parameters (C only) for phenyl groups. Three values for thermal parameters of phenyl H were also refined, for those attached to ortho, meta, or para carbons (with respect to the linkage to P), respectively. Scattering factors[36,37] and anomalous dispersion terms[37] were applied. A final difference electron density map was essentially featureless, the maximum peak being about $^2/_3$ e/Å^3. Final positional and thermal parameters are given in Table VII. A table of structure factors is available.[40]

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Registry No. **1a**, 53687-46-0; **1a**-d_1, 82808-04-6; **1b**, 53754-45-3; **1c**, 76287-18-8; Li[**2a**], 97112-45-3; K[**2a**], 97112-46-4; K[18-crown-6][**2a**], 85422-35-1; K[18-crown-6][**2a**]CH$_3$COC$_2$H$_5$·H$_2$O, 97112-47-5; [Et$_4$N][**2b**], 85422-28-2; [Me$_4$N][**2b**], 85422-36-2; [Me$_4$N][**2c**], 97112-49-7; [Et$_4$N][**3a**], 85369-53-5; [Et$_4$N][**3b**], 85369-55-7; [Et$_4$N][**3c**], 85422-32-8; [Et$_4$N][**4a**], 85422-34-0; K[18-crown-6][**4b**], 85442-20-2; [PPN][**8a**], 97112-44-2; [*closo*-3,3-(PPh$_3$)$_2$-3-Br-3,1,2-RhC$_2$P$_9$H$_{11}$], 97112-48-6; Tl$_2$C$_2$B$_9$B$_{11}$, 97102-40-4; *trans*-IrCl(CO)(PPh$_3$)$_2$, 59246-46-7.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, and parameters for atoms treated as rigid groups, a complete listing of interatomic angles, and a listing of least-squares planes for **2a** and **2b** (66 pages). Ordering information is given on any current masthead page.

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Vapor Pressures and Enthalpies of Sublimation and Evaporation of Trifluoroacetylacetonates in Helium and Helium Containing the Ligand Vapor

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The vapor pressures of 21 metal trifluoroacetylacetonates were determined in helium and in helium containing the ligand vapor by using transpiration techniques. The vapor pressure of hydrated chelates can be measured only in helium containing the ligand vapor because considerable thermal decomposition occurs in helium. The volatility is mainly dependent on their structure. The predominant factor that decides volatility of coordination-saturated trifluoroacetylacetonates such as octahedral and tetrahedral chelates is van der Waals forces, while other strong forces are apparent in square-planar and square-pyramidal chelates. From the Clausius–Clapeyron equation, sublimation enthalpies and evaporation enthalpies of coordination-saturated chelates are generally 28 ± 2 and 19 ± 2 kcal mol^{-1}, respectively, and those of cobalt(II), nickel(II), and rare-earth-metal trifluoroacetylacetonates are larger than these values. The values measured by the Freeman–Carroll method for some chelates agreed well with those of the Clausius–Clapeyron equation.

Introduction

The study of volatile metal chelates has been extended into the field of gas chromatography and other practical techniques. Particularly, β-diketonates are important and of wide range of use. However, the vapor pressures of β-diketonates are not well studied, and there are few systematic data. Berg and Truemper[1] reported the vapor pressure of various metal β-diketonates, but they found no correlation with sublimation temperature or heat of sublimation for a series of chelates. It was later pointed out that the results were erroneous because thermal decomposition accompanied the measurement by an isoteniscope. Sicre et al.[2] reported the vapor pressure of rare-earth metal 2,2,6,6-tetramethyl-3,5-heptanedionates by a spoon gauge and discussed the relation between the ionic radius and the heats of sublimation and vaporization. Wolf et al.[3] reported the vapor pressure of aluminum and chromium β-diketonates and some other thermally stable β-diketonates and discussed the volatility on the basis of the difference of ligands. Reliable data are limited to these few chelates, and other studies are often discrepant. This is because many β-diketonates are subject to partial thermal decomposition, and the products often are more volatile than chelates and interfere in the determination of vapor pressure by static methods.

The authors have reported[4] that the β-diketonates are stabilized at high temperatures and are quantitatively eluted from gas chromatographic columns by using a carrier gas containing the ligand vapor. This technique was effectively applied to measurements of vapor pressure by the transpiration method.[5] In this paper, the vapor pressures of 21 metal trifluoroacetylacetonates (M(tfa)$_n$) were measured by this method, and the results were discussed as to the structure and the volatility of the chelates.

Experimental Section

Reagents and Preparation of Chelates. Commercial 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone) was purified by refluxing in the presence of disodium hydrogenphosphate, which was added to remove trifluoroacetic acid contained as a major impurity, and distilled at 107 °C.

The following chelates were prepared: Al(tfa)$_3$, Sc(tfa)$_3$, Fe(tfa)$_3$, Ni(tfa)$_2$, Cu(tfa)$_2$, Zn(tfa)$_2$, Ga(tfa)$_3$, In(tfa)$_3$ Er(tfa)$_3$, Tm(tfa)$_3$, Yb(tfa)$_3$, and Lu(tfa)$_3$. About 1 g of metal, oxide, or salt was dissolved in acid or water, the acid used depending on the sample characteristics. For example, gallium metal and indium oxide were dissolved in hot concentrated nitric acid, scandium and rare-earth oxides in hot concentrated hydrochloric acid, and aluminum chloride, iron chloride, nickel nitrate, copper sulfate, and zinc sulfate in water. These solutions were neutralized with 1 M aqueous ammonia or, for nickel, copper, and zinc solutions, with 1 M sodium hydroxide. The precipitated metal hydroxides were centrifuged and washed twice with distilled water. A small excess over the calcualted amount of H(tfa) was added to the precipitate, and the mixture was warmed to about 80 °C. The supernatant liquid was removed by decantation, and the chelate was filtered off on a glass filter and washed successively with water and hexane. The nickel, copper, and zinc chelates were dissolved in diethyl ether, heavy rare-earth-metal chelates in diisopropyl ether, and the other chelates in benzene. The insoluble materials, if any, were removed by filtration, and the chelates were recovered by the evaporation of the organic solvent in a clean dry air stream. The other chelates used were prepared according to previously reported procedures.[6]

Vapor Pressure Measurements. A Shimadzu Model GC-6A gas chromatograph equipped with a ligand vapor generator was used. The

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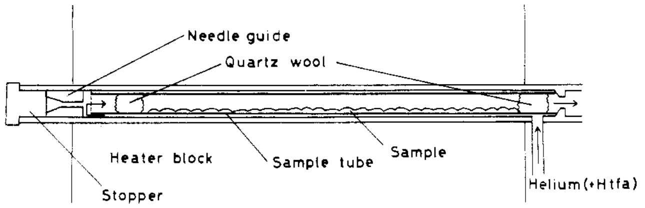

Figure 1. Sample chamber.

ligand concentration in the carrier gas was about 1.0% v/v. A Pyrex sample tube (88 mm × 3.5 mm i.d.; 0.5 mm wall thickness) was used.

A precisely weighed sample tube containing the measuring substance (15–25 mg) was inserted into the injection chamber (5-mm bore), which was preheated at a chosen temperature, and the entrance of the injection port was tightly closed with a silicone gum stopper (Figure 1). The carrier gas (helium or helium containing the vapor of trifluoroacetylacetone) was passed through the tube at a constant flow rate. The tube was kept at the temperature for a definite time, removed from the injection chamber, cooled in a desiccator, and weighed again. The temperature of the injection chamber was raised stepwise, and the procedure was repeated as above. For hydrated chelates, the samples were preheated in the carrier gas containing H(tfa) vapor for 10 min to dehydrate[7] coordinated water: $Zn(tfa)_2$, 80 °C; $Co(tfa)_2$, 90 °C; $Er(tfa)_3$, $Tm(tfa)_3$, $Yb(tfa)_3$, and $Lu(tfa)_3$, 100 °C; $Ni(tfa)_2$, 120 °C. These samples, with both ends of sample tube sealed with caps, were cooled and reserved in a desiccator until the vapor pressure measurement was carried out.

Calculation of Vapor Pressure and Sublimation Enthalpy. It is possible to calculate the vapor pressure of a sample from weight loss (amount vaporized), the flow rate, and the heating time when the vapor of a sample is saturated in a stream of carrier gas. The following equation was used:

$$P = 62.36wT/Mvt$$

where P = vapor pressure of the sample (mmHg), w = weight loss (mg), T = room temperature (K), M = molecular weight of the sample in the vapor phase, v = flow rate of the carrier gas at room temperature, and t = heating time (min). In this paper, it was assumed that all of the substances were monomeric in the vapor phase.

The sublimation and evaporation enthalpies were calculated from the slope of the Clausius–Clapeyron plots as shown by the equation

$$\ln P/760 = -\Delta H/RT + \Delta S/R$$

The accuracy of the vapor pressure and the sublimation and evaporation enthalpy determinations was confirmed by using some standard substances.[5]

Calculation of the Sublimation and Evaporation Enthalpy by Thermogravimetry. A Rigaku Model 8075 instrument was used for thermogravimetry. The temperature was calibrated by using the melting point of tin (231.9 °C) as reference. The sample taken was 10.0 mg, the flow rate was 20 mL min^{-1}, and the heating rate was 2.5 °C min^{-1}.

The sublimation and evaporation enthalpies were calculated from thermogravimetric curves according to the Freeman–Carroll equation[8]

$$\log(-\mathrm{d}X/\mathrm{d}t) - n\log X = \log A - \Delta H/2.303RT \qquad (1)$$

where $-\mathrm{d}X/\mathrm{d}t$ = rate of weight loss, n = order of reaction, X = mole fraction of chelates, A = constant, ΔH = sublimation or evaporation enthalpy, R = gas constant, and T = absolute temperature. Here, the plots of $\log(-\mathrm{d}X/\mathrm{d}t) - n\log X$ vs. T^{-1} should result in straight lines with slopes of $-\Delta H/2.303R$

The reaction order was determined by Chatterjee's method.[9] Two measurements were carried out for the same chelate, changing the initial amount of a sample, and simultaneous equations were obtained from eq 1 at the same temperature.

$$n\log X_1 - \log(-\mathrm{d}X/\mathrm{d}t)_1 = \Delta H/2.303RT_k - \log A$$

$$n\log X_2 - \log(-\mathrm{d}X/\mathrm{d}t)_2 = \Delta H/2.303RT_k - \log A$$

$$n = \{\log(-\mathrm{d}X/\mathrm{d}t)_1 - \log(-\mathrm{d}X/\mathrm{d}t)_2\}/(\log X_1 - \log X_2)$$

From the plots of n vs. T, the value of n and the temperature dependency are obtained.

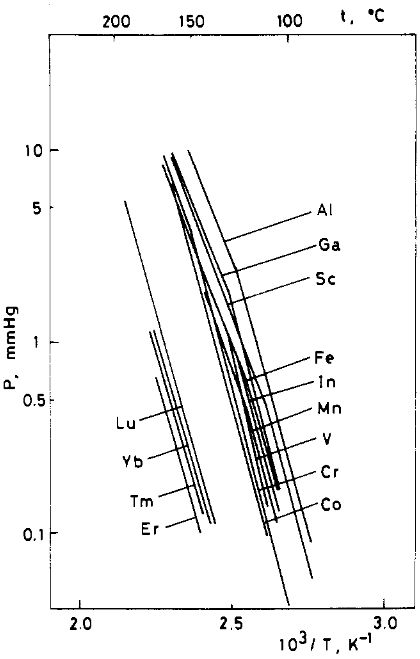

Figure 2. Clausius–Clapeyron plots for tris(trifluoroacetylacetonates). Plots for rare-earth-metal chelates were determined in helium containing H(tfa) vapor, and plots for others were determined in helium.

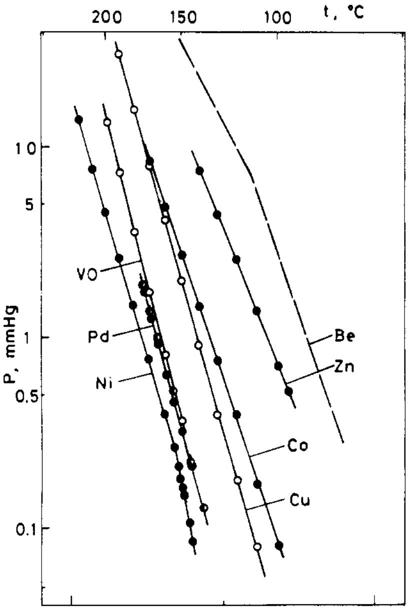

Figure 3. Clausius–Clapeyron plots for bis(trifluoroacetylacetonates): ●, in helium containing H(tfa) vapor; ○ and ◐, in helium; dashed line, from ref 15.

Measurements of the Melting Point. A Yanagimoto micro melting point apparatus was used for the measurements of the melting point of trifluoroacetylacetonates.

Results and Discussion

The prepared chelates are classified into two types of chelates, anhydrous and hydrated ones. Anhydrous[10] chelates such as $Al(tfa)_3$, $Sc(tfa)_3$, $V(tfa)_3$, $VO(tfa)_2$, $Cr(tfa)_3$, $Mn(tfa)_3$, $Fe(tfa)_3$, $Co(tfa)_3$, $Cu(tfa)_2$, $Ga(tfa)_3$, $Zr(tfa)_4$, $Pd(tfa)_2$, $In(tfa)_3$, and $Hf(tfa)_4$ show the same thermal behaviors in helium and in helium containing H(tfa) vapor. The melting points and the vapor pressures are almost identical in the two atmospheres. In contrast,

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(10) Here, "anhydrous chelates" are anhydrous as prepared. Hydrated chelates that are dehydrated in the carrier gas containing H(tfa) vapor are described as "dehydrated chelates".

Table I. Vapor Pressure, Sublimation Enthalpy, and Evaporation Enthalpy for Trifluoroacetylacetonates

chelates	*A*[a]	*B*[a]	sublim enthalpy, kcal mol^{-1}	evap enthalpy, kcal mol^{-1}	measd temp range, °C	mp,[b] °C
$Al(tfa)_3$	35.2 ± 0.4	13.6 ± 0.1	27.1 ± 0.3		90–150	122–123 (120)
	24.9 ± 0.4	9.6 ± 0.2		19.0 ± 0.3		
$Sc(tfa)_3$	36.2 ± 0.5	14.1 ± 0.2	28.1 ± 0.4		90–160	107–109 (108)
	24.6 ± 0.3	9.7 ± 0.1		19.3 ± 0.2		
$V(tfa)_3$	35.4 ± 0.6	14.3 ± 0.2	28.3 ± 0.5		110–160	133–134 (133)
	23.4 ± 0.2	9.4 ± 0.09		18.6 ± 0.2		
$VO(tfa)_2$	33.0 ± 0.2	14.4 ± 0.1	28.6 ± 0.2		150–200	229–235[c]
$Cr(tfa)_3$	34.0 ± 0.3	13.9 ± 0.1	27.5 ± 0.2		100–165	157 (154)
	22.9 ± 0.2	9.1 ± 0.08		18.0 ± 0.2		
$Mn(tfa)_3$	36.3 ± 2.8	14.5 ± 1.1	28.8 ± 2.2		105–140	119–120 (115)
	26.2 ± 1.7	10.6 ± 0.7		21.1 ± 1.4		
	[36.5 ± 0.8]	[14.7 ± 0.3]	[29.1 ± 0.6]		[105–150]	[(119)]
	[25.5 ± 0.4]	[10.4 ± 0.2]		[20.6 ± 0.3]		
$Fe(tfa)_3$	31.5 ± 0.3	12.6 ± 0.1	25.0 ± 0.2		105–165	118 (119)
	24.0 ± 0.2	9.6 ± 0.07		19.1 ± 0.1		
$Co(tfa)_3$	31.9 ± 0.2	13.1 ± 0.06	26.0 ± 0.1		110–160	160–161
$Co(tfa)_2$	[26.8 ± 0.2]	[11.0 ± 0.1]		[21.8 ± 0.2]	[100–170]	
$Ni(tfa)_2$	[43.2 ± 0.9]	[19.0 ± 0.4]	[37.7 ± 0.8]		[143–220]	[(153)]
	[27.9 ± 0.2]	[12.5 ± 0.1]		[24.8 ± 0.2]		
$Cu(tfa)_2$	32.0 ± 0.2	13.3 ± 0.09	26.3 ± 0.2		110–190	203–204
$Zn(tfa)_2$	[23.9 ± 0.2]	[9.0 ± 0.07]		[17.9 ± 0.1]	[95–140]	
$Ga(tfa)_3$	36.1 ± 0.5	14.3 ± 0.2	28.4 ± 0.4		105–160	131–132 (129)
	23.5 ± 0.4	9.2 ± 0.2		18.3 ± 0.4		
$Zr(tfa)_4$	37.2 ± 0.5	15.2 ± 0.2	30.2 ± 0.4		110–165	130–133 (130)
	25.1 ± 0.5	10.3 ± 0.2		20.5 ± 0.5		
	[34.9 ± 0.5]	[14.4 ± 0.2]	[28.5 ± 0.4]		[110–165]	[(135)]
	[25.1 ± 0.4]	[10.4 ± 0.2]		[20.6 ± 0.3]		
$Pd(tfa)_2$	30.4 ± 0.6	13.4 ± 0.3	26.5 ± 0.5		170–175	230–240[c]
	[28.8 ± 0.3]	[12.7 ± 0.1]	[25.1 ± 0.2]		[150–175]	
$In(tfa)_3$	33.8 ± 0.4	13.5 ± 0.2	26.8 ± 0.3		105–155	122–124 (123)
	23.7 ± 0.7	9.5 ± 0.3		18.9 ± 0.5		
$Er(tfa)_3$	[27.8 ± 1.0]	[12.6 ± 0.4]		[25.9 ± 0.9]	[145–170]	
$Tm(tfa)_3$	[28.2 ± 0.5]	[12.6 ± 0.2]		[25.1 ± 0.5]	[145–175]	
$Yb(tfa)_3$	[28.4 ± 0.7]	[12.6 ± 0.3]		[25.0 ± 0.6]	[140–170]	
$Lu(tfa)_3$	[28.5 ± 0.2]	[12.5 ± 0.2]		[24.8 ± 0.4]	[140–190]	
$Hf(tfa)_4$	38.3 ± 1.1	15.6 ± 0.4	31.0 ± 0.9		110–165	130 (129)
	25.7 ± 0.7	10.5 ± 0.3		20.9 ± 0.6		
	[36.8 ± 1.2]	[15.0 ± 0.5]	[29.8 ± 0.9]		[110–165]	[(130)]
	[25.0 ± 0.5]	[10.3 ± 0.2]		[20.4 ± 0.4]		

[a] *A* and *B* are values shown by the equation $\ln P\ (\mathrm{mmHg}) = A - 1000B/T$; those for the sublimation process are in the upper row, and those for the evaporation process are in the lower row. In brackets are the values in helium containing H(tfa) vapor. The errors are expressed by the standard deviation. [b] The melting point in parentheses is obtained from the break point of the Clausius–Clapeyron plots. [c] The values are not reproducible.

hydrated chelates such as $Co(tfa)_2$, $Ni(tfa)_2$, $Zn(tfa)_2$, $Er(tfa)_3$, $Tm(tfa)_3$, $Yb(tfa)_3$, and $Lu(tfa)_3$ show considerable thermal decomposition in helium atmosphere and their vapor pressure is measurable only in helium containing H(tfa) vapor. The results are shown in Figures 2–4.

Structural Consideration of Vapor Pressure. As shown in Figure 2, tris chelates except rare-earth-metal chelates have very similar vapor pressures compared with those of the bis chelates. For example, the former has the vapor pressure range of 1.3 mmHg of $Co(tfa)_3$ to 5.6 mmHg of $Al(tfa)_3$ and the latter has the range of less than 0.1 mmHg of $Ni(tfa)_2$ to 24 mmHg of $Be(tfa)_2$ at 140 °C. This is because the tris chelates have the octahedral and coordination-saturated structure, and the predominant factor that decides volatility is the molecular interaction by van der Waals forces. In contrast, bis chelates are divided into several structural types of chelates such as tetrahedral, square planar, and square pyramidal: $Be(tfa)_2$, $Cu(tfa)_2$ and $Pd(tfa)_2$, and $VO(tfa)_2$, respectively. The volatility depends on the difference in the structure of chelates. $Zn(tfa)_2$ is square pyramidal in the hydrated state. But, it is estimated that $Zn(tfa)_2$ becomes a tetrahedral monomer when dehydrated and melted in helium containing H(tfa) vapor. This is the only bis chelate, except for tetrahedral $Be(tfa)_2$, that is more volatile than all the tris chelates. It is consistent with the assumption applied to tris chelates that the molecular interaction of coordination-saturated trifluoroacetylacetonates is mainly dominated by van der Waals forces. Graddon and Weeden[11] reported that $Zn(tfa)_2$ is monomeric and presumably tetrahedral in triphenylmethane, biphenyl, and diphenylamine though $Ni(tfa)_2$ and $Co(tfa)_2$ are trimeric in nondonor solvents. Moreover, Buckingham et al.[12] studied the polymerization of iron β-diketonates in noncoordinating solvent by changing the ligands and reported $Fe(tfa)_2$ and $Fe(hfa)_2$ (iron hexafluoroacetylacetonate) in benzene are close to monomeric though $Fe(acac)_2$ (iron acetylacetonate) is monomeric to hexameric as a function of concentration. This fact supports the assumption that the structure of melted $Zn(tfa)_2$ is a tetrahedral monomer from the standpoint of ligands. On the other hand, $VO(tfa)_2$, $Co(tfa)_2$, $Ni(tfa)_2$, $Cu(tfa)_2$, and $Pd(tfa)_2$ were much less volatile than $Zn(tfa)_2$. It suggests that a strong molecular interaction other than van der Waals forces is affected in these chelates.

It is welll-known that the volatility of rare-earth-metal β-diketonates depends on the ionic radius of central atoms.[13] This is true for trifluoroacetylacetonates in ligand vapor atmosphere as shown in Figure 2.

Melting Points of Chelates. The melting points of anhydrous tris chelates obtained as break points of the Clausius–Clapeyron plots agree well with the results measured by a micro melting point apparatus, but those of $VO(tfa)_2$, $Cu(tfa)_2$, and $Pd(tfa)_2$ were not observed in the temperature range of vapor pressure measurements. They are above 200 °C and are extremely higher than those of tris chelates, which are over the range 110–160 °C. The results

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(11) Graddon, D. P.; Weeden, D. G. *Aust. J. Chem.* **1963**, *16*, 980.

(12) Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* **1967**, *20*, 281.

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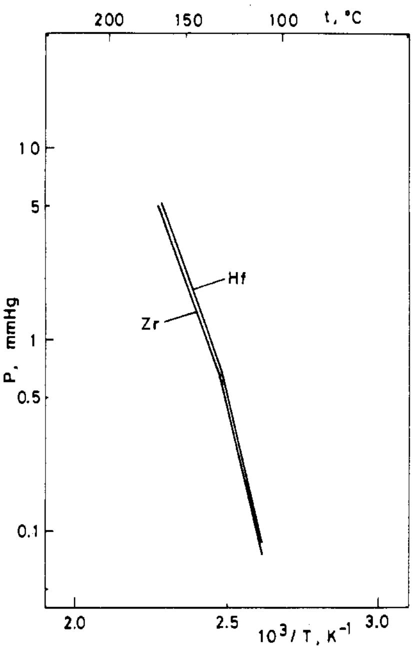

Figure 4. Clausius–Clapeyron plots of tetrakis(trifluoroacetylacetonates) measured in helium.

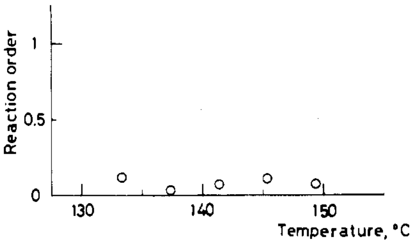

Figure 5. Reaction order of evaporation of $Al(tfa)_3$. Initial sample weights were 10 and 20 mg.

indicate these chelates have strong molecular interactions.

$Co(tfa)_2$, $Ni(tfa)_2$, and $Zn(tfa)_2$ did not melt up to their decomposition temperature in air, but melted in helium containing H(tfa) vapor. In Figure 3, the line for $Ni(tfa)_2$ shows a clear break at the melting point, 153 °C. $Co(tfa)_2$ and $Zn(tfa)_2$ melted below the plotted temperature, and a similar break was not observed.

Sublimation and Evaporation Enthalpies of Trifluoroacetylacetonates. As shown in Table I, the sublimation and evaporation enthalpies of anhydrous trifluoroacetylacetonates are generally 28 ± 2 kcal mol^{-1} and 19 ± 2 kcal mol^{-1}, respectively, and those of dehydrated chelates are larger than these values.

Figure 5 shows the reaction order of vaporization of $Al(tfa)_3$ calculated by Chatterjee's method as a function of temperature. The experimentally measured reaction order was from 0.04 to 0.12 over the temperature range 133–150 °C. The value is actually estimated to be zero; that is, the rate of evaporation is independent of the amount of a chelate. As shown in Table II, the enthalpies of sublimation and evaporation calculated by the Freeman–Carroll method agree well with the values calculated from the Clausius–Clapeyron equation.

The previously reported sublimation and evaporation enthalpies of β-diketonates of aluminum, chromium, iron, and copper are listed in Table III. The italicized values can be selected as reliable ones on the basis of their mutual agreement and are found to be within or near the range of those of the trifluoroacetylacetonates mentioned above. It is estimated that these sublimation and evaporation enthalpies are characteristic of coordination-saturated β-diketonates.

Table II. Sublimation and Evaporation Enthalpies of Trifluoroacetylacetonates Calculated by the Freeman–Carroll Equation[a]

chelates	sublim enthalpy, kcal mol^{-1}	evap enthalpy, kcal mol^{-1}
$Al(tfa)_3$		17.5 ± 0.5
$V(tfa)_3$		19.4 ± 0.2
$VO(tfa)_2$	26.6 ± 0.3	
$Fe(tfa)_3$		18.2 ± 0.2
$Cu(tfa)_2$	25.6 ± 0.2	
$Ga(tfa)_3$		19.0 ± 0.6
$Zr(tfa)_4$		[20.3 ± 0.7]
$In(tfa)_3$		19.7 ± 0.3
$Hf(tfa)_4$		[18.7 ± 0.7]

[a] The values in brackets are measured in helium containing H(tfa) vapor.

Table III. Sublimation and Evaporation Enthalpies of β-Diketonates[l]

chelates[o]	sublim enthalpy, kcal mol^{-1}	evap enthalpy, kcal mol^{-1}
$Al(tfa)_3$	9.6,[a] 22.4,[e] 24.5,[d] 27.1[w]	15.8,[e] 16.6,[d] *17.8,*[b] *18.8,*[c] *19.0*[w]
$Al(hfa)_3$	26.2[e]	12.1,[e] 14.3[b]
$Al(dpm)_3$	20.9[d]	15.6[d]
$Al(fod)_3$	17.0,[e] 21.0[b]	17.5[b]
$Al(aa)_3$	4.6,[a] 10.8,[g] 15.8,[e] 24.0,[c] 25.9,[d] 28.3,[f] 30.0,[h] 30.8[i]	18.6,[d] 22.5[i]
$Al(pta)_3$		16.6[d]
$Cr(tfa)_3$	*26.0,*[e] *26.9,*[j] *27.5*[w]	*17.3,*[b] *18.0,*[w] *18.3*[j]
$Cr(hfa)_3$	29.4[e]	*15.5,*[b] *16.6*[e]
$Cr(fod)_3$	9.0[e]	17.6[b]
$Cr(aa)_3$	6.6,[k] 9.6,[e] 20.5[r] *26.5,*[m] *26.5,*[p] *26.5,*[q] *26.8,*[n] 29.9,[i] 34.4[c]	19.7,[p] 21.5[i]
$Fe(tfa)_3$	20.8,[a] 25.0[w], 30.8[n]	*19.1,*[w] *20.8*[j]
$Fe(dpm)_3$	25.5[s]	
$Fe(fod)_3$		19.5[b]
$Fe(aa)_3$	4.7,[a] 15.6,[k] 23.7,[p] 23.9,[q] *27.2,*[f] *27.3,*[n] *27.5,*[r] *27.7*[i]	17.5,[p] 19.6[i]
$Cu(tfa)_2$	12.1,[a] 19.2,[c] *26.3,*[w] *27.6*[t]	
$Cu(dpm)_2$	26.7[u]	*17.8,*[v] *18.6*[u]
$Cu(fod)_2$		16.2[b]
$Cu(aa)_2$	12.9,[g] 13.7,[i] *25.3,*[q] *25.4,*[c] *25.4,*[r] *25.5,*[t] *26.2*[n]	
$Cu(pta)_2$		17.5[d]

[a] Reference 1. [b] Reference 3. [c] Reference 22. [d] Reference 24. [e] Reference 20. [f] Reference 27. [g] Reference 28. [h] Reference 32. [i] Reference 30. [j] Reference 14. [k] Reference 16. [l] The italicized values are explained in the text. [m] Reference 17. [n] Reference 18. [o] Abbreviations of ligands: hfa, 1,1,1,5,5,5-hexafluoropentane-2,4-dione; dpm, 2,2,6,6-tetramethylheptane-3,5-dione; fod, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione; aa, pentane-2,4-dione; pta, 1,1,1-triluoro-5,5-dimethylhexane-2,4-dione. [p] Reference 19. [q] Reference 31. [r] Reference 29. [s] Reference 21. [t] Reference 23. [u] Reference 25. [v] Reference 26. [w] This paper.

Thermal Stability of Chelates. Many of the chelates studied were stable in the temperature range of the vapor pressure measurements, but several chelates showed thermal decomposition. $Pd(tfa)_2$ was decomposed considerably above 180 °C and the Clausius–Clapeyron plot was curved. This phenomenon was not improved even in helium containing H(tfa) vapor. $Mn(tfa)_3$ is reported to be thermally unstable, and the vapor pressure was not measured by a spoon gauge.[14] However, a straight line for the

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Clausius–Clapeyron plots was obtained over the range of 105–140 °C in helium and 105–150 °C in helium containing H(tfa) vapor. As previously pointed out,[4d] above 150 °C $Mn(tfa)_3$ is gradually reduced to $Mn(tfa)_2$ in helium containing H(tfa) vapor and the decomposition of $Mn(tfa)_3$ is accelerated in the presence of $Mn(tfa)_2$. $Co(tfa)_3$ is an inert complex and thermally stable below the melting point, but above the temperature it was difficult to determine the accurate evaporation enthalpy because the deviation of vapor pressure became large in helium. $Zr(tfa)_4$ and $Hf(tfa)_4$ have about the same vapor pressures in helium and helium containing H(tfa) vapor, but there is suspicion of some thermal decomposition in helium because the chelates condensed from the vapor phase were colored yellow, while in helium containing H(tfa) vapor these chelates were recovered as white original samples. $Er(tfa)_3$, $Tm(tfa)_3$, and $Yb(tfa)_3$ were accompanied with thermal decomposition above 180 °C even in helium containing H(tfa) vapor because the lines of the Clausius–Clapeyron plots were curved.

Registry No. $Al(tfa)_3$, 14354-59-7; $Sc(tfa)_3$, 14634-68-5; $V(tfa)_3$, 15695-88-2; $VO(tfa)_2$, 14871-96-6; $Cr(tfa)_3$, 14592-89-3; $Mn(tfa)_3$, 14526-24-0; $Fe(tfa)_3$, 14526-22-8; $Co(tfa)_3$, 16827-64-8; $Co(tfa)_2$, 47115-08-2; $Ni(tfa)_2$, 14324-83-5; $Cu(tfa)_2$, 14324-82-4; $Zn(tfa)_2$, 16038-29-2; $Ga(tfa)_2$, 15453-83-5; Zr(tfa), 17499-68-2; $Pd(tfa)_2$, 63742-52-9; $In(tfa)_3$, 15453-87-9; $Er(tfa)_3$, 67118-77-8; $Tm(tfa)_3$, 97011-37-5; $Yb(tfa)_3$, 97042-23-4; $Lu(tfa)_3$, 78683-50-8; $Hf(tfa)_3$, 17475-68-2; He, 7440-59-7.

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Notes

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Chelation and Oligomerization in an Organochromium(III) System

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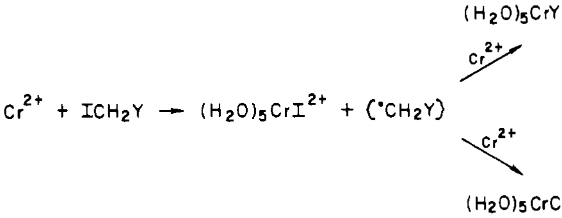
The reaction of chromium(II) and iodoacetic acid was studied by Sevcik and Jakubcova,[1] and the results reported indicate that the reaction follows the expected course, represented by the equation

$$2Cr^{2+} + ICH_2CO_2H \rightarrow (H_2O)_5CrI^{2+} + (H_2O)_5CrCH_2CO_2H^{2+}. \quad (1)$$

However some $(H_2O)_5CrO_2CCH_3^{2+}$ should form in reaction 1 on the basis of studies of ICH_2CN,[2] ICH_2CONH_2,[3] and Cl_2CHCO_2H.[4] This prediction is based on the general mechanism



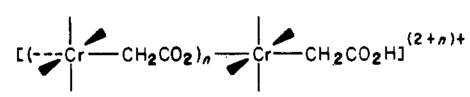
$$Cr^{2+} + ICH_2Y \rightarrow (H_2O)_5CrI^{2+} + ({}^{\bullet}CH_2Y) \begin{cases} \xrightarrow{Cr^{2+}} (H_2O)_5CrYCH_3 \\ \xrightarrow{Cr^{2+}} (H_2O)_5CrCH_2Y \end{cases} \quad (2)$$

The results reported here show that this expectation is correct and, of perhaps more general importance, that the organochromium(III) product has several unusual properties not consistent with its formulation in eq 1.

The first unusual property of the organochromium species formed by reaction 1 was noted during ion-exchange separation experiments. The reaction solution, which contained 0.15 M $Cr(ClO_4)_2$ and 0.105 M ICH_2CO_2H in 0.75 M $HClO_4$, was allowed to react for 10 min at 22 °C before being chromatographed at 5 °C on a 20 × 2.5 cm diameter column of Dowex 50W-X2 (H^+) (100–200 mesh). As elution proceeds with the concentration of $HClO_4$ increasing from 0.20 to 2.0 M, the products seem to elute normally with green $(H_2O)_5CrI^{2+}$ followed by a red-brown band (typical color of organochromium(III) species) and then some $Cr(OH_2)_6^{3+}$ (from aquation of $(H_2O)_5CrI^{2+}$). Unexpectedly, a substantial amount of red-brown species remained on the ion-exchange resin. Furthermore, when the first red-brown band was again ion exchanged on Dowex 50W-X8 (H^+)[5] almost all of the red-brown product remained on the resin even on treatment with 2 M $HClO_4$. This was unexpected because the species originally had been removed easily from Dowex 50W-X2 with 0.5 M $HClO_4$.

The separation on Dowex 50W-X8 was partially successful in that the initial red-brown eluent in 0.5 M $HClO_4$ was followed closely by a blue band. The electronic spectrum confirmed that this blue species was $(H_2O)_5CrO_2CCH_3^{2+}$.[6] At this stage it might be argued that this blue product is a result of the transformation which made the red-brown material so difficult to elute. However results described below show that $(H_2O)_5CrO_2CCH_3^{2+}$ is a product of the initial reaction.

The ion-exchange behavior can be explained by oligomerization occurring on the ion-exchange resin. The system appears to take advantage of the high local concentrations on the resin and the lability of the trans water molecule[7] in organopentaaquochromium(III) species to condense to give polymeric species, e.g.



The greater extent of the reaction (larger *n*) on X8 compared to X2 resin may be attributed to the greater density of anionic sites on the former, giving a greater concentration of the adsorbed cation.

The conclusion that the oligomerization occurs on the resin is substantiated by the observation that a solution of the red-brown eluent in 0.50 M $HClO_4$ shows no spectrophotometric change on storage at 5 °C for 24 h or at 25 °C for 30 min.

The behavior of the organochromium species on the ion-exchange column complicates a study of the true products of reaction 1. However a detailed analysis of the electronic spectra of various fractions eluted from Dowex 50W-X2 (H^+) at 5 °C shows that the products are not just $(H_2O)_5CrI^{2+}$ and $(H_2O)_5CrCH_2CO_2H^{2+}$.

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