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Note

A VACUUM DSC STUDY OF Ni(II), Cu(II) AND Co(III) DIETHYLDITHIOCARBAMATE COMPLEXES

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Volatile metal complexes are of topical interest in the context of providing a means for separating neighbouring metals in the Periodic Table by gas chromatography [1]. A few metal dithiocarbamate complexes are volatile without decomposition but the majority are involatile. The first quantitative data on the volatility of these complexes were published by D'Ascenzo and Wendlandt [2] who used an isoteniscope to obtain vapour pressure/temperature data for tris(diethyldithiocarbamato)iron(III). ΔH_{sub} $Fe(Et_2dtc)_3$, 246°C was reported as 15.7 ± 0.4 kcal $mole^{-1}$. Subsequently [3] ΔH_{sub} for the corresponding Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Hg(II) complexes was reported. Sceney et al. [4] subjected $Cu(Et_2dtc)_2$ to a TG/DTA study in air and nitrogen atmospheres and in vacuum (0.8 τ), and stated that the complex was volatile without decomposition when heated in vacuum within the range 190–260°C. Since no direct measurements of ΔH_{sub} of metal dithiocarbamate complexes have been published, the present paper reports ΔH_{sub} for Ni(II), Cu(II) and Co(III) diethyldithiocarbamate complexes as derived from vacuum DSC data.

EXPERIMENTAL

The metal diethyldithiocarbamate complexes were synthesised by well-established methods [5]. The complexes were purified by repeated sublimation. Relevant melting point and microanalysis data are given in Table 1.

A Rigaku–Denki Differential Scanning Calorimeter (type: Thermoflex 8085) was employed throughout. The Beech–Lintonbon [6] sample preparation technique was used — samples (mass range 3–5 mg) were crimped in aluminium pans and a 0.1 mm diameter hole in the pan lid allowed escape of volatile sample. Samples were heated in a dry nitrogen atmosphere or in vacuum, 5×10^{-3} τ. Heating rates of 5, 10 and 20°C min^{-1} were employed — for thermal analysis in a nitrogen atmosphere, the higher heating rates yield superior separation of fusion and volatilisation peaks. Peak areas were determined using an on-line integrator (type PADAC). For thermal analysis in a nitrogen atmosphere, the DSC was calibrated using pure indium metal (ΔH_{fus} = 3.35 kJ $mole^{-1}$) [7] and for thermal analysis in vacuum, pure benzoic acid was used as calibrant [8]. (ΔH_{sub} = 90 ± 2 kJ $mole^{-1}$).

TABLE 1

Melting point and microanalysis data for metal diethyldithiocarbamate complexes

Compound	M.p. (°C)	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulphur (%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Ni[S_2CN(CH_2CH_3)_2]_2$	234—236	33.8	34.0	5.7	5.8	7.9	7.8	36.1	35.9
$Cu[S_2CN(CH_2CH_3)_2]_2$	190—192	33.4	33.7	5.6	5.7	7.8	7.8	35.7	35.6
$Co[S_2CN(CH_2CH_3)_2]_2$	262—265	35.8	35.8	6.0	6.1	8.3	8.3	38.2	38.0

TABLE 2

DSC data for $Ni(Et_2dtc)_2$

Run No.	Atmosphere	ΔH_{fus} (kJ mole^{-1})	ΔH_{vap} (kJ mole^{-1})	ΔH_{sub} (kJ mole^{-1})	Approx. temp. of sublimation (K)
1	Dry N_2	30.4	73.8	104.2	507—650
		30.7	63.2	93.9	
		30.2	68.1	98.2	
	Mean	30.4 ± 0.4	68.4 ± 6	98.8 ± 6	
1	Vacuum 5×10^{-3} τ			91.2	443—543
2				102.0	
3				87.1	
4				93.2	
5				85.7	
			Mean	91.9 ± 6	

RESULTS

ΔH_{fus}, ΔH_{vap} and ΔH_{sub} data for the three complexes are recorded in Tables 2—4. Uncertainty intervals are quoted as twice the standard deviation from the mean.

D'Ascenzo and Wendlandt [3] have reported ΔH_{sub} $Ni(Et_2dtc)_2$ = 61.1 ± 1.7 kJ mole^{-1} and ΔH_{sub} $Cu(Et_2dtc)_2$ = 87 ± 1.7 kJ mole^{-1}. These values are lower than those reported in the present work. It is well known that ΔH_{sub}

TABLE 3

DSC data for $Cu(Et_2dtc)_2$

Run No.	Atmosphere	ΔH_{fus} (kJ mole^{-1})	ΔH_{vap} (kJ mole^{-1})	ΔH_{sub} (kJ mole^{-1})	Approx. temp. range of sublimation (K)
1	Dry N_2	23.2	82.0	105.3	455—597
2		22.9	79.6	102.5	
3		23.7	83.4	107.1	
	Mean	23.3(±0.5)	81.7(±2)	104.9(±3)	
1	Vacuum 5×10^{-3} τ			100.4	423—513
2				102.7	
3				104.2	
4				104.0	
5				107.7	
			Mean	103.8(±2.4)	

TABLE 4

Vacuum DSC data for $Co(Et_2dtc)_3$

Run No.	Atmosphere	ΔH_{sub} (kJ mole^{-1})	Approx. temp. range of sublimation (K)
1	Vacuum 5×10^{-3} τ	91.7	448—587
2		86.0	
3		103.8	
4		99.4	
5		94.2	
	Mean	95 ± 6	

data for metal acetylacetonates based on isoteniscopic vapour pressure/temperature data are consistently lower than corresponding values obtained by other methods [9—12] such as the sublimation bulb technique [13]. Incomplete outgassing of the sample appears to be the major source of error with the isoteniscopic technique. Despite relatively low precision and moderate accuracy, vacuum DSC offers several advantages over other methods for deriving sublimation enthalpies. The technique is experimentally simple, rapid and yields enthalpy data directly. Greater precision results if extreme care is taken to remove volatile impurities, particularly water, from samples prior to a DSC study.

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