Thermochimica Acta, 223 (1993) 187–191
Elsevier Science Publishers B.V., Amsterdam

A solution calorimetric study of tris(diethyldithiocarbamato)cobalt(III)

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(Received 8 December 1992; accepted 13 January 1993)

Abstract

The standard formation enthalpy (298 K) of tris(diethyldithiocarbamato)cobalt(III) has been derived by solution calorimetry as $\Delta_f H_m^{\ominus}(\mathrm{Co[S_2CN(C_2H_5)_2]_3}) = -233.8 \pm 20\ \mathrm{kJ\ mol^{-1}}$. The thermochemical measurements are based on a ligand-exchange reaction involving the complete displacement of pentane-2,4-dionate in tris(pentane-2,4-dionato)cobalt(III) by the diethyldithiocarbamato anion. The homolytic thermochemical bond dissociation enthalpy, $\langle D \rangle$(Co–S), has subsequently been calculated as 200 ± 25 kJ. These thermochemical data are assessed in conjunction with the corresponding data for the bis(diethyldithiocarbamato)nickel(II), -copper(II) and -zinc(II) complexes.

INTRODUCTION

The two major reviews [1, 2] of the thermochemistry of the metal dithiocarbamate complexes have shown that sufficient empirical enthalpy data are available for these systems for trends to be formulated. However, empirical enthalpy data for tris(diethyldithiocarbamato)cobalt(III) are conspicuously absent. It has long been known that many of these complexes are volatile but the sublimation enthalpies of only a few have been determined. Larionov [3] has reviewed the early data. These data are essential for the ultimate determination of the corresponding metal–sulphur bond dissociation enthalpies.

Conventional solution calorimetry has been applied to determine the standard formation enthalpies of several metal dithiocarbamate complexes $\mathrm{M(S_2CNR_2)}_n$: M = Pb(II), Zn(II), Cd(II), R = H, $n = 2$ [4]; M = Ni(II), $\mathrm{R = C_2H_5}$, $n = 2$ [5, 6]; M = Ni(II), $\mathrm{R = C_3H_7}$, $\mathrm{CH(CH_3)_2}$, $\mathrm{C_4H_9}$, $\mathrm{CH_2CH(CH_3)_2}$, $n = 2$ [6]; M = Cu(II), $\mathrm{R = C_2H_5}$, $n = 2$ [7, 8]; M = Cu(II), $\mathrm{R = C_3H_7}$, $\mathrm{CH(CH_3)_2}$, $\mathrm{C_4H_9}$, $\mathrm{CH_2CH(CH_3)_2}$, $n = 2$ [8]; M = Zn(II),

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$R = C_2H_5$, $n = 2$ [9]; M = Zn(II), Cd(II), Hg(II), $R = C_3H_7$, $n = 2$ [10]; M = Zn(II), Cd(II), Hg(II), $R = C_4H_9$, $n = 2$ [11]; M = P(III), As(III), $R = C_2H_5$, $n = 3$ [12]; M = Sb(III), Bi(III), $R = C_2H_5$, $n = 3$ [13]; and M = P(III), As(III), Sb(III), Bi(III), $R = C_4H_9$, $n = 3$ [14]. In all cases, the mean homolytic metal–sulphur bond dissociation enthalpies have been calculated and their magnitudes rationalised in terms of the structures of the complexes. Trends in these data are also highlighted and discussed.

This paper reports the standard formation enthalpy of tris(diethyldithiocarbamato)cobalt(III) as derived by conventional solution calorimetry. A ligand-exchange reaction between tris(pentane-2,4-dionato)cobalt(III) and diethylammonium diethyldithiocarbamate forms the basis of the required thermochemical cycle for the solution calorimetry. The cobalt–sulphur homolytic bond dissociation enthalpy is subsequently calculated and its magnitude is compared with those for the related bis(diethyldithiocarbamato)nickel(II), -copper(II) and -zinc(II) complexes.

EXPERIMENTAL

Reagents

1,4-Dioxan, diethylamine and pentane-2,4-dione were purified according to the well-established procedures [15]. Diethylammonium diethyldithiocarbamate was prepared and purified as described previously [16]. Tris(diethyldithiocarbamato)cobalt(III) was prepared and purified by the well-established procedures [17]; found: C, 35.8; H, 6.1; N, 8.3; S, 38.0; Co (by AAS), 11.4%: calc. for $C_{15}H_3N_3S_6Co$: C, 35.8; H, 6.0; N, 8.3; S, 38.2; Co, 11.7%. Tris(pentane-2,4-dionato)cobalt(III) was prepared by the well-established procedures [18]; found: C, 50.2; H, 6.1; Co (by AAS), 16.3%: calc. for $C_{15}H_{21}O_6Co$: C, 50.6; H, 5.9; Co, 16.5%. These microanalysis data were provided by the Chemistry Department Microanalytical Service, National University of Singapore.

Calorimeter and assessories

The isoperibol solution calorimetric system used, together with the measurement and data analysis procedures, have been described in detail previously [5]. The system was calibrated chemically using the THAM (tris(hydroxymethyl)aminomethane) test reaction. The measured molar enthalpy of a solution of THAM in 0.1 M HCl was -29.75 ± 0.08 kJ mol^{-1}, based on 5 determinations (-29.757 ± 0.008 kJ mol^{-1} in ref. 19). The system was further calibrated using the dissolution of KCl in water as a standard test reaction. The measured molar enthlapy of solution was 17.55 ± 0.12 kJ mol^{-1}, based on five determinations (17.548 ± 0.012 kJ

mol^{-1} in ref. 20). The quoted uncertainty intervals are the standard deviation of the mean.

Calorimetric procedure

The general experimental procedure for the determination of the standard formation enthalpy of metal complexes is well established and has been widely applied. The basic principle is to consider the reaction leading to the formation of the metal complex of interest as the basis of a thermochemical cycle interrelating metal complex formation in a heterogeneous system to that in a homogeneous solution phase. Thus, a key prerequisite is the selection of a solvent which dissolves all reactants and products of the metal complex formation reaction. The present system is associated with five calorimetric measurements, as detailed in Table 1. Measured molar enthalpies are referenced to 298 K and the infinitely dilute solution state. The relevant molar enthalpies are quoted as the mean and standard deviation of at least five determinations.

TABLE 1

Solution calorimetric data yielding $\Delta_f H_m^{\ominus}(\mathrm{Co[S_2CN(C_2H_5)_2]_3})$ at 298 K

i	Calorimetric reaction	$\Delta_i H_m^{\ominus}$ [b]/kJ mol^{-1} (298 K)
1	Solvent [a] + $\mathrm{Co(C_5H_7O_2)_3(c)} \rightarrow$ Solution $\mathrm{S_A}$	-15.3 ± 1.5
2	$\mathrm{S_A} + \mathrm{(C_2H_5)_2NH_2S_2CN(C_2H_5)_2(c)} \rightarrow$ Solution $\mathrm{S_B}$	$+38.8 \pm 0.4$
3	Solvent [a] + $\mathrm{Co[S_2CN(C_2H_5)_2]_3(c)} \rightarrow$ Solution $\mathrm{S_C}$	-17.7 ± 1.3
4	$\mathrm{S_C} + \mathrm{(C_2H_5)_2NH_{(2)}} \rightarrow$ Solution $\mathrm{S_D}$	$+15.3 \pm 1.7$
5	$\mathrm{S_D} + \mathrm{C_5H_8O_2(l)} \rightarrow$ Solution $\mathrm{S_E}$	-32.4 ± 0.9
	$\mathrm{S_B} \rightarrow \mathrm{S_E}$	0.0

[a] Solvent = dioxan/ethanol (75/25, vv). [b] Quoted as the mean and standard deviation of five determinations.

RESULTS AND DISCUSSION

The following heterogeneous stoichiometric ligand-exchange reaction was used as the basis for the calculation of the standard formation enthalpy of tris(diethyldithiocarbamato)cobalt(III)

$$\mathrm{Co(C_5H_7O_2)_3(c)} + 3\mathrm{(C_2H_5)_2NH_2S_2CN(C_2H_5)_2(c)} \rightarrow$$
$$\mathrm{Co[S_2CN(C_2H_5)_2]_3(c)} + 3\mathrm{(C_2H_5)_2NH(l)} + 3\mathrm{C_5H_8O_2(l)}$$

All five components in this reaction dissolve rapidly and quantitatively in 1,4-dioxan/ethanol (75/25, v/v) at 298 K. The relevant empirical enthalpy data are summarised in Table 1. The standard molar enthalpy change ($\Delta_R H_m^{\ominus}$) for the reference ligand-exchange reaction is related to the measured standard molar solution enthalpies by the equation

$$\Delta_R H^\ominus_m = \Delta_1 H^\ominus_m + 3\Delta_2 H^\ominus_m - \Delta_3 H^\ominus_m - 3\Delta_4 H^\ominus_m - 3\Delta_5 H^\ominus_m$$

Thus, $\Delta_R H^\ominus_m = 170.1 \pm 12$ kJ mol^{-1}. Standard formation enthalpies of tris(pentane-2,4-dionato)cobalt(III), diethylammonium diethyldithiocarbamate, diethylamine, and pentane-2,4-dione are -1233.9 ± 3.8 [21], -249.2 ± 2.0 [22], -103.7 ± 1.2 [23] and -425.5 ± 1.0 kJ mol^{-1} [24], respectively. Hence, $\Delta_f H^\ominus_m(Co[S_2CN(C_2H_5)_2]_3 = -223.8 \pm 20$ kJ mol^{-1}. The well-established method for the derivation of metal–sulphur coordinate bond dissociation enthalpies for metal dithiocarbamate complexes has been described in detail previously and the symbolsim has also been defined [5–14]. The following relevant additional enthalpy data are taken from the literature: $\Delta_c^g H^\ominus_m(Co[S_2CN(C_2H_5)_2]_3]) = 95 \pm 6$ [25]; $\Delta_c^g H^\ominus_m$, Co = 424.7 ± 4.2 [26]; $\Delta_f H^\ominus_m(\dot{S}_2CN(C_2H_5)_2) = 215.9 \pm 6.5$ [13] kJ mol^{-1}. Hence the homolytic cobalt–sulphur bond dissociation enthalpy, $\langle D\rangle$(Co–S) is derived as 200 ± 25 kJ.

It is relevant to compare $\langle D\rangle$(Co–S) for tris(diethyldithiocarbamato)cobalt(III) with $\langle D\rangle$(M–S) for the related nickel(II), copper(II) and zinc(II) complexes. The metal ionic radius, the metal–sulphur bond length and the $\langle D\rangle$(M–S) data for this group of complexes are listed in Table 2. It appears that for the Ni(II), Cu(II) and Zn(II) complexes, a direct correlation exists between $\langle D\rangle$(M–S) and the M–S bond length in these complexes. The corresponding data for the Co(III) complex are clearly consistent with this trend. Any real trend in these data is however masked by profound differences in the crystal structures of these complexes. The Co(III) complex has a distorted octahedral structure of D_3 symmetry [28]; the Ni(II) complex has a square-planar structure [29]; the Cu(II) complex is dimeric in the solid state [29]; and the zinc(II) complex has the metal located in a 5-coordinate environment and is also dimeric in the solid state, and is essentially isostructural with the Cu(II) complex [30]. Because the $\langle D\rangle$(M–S) and the M–S bond length for

TABLE 2

Metal ionic radius, metal–sulphur bond length and metal–sulphur homolytic bond dissociation enthalpy for some metal dithiocarbamate complexes

$M[S_2CN(C_2H_5)_2]_n$	r of M^{n+} [a]/pm	M–S/pm	$\langle D\rangle$(M–S)/kJ
Co(III)	69	226 [b]	200
Ni(II)	63	220 [c]	227 [f]
Cu(II)	71	231 [d]	187 [g]
Zn(II)	82	260 [e]	177 [h]

[a] From ref. 27. [b] From ref. 28. [c] From ref. 29. [d] From ref. 29. [e] From ref. 30. [f] From ref. 6. [g] From ref. 8. [g] From ref. 9.

tris(diethyldithiocarbamato)cobalt(III) closely correlate with the corresponding data for the other complexes considered, it is concluded that metal–sulphur π-bonding in the Co(III) complex is insignificant, as compared with the metal–sulphur σ-bond strength and further that these metal-sulphur bond dissociation enthalpies are little influenced by the geometry of the metal centre and the overall structure of the complex.

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