Standard Enthalpy of Formation of Bis(diethyldithiocarbamato)copper(II) at 298 K and the Copper–Sulphur Bond Energy

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Solution calorimetry has been employed to determine the standard enthalpy of formation of bis(diethyldithiocarbamato)copper(II) at 298 K, $\Delta H_f^{\ominus}[Cu(S_2CNEt_2)_2,c] = -17.70 \pm 9.39$ kJ mol^{-1}. Thermochemical measurements are based on a ligand-exchange reaction, in dimethylformamide as solvent, involving the displacement of pentane-2,4-dionate in bis(pentane-2,4-dionato)copper(II) by the diethyldithiocarbamate anion. The homolytic and heterolytic copper–sulphur bond-enthalpy contributions are assessed as 143 ± 13 and 678 ± 13 kJ respectively.

THIS paper is complimentary to a previous paper reporting a solution calorimetric determination of the standard enthalpy of formation of bis(diethyldithiocarbamato)nickel(II);[1] $\Delta H_f^{\ominus} = -118.4 \pm 9.8$ kJ mol^{-1}. Also the homolytic and heterolytic nickel–sulphur bond-energy contributions were stated as 193 ± 13 and 666 ± 13 kJ respectively.

Calorimetric data for complexes containing metal–sulphur bonds, in general, and for metal dithiocarbamate complexes in particular are sparse. Thermochemical studies on metal dithiocarbamate complexes is at present limited to the metals, Pd^{II}, Zn^{II}, Cd^{II},[2] Ni^{II},[1] and Fe^{III} [3] and in only one case is metal–sulphur bond-energy data provided.[1] One further study that may be considered as relating to the present work is that of Irving and Lockyer [4] involving the solution thermochemistry of the square-planar complex, bis(5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato-*S*)nickel(II). Appropriate thermochemical calculations yielded nickel–sulphur bond-energy data.

This paper describes calorimetric experiments leading to the determination of the standard enthalpy of formation of bis(diethyldithiocarbamato)copper(II) and calculation of the thermochemical copper–sulphur bond energy. The heterogeneous standard-state, ligand-exchange reaction (1) is used as the basis for thermochemical calculations.

$$[Cu(C_5H_7O_2)_2](c) + 2[NEt_2H_2][S_2CNEt_2](c) \longrightarrow [Cu(S_2CNEt_2)_2](c) + 2NEt_2H(l) + 2\,C_5H_8O_2(l) \quad (1)$$

The corresponding homogeneous reaction in dimethylformamide is kinetically fast and quantitative at 298 K, and is ideal for calorimetric study. Dioxan is a common calorimetric solvent but is not suitable for the dissolution of bis(diethyldithiocarbamato)copper(II) due to the occurrence of adduct formation between complex and solvent.

The present data indicate that the copper–sulphur homolytic bond energy in bis(diethyldithiocarbamato)copper(II) is approximately 53 kJ less than the nickel–sulphur homolytic bond energy in bis(diethyldithiocarbamato)nickel(II) which reflects the expected trend in this parameter with change of the co-ordinating metal.

EXPERIMENTAL

The Calorimeter and Accessories.—The isoperibol reaction calorimeter and associated apparatus, together with the measurement procedure and data processing has been described in detail previously.[1] The calorimetric system was chemically calibrated using the thermochemical 'tham' [tris(hydroxymethyl)aminomethane] test reaction, the measured enthalpy of solution of 'tham' in 0.100 mol dm^{-3} HCl, $\Delta H_{tham}^{298} = -29.75 \pm 0.08$ kJ mol^{-1} based on five determinations; the accepted 'best' $\Delta H_{tham}^{298} = -29.757 \pm 0.008$ kJ mol^{-1}.[5] The system was also calibrated using the dissolution of potassium chloride in water as a standard test reaction, the measured $\Delta H_{KCl}^{298} = 17.55 \pm 0.12$ kJ mol^{-1} based on five determinations; the accepted 'best' $\Delta H_{KCl}^{298} = 17.548 \pm 0.012$ kJ mol^{-1}.[6] Uncertainty intervals associated with ΔH data are quoted as twice the standard deviation of the mean.[7]

Reagents.—Dimethylformamide,[8] diethylamine,[9] and pentane-2,4-dione [10] (B.D.H. reagent grade) were purified according to the established procedures.

Bis(diethyldithiocarbamato)copper(II) was prepared and purified by the established procedures,[11] m.p. 190—192 °C (Found: C, 33.7; H, 5.7; N, 7.8; S, 35.6. Calc. for $C_{10}H_{20}CuN_2S_4$: C, 33.4; H, 5.6; N, 7.8; S, 35.7%).

Bis(pentane-2,4-dionato)copper(II) was prepared by an established procedure.[12] The complex was purified by repeated sublimation (Found: C, 46.0; H, 5.4. Calc. for $C_{10}H_{14}CoO_4$: C, 45.9; H, 5.4%).

Microanalysis data were provided by the Australian Microanalytical Service, Melbourne.

RESULTS AND DISCUSSION

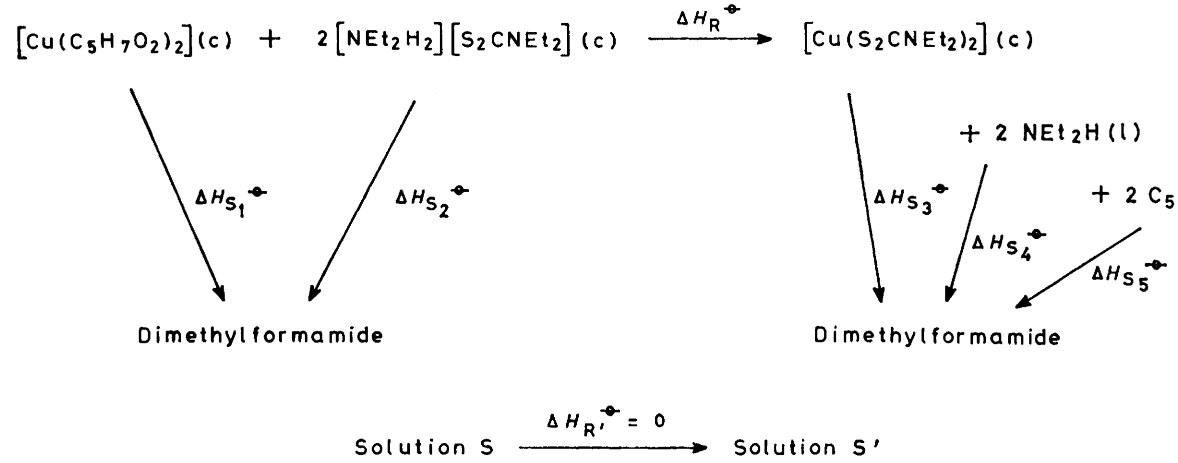
Solution Thermochemistry of Bis(diethyldithiocarbamato)copper(II).—The heterogeneous stoicheiometric ligand-exchange reaction (1) was used as the basis for the calculation of the standard enthalpy of formation of bis(diethyldithiocarbamato)copper(II) at 298 K. All five components in the formation reaction dissolve instantaneously in dimethylformamide at 298 K. The relevant thermochemical cycle is given in the Scheme. $\Delta H_{S1}^{\ominus}$ to $\Delta H_{S5}^{\ominus}$ inclusive were determined experimentally and since strict control of stoicheiometry was maintained throughout, dimethylformamide solutions S and S′ are thermodynamically equivalent and thus $\Delta H_{R'}^{\ominus}$ is zero.

Data yielding $\Delta H_{S1}^{\ominus}$ and $\Delta H_{S5}^{\ominus}$ are summarized in the Table and $\Delta H_R^{\ominus}$ is calculated from equation (2).

The combined enthalpy data in the Table yield $\Delta H_R^{\ominus}$ (298 K) $= 97.59 \pm 1.1$ kJ mol^{-1}. Standard enthalpies

$$\Delta H_R^\ominus = \Delta H_{S1}^\ominus + 2\Delta H_{S2}^\ominus - \Delta H_{S3}^\ominus - 2\Delta H_{S4}^\ominus - 2\Delta H_{S5}^\ominus \quad (2)$$

of formation of bis(pentane-2,4-dionato)copper(II), pentane-2,4-dione, and diethylamine are -776.05 ± 2.22,[13] -425.5 ± 1.0,[14] and -103.68 ± 1.21 [15] kJ mol^{-1} respectively. The standard enthalpy of formation of diethylammonium diethyldithiocarbamate has been determined by reaction calorimetry as -198.8 ± 4.1 kJ mol^{-1}.[16] Thus $\Delta H_f^\ominus[Cu(S_2CNEt_2)_2,\ c] = -17.70 \pm 9.39$ kJ mol^{-1}. The heterogeneous standard-state reaction involving the indirect formation of bis(diethyldithiocarbamato)copper(II) is endothermic; however, an increase in entropy is predicted from the stoicheiometric equation describing this reaction and it appears that the spontaneity of ligand exchange is entropy controlled.[1] The sublimation enthalpy of bis(diethyldithiocarbamato)copper(II) [17] is 116.2 ± 1.3 kJ mol^{-1} and hence $\Delta H_f^\ominus[Cu(S_2CNEt_2)_2,\ g] = 98.50 \pm 9.48$ kJ mol^{-1}.



SCHEME Thermochemical cycle for the determination of $\Delta H_f^\ominus$(298 K) of bis(diethyldithiocarbamato)copper(II)

Solution calorimetric data yielding $\Delta H_f^\ominus$ of $[Cu(S_2CNEt_2)_2]$ at 298 K

Calorimetric reaction	No. of determinations	$\Delta H^\ominus$/kJ mol^{-1} (298 K)
Solvent + $[Cu(C_5H_7O_2)_2]$ (c) $\longrightarrow$ Solution S_1	5	$\Delta H_{S_1}^\ominus$ 20.69 ± 0.41
S_1 + $[NEt_2H_2][S_2CNEt_2]$ (c) $\longrightarrow$ Solution S	5	$\Delta H_{S_2}^\ominus$ 48.58 ± 0.16
Solvent + $[Cu(S_2CNEt_2)_2]$ (c) $\longrightarrow$ Solution S_2	5	$\Delta H_{S_3}^\ominus$ 34.04 ± 0.20
S_2 + NEt_2H(l) $\longrightarrow$ Solution S_3	5	$\Delta H_{S_4}^\ominus$ -6.07 ± 0.46
S_3 + $C_5H_8O_2$(l) $\longrightarrow$ Solution S′	3	$\Delta H_{S_5}^\ominus$ -0.821 ± 0.08
S $\longrightarrow$ S′	1	$\Delta H_R'^\ominus$ 0.00

The method of obtaining the metal–sulphur homolytic bond-energy parameter has been described in detail previously and the symbolism has also been documented.[1] The following relevant thermodynamic parameters (298 K) are taken from the literature or are calculated by the well established methods given previously:[1] $\Delta H_f(H) = 217.99 \pm 0.25$,[15] $\Delta H_f(Et_2NCS_2H,\ g) = 35.13 \pm 15.00$,[1] $\bar{D}$(S–H) $(Et_2NCS_2H) = 346.6 \pm 25$,[1] $\Delta H_f(Et_2NCS_2^\cdot) = 163.8 \pm 29$,[1] $\Delta H_{sub}(Cu) = 339.32$,[18] $\Delta H_{fr} = 571.82 \pm 59$, $(I_1 + I_2)_{Cu} = 2\,702$,[19] $E_L(Et_2NCS_2^\cdot) = 200$,[1] and $\Delta H_{fi} = -2\,886 \pm 52$ kJ mol^{-1}. From these data $\bar{D}$(Cu–S) and $\bar{D}'$(Cu–S) for bis(diethyldithiocarbamato)copper(II) are derived as 143 ± 13 and 721 ± 18 kJ respectively. ΔH_{fi} is corrected for crystal-field stabilisation energy, δH, by assuming an analogous d-orbital splitting pattern for bis(diethyldithiocarbamato)copper(II) as proposed by Dingle [20] for the corresponding nickel(II) complex. δH is thus derived as -174.3 kJ mol^{-1} yielding corrected ΔH_{fi} and $\bar{D}'$(Cu–S) as $-2\,712$ kJ mol^{-1} and 678 kJ respectively.

Metal–sulphur bond lengths for the complexes $[M(S_2CNEt_2)_2]$ ($M = Ni^{II}$ or Cu^{II}) are 221 and 231 pm [21] respectively and hence the greater Cu–S bond length is consistent with the lower metal–sulphur bond energy for bis(diethyldithiocarbamato)copper(II). Conversely, the metal–sulphur heterolytic bond energy for bis(diethyldithiocarbamato)copper(II) is greater than that for the corresponding nickel(II) complex which reflects the well established trend [22] of increasing corrected enthalpy change for the gas-phase formation of the complex from the constituent ions with increasing atomic number of the metal cation.

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