub}, increases with increasing temperature.

The Clausius–Clapeyron relation between pressure (p) and temperature (T),[18] shown in equation (3), forms the basis of analysing isothermal TGA data.

$$\frac{d \ln(p)}{dT} = \frac{\Delta H_{sub}}{RT^2} \qquad (3)$$

Since m_{sub} data are obtained from TGA data, it is necessary to utilize the Langmuir equation (4) which relates the vapour pressure of a solid with its sublimation rate.[19]

$$p = \left[\frac{2\pi RT}{M_w}\right]^{0.5} m_{sub} \qquad (4)$$

After integrating equation (3) in log form and substituting equation (4), one obtains the equality given by equation 5.[15]

$$\log(m_{sub}\sqrt{T}) = \frac{-0.0522(\Delta H_{sub})}{T}$$
$$+ \left[\frac{0.0522(\Delta H_{sub})}{T_{sub}} - \frac{1}{2}\log\left(\frac{1306}{M_w}\right)\right] \qquad (5)$$

Hence, the linear slope of a $\log(m_{sub}\sqrt{T})$ versus $1/T$ plot yields ΔH_{sub}. An example of a typical plot and the corresponding ΔH_{sub} value is shown in Fig. 2. In addition, the y intercept of such a plot provides a value for T_{sub}, the calculated sublimation temperature at atmospheric pressure.

Table 1 lists the results using the TGA method for a variety of metal β-diketonates. The value determined for Fe(acac)$_3$ shows a difference of less than 4% relative to the literature value[20] and is within experimental error of the value obtained by the analogous method on a different instrument reported by Gillan et al.[15] However, the values determined for M(acac)$_3$, M(tfac)$_3$ and M(hfac)$_3$ (M = Al, Cr), and Co(acac)$_3$ differ from previously reported values.[12,21] This may be rationalized by examining the methods utilized for each compound.

For $Cr(acac)_3$ and $Co(acac)_3$, isoteniscopic and sublimation bulb techniques were used, whose accuracy have long been questioned.[20] For the aluminium β-diketonate complexes, a comparable thermogravimetric approach was employed,[12] but, their system used buffer gas pressures in excess of 100 Torr. Since the pressure of their system was sufficiently greater than that used to obtain the values listed in Table 1, it is no surprise that a sufficient discrepancy exists between the two techniques. However, since both methods illustrate the same trend in ΔH_{sub} with increasing ligand fluorination, the data offset is most likely the direct consequence of differing system pressures. Since the system used in our experiments provides the same data that we have obtained using a dynamic vacuum, it is unlikely that a systematic error is being introduced into the numbers listed in Table 1 through the utilization of a steady flow of Ar gas. Furthermore, for all metal complexes, the order of volatility follows the trend acc < tfac < hfac which agrees with the order reported for Cu(II) complexes.[22]

The entropy of sublimation is readily calculated from the ΔH_{sub} and the calculated T_{sub} data in Table 1, equation (6). The range observed for all the metal β-diketonates compounds [$\Delta S_{sub} = 130–330$ J K^{-1} mol^{-1}] would be expected for a transformation giving translational and internal degrees of freedom. Interestingly, for any particular metal the lowest ΔS_{sub} are observed for the fluorinated derivatives, see Table 1.

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}} \qquad (6)$$

While the sublimation temperature is an important parameter to determine the suitability of potential precursor compounds for CVD, it is often preferable to express a compound's volatility in terms of its vapour pressure. However, while it is relatively straightforward to determine the vapour pressure of a liquid or gas, measurements of solids is difficult (e.g., use of the isoteniscopic method).[23] Substitution of equation (4) into equation (5) allows for the calculation of the vapour pressure (p) of the metal β-diketonates compounds as a function of temperature (T). The calculated vapour pressures for each of the metal β-diketonates compounds at 150 °C are given in Table 1. We have found the TGA approach to show reasonable agreement with

previous measurements. For example, the value calculated for $Fe(acac)_3$ (e.g., 2.78 Torr at 113 °C) is slightly higher than that measured directly by the isoteniscopic method (0.53 Torr at 113 °C), however, it should be noted that measurements using the sublimation bulb method obtained values much lower (8×10^{-3} Torr at 113 °C).[24] Based on these results, we propose that this TGA method offers a suitable alternative to conventional (direct) measurements of vapour pressure.

Structural Correlations Between Calculated ΔH_{sub} Values

The measured ΔH_{sub} values for $M(acac)_3$ and $M(tmhd)_3$ complexes indicate that replacing the methyl groups with tert-butyl moieties slightly increases the volatility of the complex. Although it would be expected that the increased mass [i.e., $Al(acac)_3 = 324.31$ g mol^{-1} versus $Al(tmhd)_3 = 576.80$ g mol^{-1}] should decrease the overall volatility of the complex, the relatively low enthalpy values indicate that the C–H $\cdots$ H–C interactions between neighbouring tert-butyl groups is approximately equal in magnitude to methyl $\cdots$ methyl interactions. In all cases, the tmhd derivative has a ΔH value of between 93 and 99% of that of the acac derivative. This effect is irrespective of the number of the oxidation state of the metal, i.e., the number of β-diketonate ligands.

As was expected based upon previous workers' results, the fluorinated complexes are more volatile than the non-fluorinated derivatives. Furthermore, the higher the fluorination (i.e., hfac versus tfac versus acac) the greater the increase in volatility. This trend is expected based solely upon the difference in intermolecular C–H $\cdots$ H–C versus C–H $\cdots$ F–C versus C–F $\cdots$ F–C interactions. Fig. 3(a) represents a comparison of the ΔH_{sub} for $M(tfac)_n$ and $M(hfac)_n$ normalized to $M(acac)_n$. This shows that replacement of one CH_3 (per ligand) with CF_3 results in a decrease in ΔH_{sub} of ca. 83% for M(β-diketonate)$_3$ irrespective of the identity of the metal. Replacing the second CH_3 results in another 66% decrease in the ΔH_{sub}. It may be clearly seen from Fig. 3(a) that the amount of decrease is dependent on the oxidation state of the metal, i.e., more ligands cause a larger change in volatility. A similar trend is observed for T_{sub} (Fig. 3(b)); however, there appears to be no effect by changing the number of ligands (oxidation state).
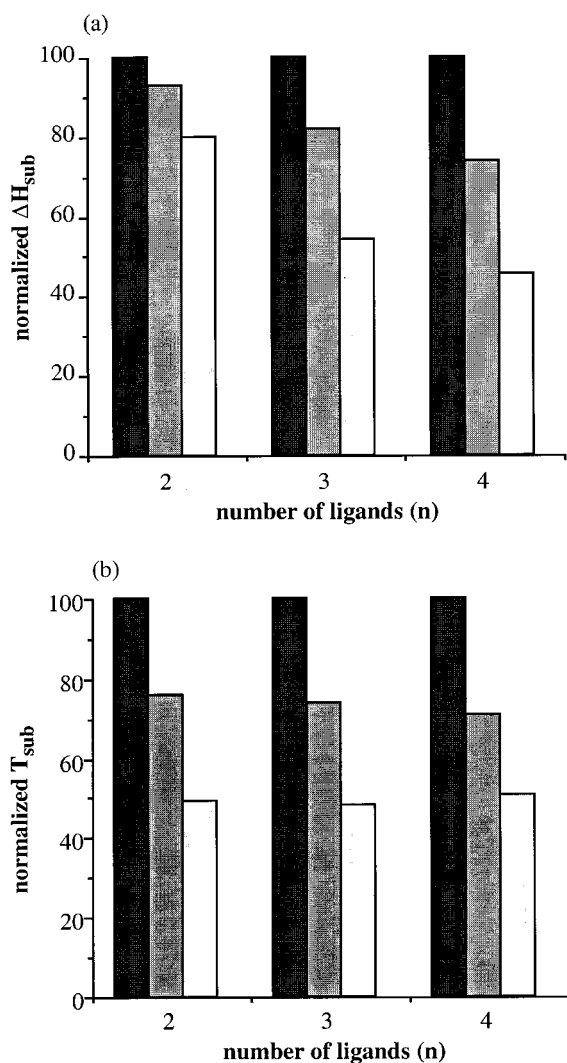
Fig. 3. Plot of relative (a) ΔH_{sub} and (b) T_{sub}, normalized to $M(acac)_n$, versus the number of β-diketonate ligands (n); acac (■), tfac (■) and hfac (□)

We propose that the relationship between the ΔH_{sub} and T_{sub} of the fluorinated derivatives as compared with the values for $M(acac)_n$ may be used to predict either quantity for a range of $M(tfac)_n$ and $M(hfac)_n$ complexes where the values for the parent $M(acac)_n$ are known. In fact, with similar trends it should be possible to determine these values for a wide range of β-diketonate complexes. An interesting application of these relationships is that the deviation from the expected trend may be used to

confirm the presence or absence of oligomers for the sterically undemanding complexes, i.e., $Ba(acac)_2$ is known to exist as an oligomer in the solid and vapour state and hence has a significantly lower volatility than $M(tmhd)_2$. Finally, the ΔH_{sub} and T_{sub} may be indirectly determined for compounds that decompose during sublimation.

The *tris*-acetylacetonate complexes of Al(III),[25] Cr(III),[26] Co(III),[27] and Ga(III)[28] form a monoclinic isomorphic set of solid state structures, crystallizing in the P2$_1$/c space group. By comparison, Fe $(acac)_3$[29] and $Sc(acac)_3$[30] each possess orthorhombic structures, in the Pbca space group. Since the structures of the Al, Cr, Co and Ga acetylacetonate complexes are isomorphous, one would expect the volatility to be related to the molecular weight of the complex, since no factors such as differing metal oxidation states or fluorinated ligands exist. Fig. 4 shows plots of sublimation enthalpies for (a) $M(acac)_3$, (b) $M(tmhd)_3$, (c) $M(tfac)_3$ and (d) $M(hfac)_3$ as a function of molecular weight. Two different trends between volatility and molecular weight are observed; d^n transition metal complexes exhibit a linear correlation whereas no correlation between molecular weight and volatility is evident for d^0 metal complexes, see Fig. 4(a). While Gillan et al.[15] discovered a link between volatility and molecular mass, they also found that the degree of branching of alkyl groups was more influential than molecular mass on the volatility of a series of gallium chalcogenide cubanes, presumably due to stronger intermolecular interactions. Since the similar volatilities between $M(acac)_3$ and $M(tmhd)_3$ complexes also indicate that molecular weight is relatively unimportant, the nature and degree of the intermolecular interactions are likely to be predominant factors in the volatilities for these complexes.

Table 2 lists the closest intermolecular interactions and number of neighbouring molecules for $M(acac)_3$ complexes. ΔH_{sub} values for the $M(acac)_3$ complexes indicate that $Co(acac)_3$ and $Fe(acac)_3$ should have the most intermolecular interactions giving rise to the lowest volatility. For $Co(acac)_3$, the closest interactions are the C–H $\cdots$ O (C $\cdots$ O = 348 Å) which is lower than the sum of the Van der Waals' radii (ca. 3.5 Å[31]). No such interaction exists for the $Fe(acac)_3$ complex, as the closest C–H $\cdots$ O distance is 3.956 Å; outside the sum of the Van der Waals' radii. However, in $Fe(acac)_3$, C–H $\cdots$ H–C (methyl . . . methyl and methyl . . . meth-
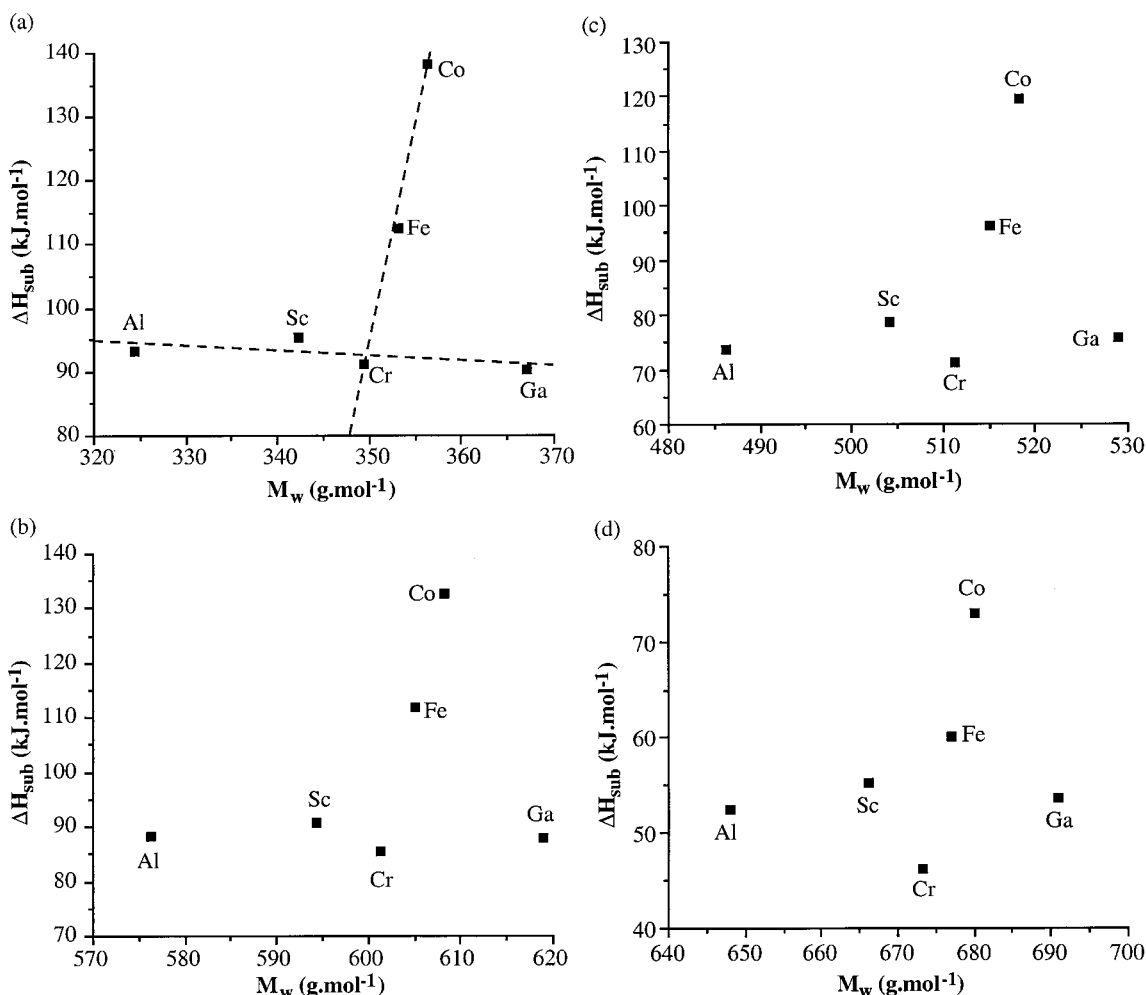
Fig. 4. Plot of ΔH_{sub} versus molecular weight for (a) M(acac)$_3$, (b) M(tmhd)$_3$, (c) M(tfac)$_3$ and (d) M(hfac)$_3$ complexes

ine) are the predominant interactions and much stronger in magnitude than the analogous contacts in Co(acac)$_3$. Hence, the lack of C–H $\cdots$ O interactions in the Fe(acac)$_3$ complex relative to the cobalt analogue most likely contributes to the observed greater volatility. The intermolecular interactions for Cr(acac)$_3$, Al(acac)$_3$, Sc(acac)$_3$ and Ga(acac)$_3$ are all comparable (see Table 2) which would correspond to the similarity in the measured ΔH_{sub} values for these complexes. The major intermolecular contacts are the C–H $\cdots$ H–C inter-

actions since the C–H $\cdots$ O distances are all greater than the sum of the Van der Waals' radii. Although Sc(acac)$_3$ crystallizes in the same space group as Fe(acac)$_3$, the CH$_3$ $\cdots$ HC distance is much shorter for Fe(acac)$_3$, which must account for the significantly lower volatility of Fe(acac)$_3$. Fig. 5 illustrates the relationship between the shortest intermolecular interaction (below the sum of the appropriate van der Waal radii) and the ΔH_{sub}. A general trend is observed of decreasing intermolecular contacts with decreasing volatility for

Table 2. Comparison of the shortest intermolecular contacts for M(acac)$_3$ complexes*

Compound	Number of nearest neighbours	C–H···O (Å)	C–H···H–C† (Å)	C–H···C‡ (Å)
Al(acac)$_3$	4	3.578	3.850	3.765
Sc(acac)$_3$	6	3.820	3.670	3.870
Cr(acac)$_3$	4	3.516	3.912	3.894
Fe(acac)$_3$	6	3.956	3.669	3.696
Co(acac)$_3$	4	3.458	3.859	3.833
Ga(acac)$_3$	4	3.587	3.890	3.774

* The sum of the Van der Waals' radii for C–H ··· O and C–H ··· H–C are *ca.* 3.5 Å and 4.0 Å, respectively.
† Methyl . . . methyl interaction.
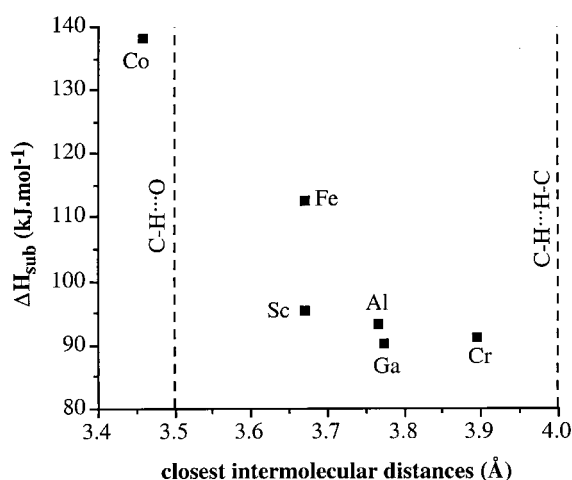‡ Methyl . . . methine interaction.

Fig. 5. Plot of the ΔH_{sub} values versus the closest intermolecular contact distances (Å) for M(acac)$_3$ complexes illustrating the general trend of increasing volatility with increasing intermolecular contacts. The sum of the Van der Waals' radii for C–H ··· O and C–H ··· H–C are shown

M(acac)$_3$ complexes. For Co(acac)$_3$, the short C–H ··· O distance appears to be most responsible for the significantly lower volatility exhibited by this complex. For all other compounds, the C–H ··· H–C interactions are predominant; their variance is roughly in accord with the measured ΔH_{sub} values.

The large inductive effect created by CF$_3$ groups should give rise to a significantly different charge distribution in the chelate ring and a correspondingly different co-ordination sphere in fluorinated derivatives relative to acac complexes.[32] However, the co-ordination environments in

Al(tfac)$_3$,[33] Co(tfac)$_3$,[33] Fe(hfac)$_3$,[34] Cu(hfac)$_2$[35,36] and Cu(tmhd)$_2$[37] are essentially isostructural to their acac counterparts. Hence, as expected, the same overall volatility trends previously described for M(acac)$_3$ complexes are observed for the tfac and hfac analogues (Fig. 4).

CONCLUSIONS

The sublimation enthalpies (ΔH_{sub}) and sublimation temperatures (T_{sub}) for a series of metal β-diketonate complexes, M(β-diketonate)$_n$, were determined using thermogravimetric analysis. Replacing methyl groups in M(acac)$_n$ with *tert*-butyl groups in M(tmhd)$_n$ had little effect on the volatility (although the effect is to generally increase the volatility). In contrast, replacement of methyl with CF$_3$ units significantly increased the volatility in the order M(acac)$_n$ < M(tfac)$_n$ < M(hfac)$_n$. The relationship between this homologous series may be used to predict the ΔH_{sub} and/or T_{sub} for unknown members of the series.

For the d^n transition metal, *tris*-β-diketonate complexes investigated, the increase in volatility of a series of homologous compounds was observed to increase linearly with the molecular weight of the complex. By contrast, the volatility of analogous d^0 metal chelates was independent of molecular weight and the degree and nature of intermolecular interactions. Investigation of the closest intermolecular interactions shows that this appears to be the controlling factor in determining the sublimation enthalpies (ΔH_{sub}).

EXPERIMENTAL SECTION

Compounds Sc(hfac)$_3$, Cr(hfac)$_3$, Fe(hfac)$_3$, Co(hfac)$_3$, Co(tmhd)$_3$, Cu(hfac)$_2$.xH$_2$O Zr(tfac)$_4$ and Zr(hfac)$_4$ were prepared by the literature method.[38] All other metal β-diketonate complexes were purchased (Strem or Aldrich) and were purified by recrystallization in acetone or by vacuum sublimation prior to use. Compound Cu(hfac)$_2$ was synthesized by sublimation of Cu(hfac)$_2$.xH$_2$O under dynamic vacuum at 60–70 °C. Upon exposure to air, the blue anhydrous crystals rapidly turned green due to hydrate formation. Although all compounds are available commercially, there

Table 3. Multinuclear NMR characterization of synthesized metal β-diketonates*†

Compound	^{1}H	^{13}C	^{19}F
Al(tfac)$_3$	5.63 (C$\underline{H}_3$)	191.2 ($\underline{C}$OCH$_3$)	−75.89
	1.47 (C$\underline{H}$)	173.2 ($\underline{C}$OCF$_3$)	
		117.2 ($\underline{C}$F$_3$)	
		97.6 ($\underline{C}$H)	
		28.1 ($\underline{C}$H$_3$)	
Al(hfac)$_3$	0.94 (C$\underline{H}$)	181.2 ($\underline{C}$O)	−75.90
		116.6 ($\underline{C}$F$_3$)	
		94.8 ($\underline{C}$H)	
Cr(hfac)$_3$	0.92 (C$\underline{H}$)	180.9 ($\underline{C}$O)	−75.72
		115.9 ($\underline{C}$F$_3$)	
		94.0 ($\underline{C}$H)	
Fe(hfac)$_3$	0.89 (C$\underline{H}$)	180.1 ($\underline{C}$O)	−75.18
		115.6 ($\underline{C}$F$_3$)	
		93.2 ($\underline{C}$H)	
Co(tfac)$_3$	5.51 (C$\underline{H}_3$)	188.9 ($\underline{C}$OCH$_3$)	−75.64
	1.28 (C$\underline{H}$)	171.0 ($\underline{C}$OCF$_3$)	
		116.0 ($\underline{C}$F$_3$)	
		26.9 ($\underline{C}$H$_3$)	
		94.5 ($\underline{C}$H)	
Cu(tfac)$_2$	5.22 (C$\underline{H}_3$)	190.1 ($\underline{C}$OCH$_3$)	−76.05
	1.32 (C$\underline{H}$)	168.5 ($\underline{C}$OCF$_3$)	
		116.7 ($\underline{C}$F$_3$)	
		96.2 ($\underline{C}$H)	
		27.5 ($\underline{C}$H$_3$)	
Cu(hfac)$_2$	0.91 (C$\underline{H}$)	183.1 ($\underline{C}$O)	−76.35
		117.1 ($\underline{C}$F$_3$)	
		95.5 ($\underline{C}$H)	
Zrtfac)$_4$	5.73 (C$\underline{H}_3$)	190.8 ($\underline{C}$OCH$_3$)	−75.38
	1.55 (C$\underline{H}$)	172.8 ($\underline{C}$OCF$_3$)	
		116.9 ($\underline{C}$F$_3$)	
		95.2 ($\underline{C}$H)	
		27.4 ($\underline{C}$H$_3$)	

* Chemical shifts (δ) in ppm.
† Assignments given in parentheses.

are incomplete reports of their NMR characterization in the literature. Hence, ^{19}F, ^{13}C and ^{1}H NMR characterizations were performed on the synthesized complexes (Table 3) using a Bruker 250 MHz and 400 MHz multinuclear spectrometer.

Thermogravimetric analyses experiments were performed on a TA Instruments Simultaneous Differential Techniques (SDT 2960) TGA-DTA system using the methods previously described.[15] The argon flow rate was set to 90.0 ml min^{-1} and was carefully monitored to ensure a steady flow rate during runs and an identical flow rate from one set of data to the next. Samples of iron acetylacetonate was used as a calibration standard through ΔH_{sub} determinations before each day of use. If the measured value of the sublimation enthalpy for Fe(a-

cac)$_3$ was found to differ from the literature value by more than 5%, the sample was reanalysed and the flow rates were optimized until an appropriate value was obtained. Only after such a calibration was optimized would other metal complexes be analysed in this manner. As the surface area of a given crystallite decreases during the experiment, the sublimation rate will also decrease, therefore, to ensure that the solid displayed a near constant surface area, data were taken over small temperature ranges (*ca.* 30–40 °C) and the overall mass loss was kept relatively low. This latter condition was imposed on the experiments since we have previously found that 25% overall mass loss corresponded to a change in surface area of less than 15%.[15] The mass loss versus time curves were monitored for the compounds being investigated to ensure linearity was maintained. Any *n*th order deviations for these trends would correspond to decomposition processes for the solids being investigated. Also, through the utilization of a simultaneous TG/DTA system, it would have been possible to observe such exothermic events for a particular solid. No such features were observed for the compounds over the temperature ranges investigated. All the compounds investigated exhibited full sublimation/vaporization, leaving less than 3% residue in most cases. Since the enthalpies of sublimation were to be compared, the isothermal ranges investigated were those below the melting points of the compounds studied (see Table 1). For the M(hfac)$_n$ complexes this required that temperature ranges close to ambient were used for the analyses.

REFERENCES

1. Rees WS Jr. *CVD of Nonmetals*. VCH: New York, 1996.
2. Kodas T, Hampden-Smith M. *The Chemistry of Metal CVD*. VCH: New York, 1996.
3. Samuels JA, Folting K, Huffman JC, Caulton KG. *Chem. Mater.* 1995; **7**: 929.

4. See, for example, (a) Jefferies PM, Wilson SR, Girolami GS. *Inorg. Chem.* 1992; **31**: 4503; (b) Bradley DC, Chudzynska H, Hammond ME, Hursthouse MB, Motevalli M, Ruowen W. *Polyhedron* 1992; **11**: 375; (c) Purdy AP, Berry AD, Holm RT, Fatemi M, Gaskill DK, *Inorg. Chem.* 1989; **28**: 2799; (d) Thompson SC, Cole-Hamilton DJ, Gilliland DD, Hitchman ML, Barnes JC. *Adv. Mater. Optics Electron* 1992; **1**: 81; (e) Belcher R, Cranley CR, Majer JR, Stephen WI, Uden PC. *Anal. Chim. Acta* 1972; **60**: 109.

5. Reed TM III. In *Fluorine Chemistry*, Vol. 5, Simons JH (ed). Academic Press: New York, 1964; 133.

6. Gleizes A, Julve M, Kuzimina N, Alikhanyan A, Lloret F, Malkerova I, Sanz JL, Senoca F. *Eur. J. Inorg. Chem.* 1998; **8**: 1169.

7. Westwell MS, Searle MS, Wales DJ, Williams DH. *J. Am. Chem. Soc.* 1995; **117**(18): 5013.

8. Hill JO, Murray JP. *Rev. Inorg. Chem.* 1993; **13**: 125.

9. Beech G, Lintonbon RM. *Thermochim. Acta* 1971; **3**: 97.

10. Murray JP, Cavell KJ, Hill JO. *Thermochim. Acta* 1980; **36**: 97.

11. Torres-Gomez LA, Barreiro-Rodriquez G, Galarza-Mondragon A. *Thermochim. Acta* 1988; **124**: 229.

12. Pauleau Y, Dulac O. *Chem. Mater.* 1991; **3**(2): 281.

13. Bukovec N, Bukovec P, Siftar J. *Thermochim. Acta* 1980; **35**: 85.

14. Slifirski J, Huchet G, Marty A, Teyssandier F. *Chem. Mater.* 1995; **7**: 622.

15. Gillan EG, Bott SG, Barron AR. *Chem. Mater.* 1997; **9**(3): 796.

16. Ashcroft SJ. *Thermochim. Acta* 1971; **2**: 512.

17. Turi EA, Khanna YP, Taylor TJ. In *A Guide to Materials Characterization and Analysis*, Sibilia JP (ed). VCH: New York, 1988; chapter 9.

18. Atkins PW. *Physical Chemistry*, 5th edn. W.H. Freeman: New York, 1994; 198.

19. Langmuir I. *Phys. Rev.* 1913; **2**: 329.

20. Sabbah R, Tabet D, Belaadi S. *Thermochim. Acta* 1994; **247**: 193.

21. Ribeiro da Silva MAV, Ferrao MLCCH. *Pure and Appl. Chem.* 1988; **60**(8): 1225.

22. Baidina IA, Sabnikov PA, Igumenov IK, Borisov SV. *Koord. Khim.* 1984; **10**: 948.

23. Arm H, Daeniker H, Schaller R. *Helv. Chim. Acta* 1966; **48**: 1772.

24. Sachinidis J, Hill JO. *Thermochimica Acta* 1980; **35**: 59.

25. (a) Hon PK, Pfluger CE. *J. Coord. Chem.* 1973; **3**; 67; (b) Rahman A, Ahmed SN, Khair MA, Zangrando E, Randaccio L, *J. Bangladesh Acad. Sci* 1990; **14**: 161.

26. Morosin B. *Acta Crystallogr.* 1965; **19**: 131.

27. Kruger GJ, Reynhardt EC. *Acta Cryst.* 1974; **B30**: 822.

28. Dymock K, Palenik GJ. *Acta Cryst.* 1974; **B30**: 1364.

29. Roof RB. *Acta Cryst.* 1956; **9**: 781.

30. Anderson TJ, Newman MA, Melson GA. *Inorg. Chem.* 1973; **12**: 927.

31. *Handbook of Chemistry and Physics*, 60th edn. CRC Press: Boca Raton, 1980.

32. Watkins CL, Harris ME. *J. Inorg. Nucl. Chem.* 1978; **40**: 1769.

33. Vogelson CT, Edwards CL, Kobylivker AN, Chacko SB, Moran CE, Dalton K, Stewart SM, Werner BC, Bott SG, Barron AR. *J. Chem. Cryst.* 1998; **28**(11): 815.

34. Pfluger CE, Haradem PS. *Inorg. Chim. Acta* 1983; **69**: 141.

35. Jain A, Kodas TT, Corbitt TS, Hampden-Smith MJ. *Chem. Mater.* 1996; **8**: 1119.

36. Pinkas J, Huffman JC, Baxter DV, Chisholm MH, Caulton KG. *Chem. Mater.* 1995; **7**: 1589.

37. Patnaik S, Guru Row TN, Raghunathan L, Devi A, Goswami J, Shivashankar SA, Chandrasekaran S, Robinson WT. *Acta Cryst.* 1996; **C52**: 891.

38. Morris ML, Moshier RW, Sievers RE. *Inorg. Chem.* 1963; **2**: 411.

39. Ribeiro da Silva MAV, Ferrao MLCCH. *J. Chem. Thermodyn.* 1994; **26**: 315.