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DSC DETERMINATION OF THE SUBLIMATION ENTHALPY OF TRIS(2,4-PENTANEDIONATO)COBALT(III) AND BIS(2,4-PENTANEDIONATO)NICKEL(II) AND -COPPER(II)

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ABSTRACT

The sublimation enthalpies of tris(2,4-pentanedionato)cobalt(III) and bis(2,4-pentanedionato)nickel(II) and -copper(II) have been determined by differential scanning calorimetry as 142.6 ± 6.9, 108.2 ± 4.9 and 107.1 ± 5.7 kJ mol^{-1}, respectively. An assessment of the sublimation characteristics of tris(2,4-pentanedionato)manganese(III) is also reported.

INTRODUCTION

The sublimation enthalpies of metal complexes continues to be a subject associated with considerable controversy. However, much interest is routinely focussed on their determination as a consequence of the need for such data in the calculation of metal–ligand thermochemical bond energies.

The existing sublimation enthalpy data for each of the title complexes reflect much inconsistency and, in general, are not referred to a defined temperature or temperature range. Hence, recognising the deficiency and following standardisation of DSC calibration procedures [1], a systematic redetermination of the sublimation enthalpies of metal acetylacetonates has been initiated [2,3] and the present paper extends this study.

For tris(2,4-pentanedionato)manganese(III), considerable doubt exists as to whether the complex sublimes on heating or whether decomposition is associated with sublimation [4]. Previous solid–gas phase transition studies of this complex, which have assumed sublimation with the formation of a gaseous monomeric species, have yielded ΔH_{sub} as 77.8 ± 0.8 [5], 113.0 [6] and 117.3 kJ mol^{-1} [7], respectively. Wood and Jones [5] used the isoteniscopic method, Gotze et al. [6] essentially used the method of Gruner [8],

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which involves determination of the mass of complex volatilised at a given temperature by condensation in a cold trap, and Ashcroft [7] used the thermogravimetric method. It should be noted that these various techniques are unable to differentiate between pure sublimation and sublimation coupled with decomposition.

For tris(2,4-pentanedionato)cobalt(III), ΔH_{sub} has been previously determined as 74.9 ± 4.6 [5], 107.1 [6] and 86.3 kJ mol^{-1} [7] using the respective methods described for the corresponding Mn(III) complex.

For bis(2,4-pentanedionato)nickel(II), ΔH_{sub} has been previously determined as 69.0 [9] and 95.4 kJ mol^{-1} [6] using the isoteniscopic and vapour phase condensation methods, respectively, and Burkinshaw and Mortimer [10] have reported ΔH_{sub} as 132 ± 10 kJ mol^{-1} based on the application of a differential Knudsen effusion technique.

For bis(2,4-pentanedionato)copper(II), ΔH_{sub} has been previously estimated as 62.8 kJ mol^{-1} by Jones et al. [11] and determined as 81.2 [6] and 106.1 kJ mol^{-1} [7] by the vapour phase condensation and TG methods, respectively. Beech and Lintonbon [4] have reported $\Delta H_{sub} = 57.3$ kJ mol^{-1} based on DSC determination and Teghil et al. [12] have reported $\Delta H_{sub} = 57.1 \pm 1$ kJ mol^{-1} using the torsion effusion method.

An assessment of these previous data is made in conjunction with new sublimation enthalpy data for the title complexes as determined by DSC using benzoic acid [1] as calibrant.

EXPERIMENTAL

Tris(2,4-pentanedionato)manganese(III) was prepared according to the method of Charles and Bryant [13] and was twice recrystallised from benzene/petroleum ether, 80 : 20 v/v, and dried at ambient temperature in vacuo over calcium chloride. Tris(2,4-pentanedionato)cobalt(III) was prepared according to the method of Fernelius and Bryant [14] and was twice recrystallised from benzene/petroleum ether, 80 : 20 v/v (m.p. 214; lit. 213°C [14]). Bis(2,4-pentanedionato)nickel(II) was prepared according to the

TABLE 1

Microanalysis data for Mn(III), Co(III), Ni(II) and Cu(II) acetylacetonate complexes

Complex	Calculated %		Found %	
	C	H	C	H
$(C_5H_7O_2)_3Mn$	51.1	6.0	51.9	6.0
$(C_5H_7O_2)_3Co$	50.6	5.9	50.8	5.9
$(C_5H_7O_2)_2Ni$	46.8	5.5	47.0	5.4
$(C_5H_7O_2)_2Cu$	45.9	5.4	46.0	5.4

original method of Debierne and Urbain [15] and was purified by repeated sublimation. Bis(2,4-pentanedionato)copper(II) was prepared according to an established procedure [15] and was purified by repeated sublimation. Microanalysis data (Amdel Microanalytical Service, Melbourne, Australia) for these complexes are given in Table 1.

The DSC, calibration, sample preparation, experimental procedures and data analysis have been described in detail previously [1].

RESULTS AND DISCUSSION

A typical DSC thermogram for tris(2,4-pentanedionato)manganese(III) is shown in Fig. 1 and derived enthalpy data are recorded in Table 2.

The derived mean $\Delta H_{\text{sub}} = 33.5 \pm 4.5$ kJ mol^{-1} is much lower than all previously reported sublimation enthalpies for this complex [5–7] and thus it is concluded that extensive decomposition is associated with the sublimation of $(C_5H_7O_2)_3Mn$ and this is verified from the irregular DSC profile for this complex which exhibits shoulders at 147 and 156°C and a secondary endotherm at 180°C. Hence no meaningful ΔH_{sub} can be ascribed to tris(2,4-pentanedionato)manganese(III).

A typical TG/DSC thermogram for tris(2,4-pentanedionato)cobalt(III) is shown in Fig. 2 and derived sublimation enthalpy data are recorded in Table 3.

The mass loss over the sublimation range 132–204°C corresponds to 100% and thus sublimation without decomposition is confirmed for $(C_5H_7O_2)_3Co$. The scatter of the previously reported ΔH_{sub} values for this

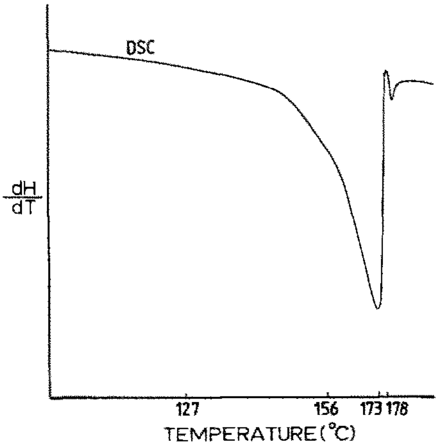

Fig. 1. Typical DSC thermogram of $(C_5H_7O_2)_3Mn$. Sample mass, 7.89 mg; sublimation range, 127–178°C; sublimation peak temperature, 173°C.

TABLE 2

"Sublimation" enthalpy of tris(2,4-pentanedionato)manganese(III)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
7.89	±4	29.8
6.72	±4	37.6
9.15	±4	37.4
11.00	±4	33.2
8.00	±4	25.5
12.43	±2	32.7
8.16	±4	31.4
7.33	±4	40.6
		Mean = 33.5 ± 4.5

complex [5–7], together with the present value, is too great to permit a "selected value" to be decided.

A typical DSC thermogram for bis(2,4-pentanedionato)nickel(II) is shown in Fig. 3 and derived sublimation enthalpy data are recorded in Table 4.

Neglecting the isoteniscopic $\Delta H_{sub} = 69.0$ kJ mol^{-1} reported by Berg and Truemper [9], $\Delta H_{sub}(C_5H_7O_2)_2Ni$ is selected as 111.9 ± 10.0 based on the present value and the data of Gotze et al. [6] and Burkinshaw and Mortimer [10].

A typical TG/DSC thermogram for bis(2,4-pentanedionato)copper(II) is shown in Fig. 4 and derived sublimation enthalpy data are recorded in Table 5.

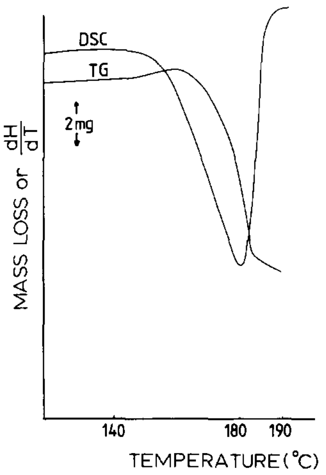

Fig. 2. Typical TG–DSC thermogram of $(C_5H_7O_2)_3Co$. Sample mass, 9.37 mg; sublimation temperature range, 132–204°C; sublimation peak temperature, 198°C.

TABLE 3

Sublimation enthalpy of tris(2,4-pentanedionato)cobalt(III)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
10.09	±4	137.7
8.95	±8	143.1
12.68	±4	134.7
9.37	±4	131.9
6.25	±4	149.9
7.76	±4	151.2
6.67	±2	150.1
8.04	±2	142.2
		Mean = 142.6 ± 6.9

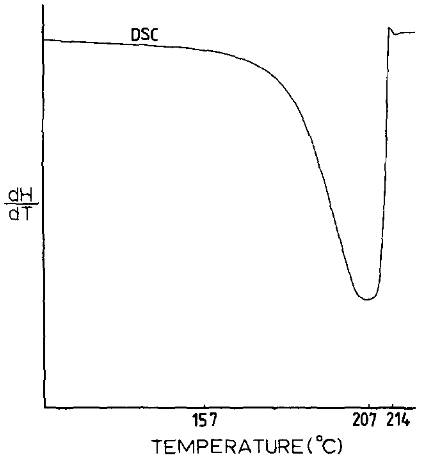

Fig. 3. Typical DSC thermogram of $(C_5H_7O_2)_2Ni$. Sample mass, 7.27 mg; sublimation temperature range, 157–214° C; sublimation peak temperature, 207° C.

TABLE 4

Sublimation enthalpy of bis(2,4-pentanedionato)nickel(II)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
5.88	±4	108.5
7.27	±4	104.7
8.36	±4	100.1
11.59	±16	115.4
13.60	±8	111.8
8.49	±8	108.4
		Mean = 108.2 ± 4.9

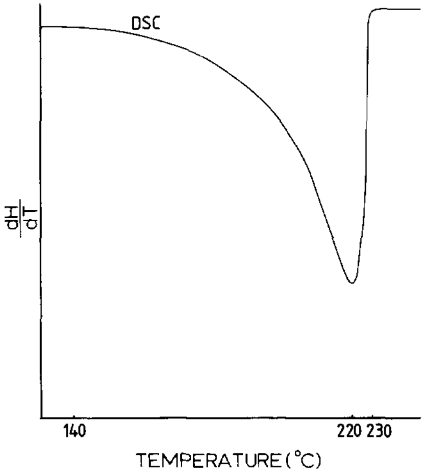

Fig. 4. Typical TG–DSC thermogram of $(C_5H_7O_2)_2Cu$. Sample mass, 3.71 mg; sublimation temperature range, 172–224°C; sublimation peak temperature, 219°C.

The mass loss over the sublimation range 172–224°C corresponds to 100% and thus sublimation without decomposition is confirmed for $(C_5H_7O_2)_2Cu$. Neglecting the estimated ΔH_{sub} for this complex reported by Jones et al. [11] and the torsion effusion value of Teghil et al. [12], $\Delta H_{sub}(C_5H_7O_2)_2Cu$ is selected as 98.1 ± 10.0 kJ mol^{-1} based on the present value and the data of Gotze et al. [6] and Ashcroft [7].

It is apparent that in the determination of sublimation enthalpies of metal acetylacetonate complexes, the divergence of separately derived data for a particular complex is most probably due to decomposition and sublimation occurring concurrently under the conditions imposed. This has been confirmed in the present work for tris(2,4-pentanedionato)manganese(III). Beech and Lintonbon [4] have suggested that mass spectrometry may be employed

TABLE 5

Sublimation enthalpy of bis(2,4-pentanedionato)copper(II)

Sample mass (mg)	DSC range (mcal s^{-1})	ΔH_{sub} (kJ mol^{-1})
5.35	±4	103.4
7.61	±8	100.7
9.62	±4	112.0
7.91	±16	106.7
5.98	±4	109.7
4.73	±4	100.9
3.71	±4	104.6
2.92	±4	118.6
		Mean = 107.1 ± 5.7

to determine the extent of decomposition of metal acetylacetonate complexes in vacuum. Since the conditions associated with mass spectrometry and vacuum DSC are similar, mass spectrometry data may be correlated with corresponding thermal data for a particular complex. In the case of pure sublimation, a smooth, single DSC peak is obtained and only parent-ion peaks appear in the mass spectrum corresponding to $[M(acac)_3]^+$ or $[M(acac)_2]^+$ for M(III) and M(II) complexes, respectively. In this way, Beech and Lintonbon [4] have confirmed that Al(III), Sc(III), V(III), Cr(III) and Zn(II) acetylacetonate complexes sublime whereas Ti(IV), Mn(II) and Mn(III) acetylacetonate complexes decompose.

It is relevant to note that Dilli and Robards [16] have studied the volatility characteristics of a wide variety of aryl-substituted Cu(II)–β-diketonate complexes using TG/DTA. Volatility of these complexes is increased by fluorination of the terminal aromatic ring substituents and decreased in the case of chlorine, bromine and methyl aromatic ring substituents. These data are of prime significance in the gas chromatographic separation of these complexes and suggest that fluorinated copper(II) acetylacetonate complexes sublime without decomposition.

Volkov et al. [17] have confirmed sublimation for the acetylacetonates, trifluoroacetylacetonates and hexafluoroacetylacetonates of Al(III), Cr(III), Cu(II) and Fe(III) and have reported sublimation enthalpies and entropies for these complexes.

Cardwell and Lorman [18] have recently investigated by TG/DTA the volatility characteristics of Cr(III) and Co(III) acetylacetonates containing bromine substituents on the β-carbon atom of the ligand. The thermal analysis data are consistent with the parent complex being more thermally stable than the corresponding brominated species and further, it is apparent that thermal stability decreases as the extent of bromination of these chelates increases and, overall, the Cr(III) complexes are more volatile than the corresponding Co(III) complexes.

Sublimation/degree of volatility of metal acetylacetonate complexes continues to be a controversial subject. With respect to first-row transition metal acetylacetonate complexes, it is apparent that further studies are necessary to confirm the degree of sublimation of the Ti(IV), Mn(II) and Mn(III) complexes, whereas for the remaining complexes of this group sublimation enthalpies now appear to be well established.

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