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

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The standard enthalpy of formation of bis(diethyldithiocarbamato)nickel(II) has been derived by solution calorimetry, $\Delta H_f^\ominus$ (298 K) = −118.4 ± 9.8 kJ mol^{-1}. Thermochemical measurements are based on a ligand-exchange reaction involving the complete displacement of pentane-2,4-dionate in bis(pentane-2,4-dionato)nickel(II) by the diethyldithiocarbamate anion. The homolytic and heterolytic nickel–sulphur bond-energy parameters are calculated to be 193 ± 13 and 666 ± 13 kJ respectively.

In recent years, the number of publications dealing with various aspects of the chemistry of metal dithiocarbamates has burgeoned.[1-3] However, although considerable interest is currently directed to thermochemical bond energies in general, and metal–ligand bond energies of complexes in particular,[4,5] the thermodynamic properties of the metal dithiocarbamates have received little attention, the bulk of the data available being stability constants.[6-13] Further, although calorimetric data for metal complexes containing oxygen and nitrogen ligands are considerable,[4] such data for metal complexes containing sulphur ligands, in particular, metal dithiocarbamate complexes, are sparse. Bernard and Borel [14] have published standard heats of formation of several bis(dithiocarbamato)metal(II) complexes, $[M(S_2CNH_2)_2]$ (M = Pb, Zn, or Cd), as derived by reaction calorimetry. Annuar *et al.*[15] have determined the enthalpy change (303 K) for the standard-state solid-phase complexation reaction (1) by conventional reaction calorimetry.

$$FeCl_3(c) + 3Na[S_2CNEt_2](c) \longrightarrow [Fe(S_2CNEt_2)_3](c) + 3NaCl(c) \quad (1)$$

Cavell *et al.*[16] have derived the standard heat of formation of diethylammonium diethyldithiocarbamate by reaction calorimetry. Sublimation enthalpies have been reported for $[M^{II}(S_2CNEt_2)_2]$ complexes (M = Cu, Ni, Zn, Co, Cd, or Hg) and for $[Fe(S_2CNEt_2)_3]$ as derived from isoteniscopic vapour pressure–temperature data.[17,18] Cavell *et al.*[19] have recently reported ΔH_{sub} values for nickel(II) and copper(II) diethyldithiocarbamates as derived by the sublimation-bulb technique. No further enthalpy data for metal dithiocarbamate complexes exist.

This paper describes calorimetric experiments leading to the determination of the standard enthalpy of formation of bis(diethyldithiocarbamato)nickel(II), and calculation of the thermochemical nickel–sulphur bond energy. The heterogeneous standard-state ligand-exchange reaction (2) is used as the basis for thermochemical

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

measurements. The corresponding homogeneous reaction in dioxan is kinetically fast and quantitative at 298 K, and is ideal for calorimetric study.

It appears that the well established trend relating the metal cationic radius to the gas-phase enthalpy of formation of the complex as corrected for crystal-field effects, for complexes containing metal–oxygen co-ordinate bonds,[20] may exist for transition-metal complexes of dithiocarbamic acids.

EXPERIMENTAL

The Calorimeter and Accessories.—The isoperibol reaction calorimeter used was the Tronac model 450 thermometric titration–reaction calorimeter (Tronac Inc., Orem, Utah, U.S.A.). The calorimeter was a rapid-response, glass, vacuum Dewar of 40 cm^3 capacity. An all-glass stirrer-ampoule breaker was employed and glass ampoules of *ca.* 0.5 cm^3 capacity were used. The thermostat bath was maintained at 25.0 ± 0.001 °C by employing the Tronac model 1040 precision temperature controller. Potential measurements were made using a Systron–Donner model 7005A digital voltmeter and thermograms were recorded using a Perkin-Elmer 56 multi-range strip-chart recorder. The well defined standard procedure [21] for the measurement of enthalpy change was adopted. The calorimetric system was calibrated electrically by the standard method [21] and the total heat capacity of the calorimeter and contents, ε, was calculated according to the equation $\varepsilon = V_1V_2t(R_s\theta_c)^{-1}$ where V_1 and V_2 are the potential differences (volts) across the series standard resistance R_s (= 100.07 Ω) and across the calorimeter calibration heater respectively, t (s) is the calibration heating period, and θ_c is proportional to the corrected temperature rise during electrical calibration. For the reaction of interest, $\Delta H_R = \varepsilon\theta_R n_R^{-1}$ where θ_R is proportional to the corrected temperature change for the reaction as determined by Dickinson's graphical method [22,23] and n_R is the number of moles of the reactant defining unit reaction. The system was chemically calibrated using the thermochemical 'tham' test reaction,* the measured enthalpy of solution of tham in 0.100 0 mol dm^{-3} HCl being $\Delta H_{tham}^{298} = -29.757 \pm 0.008$ kJ mol^{-1} based on five determinations; the accepted 'best' $\Delta H_{tham}^{298} = -29.757 \pm 0.008$ kJ mol^{-1}.[24] 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}.[25] Uncertainty intervals associated with ΔH data are quoted as twice the standard deviation of the mean.[26]

Reagents.—Dioxan,[27] diethylamine,[27] and pentane-2,4-dione [28] (B.D.H. reagent grade) were purified according to the well established procedures.

Bis(diethyldithiocarbamato)nickel(II) was prepared and purified by the well established procedures,[1] m.p. 234—236 °C (Found: C, 34.0; H, 5.8; N, 7.8; S, 35.9. Calc. for

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* tham = Tris(hydroxymethyl)aminomethane.

$C_{10}H_{20}N_2NiS_4$: C, 33.8; H, 5.7; N, 7.9; S, 36.1%). Bis(pentane-2,4-dionato)nickel(II) was prepared, anhydrous, by a well established procedure.[29] The complex was purified by repeated sublimation (Found: C, 47.0; H, 5.4. Calc. for $C_{10}H_{14}NiO_4$: C, 46.8; H, 5.5%).

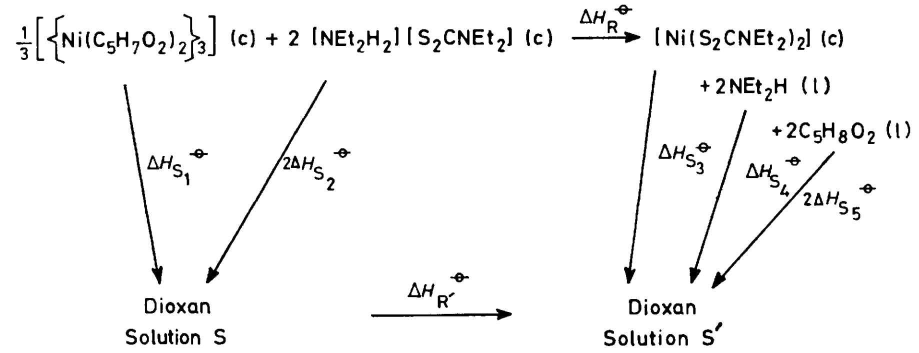
Microanalysis data were provided by the Australian Microanalytical Service, Melbourne.

RESULTS AND DISCUSSION

Solution Thermochemistry of Bis(diethyldithiocarbamato)nickel(II).—The heterogeneous stoicheiometric ligand-exchange reaction (3) was used as the basis for the

$$\tfrac{1}{3}[\{Ni(C_5H_7O_2)_2\}_3](c) + 2[NEt_2H_2][S_2CNEt_2](c) \longrightarrow [Ni(S_2CNEt_2)_2] + 2NEt_2H(l) + 2C_5H_8O_2(l) \quad (3)$$

calculation of the standard enthalpy of formation of bis(diethyldithiocarbamato)nickel(II) at 298 K. All five components in the formation reaction dissolve instantaneously in dioxan at 298 K. The relevant thermochemical cycle is given in the Scheme. $\Delta H_{S_1}^{\ominus}$ to $\Delta H_{S_5}^{\ominus}$ inclusive were determined experimentally and since strict control of stoicheiometry was maintained throughout, dioxan solutions S and S′ are thermodynamically equivalent and thus $\Delta H_{R}'^{\ominus}$ is zero. Data yielding $\Delta H_{S_1}^{\ominus}$—$\Delta H_{S_5}^{\ominus}$ are summarised in Table 1 and $\Delta H_{R}^{\ominus}$ is calculated from equation (4).



SCHEME Thermochemical cycle for the derivation of $\Delta H_f^{\ominus}$ (298 K) of bis(diethyldithiocarbamato)nickel(II)

$$\Delta H_R^{\ominus} = \Delta H_{S_1}^{\ominus} + 2\Delta H_{S_2}^{\ominus} - \Delta H_{S_3}^{\ominus} - 2\Delta H_{S_4}^{\ominus} - \Delta H_{S_5}^{\ominus} \quad (4)$$

Substituting mean values of $\Delta H_{S_1}^{\ominus}$ to $\Delta H_{S_5}^{\ominus}$ into equation (4) yields $\Delta H_R^{\ominus}$ (298 K) = 94.5 ± 2.0 kJ mol^{-1}. Standard enthalpies of formation of tris[bis(pentane-2,4-dionato)nickel(II)], pentane-2,4-dione, and diethylamine are −2 610.9 ± 0.330,[30] −423.8 ± 1.5,[31] and −103.68 ± 1.21 [31] 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 $\Delta H_f^{\ominus}[Ni(S_2CNEt_2)_2]$ = −118.4 ± 9.8 kJ mol^{-1}. The heterogeneous standard-state reaction involving the indirect formation of bis(diethyldithiocarbamato)nickel(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. A necessary preliminary to the calculation of nickel–sulphur bond energies is to derive the gas-phase enthalpy of formation of bis(diethyldithiocarbamato)nickel(II). The sublimation enthalpy of this complex is 102.6 ± 1.5 kJ mol^{-1} [19] and hence $\Delta H_f^{\ominus}[Ni(S_2CNEt_2)_2,g]$ = −15.9 ± 9.9 kJ mol^{-1}. Two nickel–sulphur bond-energy parameters are of theoretical significance. The homolytic bond-energy parameter, $\bar{D}$(Ni–S), is calculated from ΔH_{fr}, the gas-phase enthalpy change corresponding to the formation of gaseous bis(diethyldithiocarbamato)nickel(II) from gaseous nickel atoms and gaseous ligand radicals in the lowest energy state [equation (5)]. Since the reorganisational energy

$$Ni(g) + 2Et_2NCS_2{\cdot}(g) \xrightarrow{\Delta H_{fr}} [Ni(S_2CNEt_2)_2](g) \quad (5)$$

associated with the ligand upon complexation is normally neglected and, since the four metal–sulphur co-ordinate bonds are considered equivalent, due to resonance within the dithiocarbamate moiety, $\Delta H_{fr} = -4\bar{D}$(Ni–S). The heterolytic bond-energy parameter, $\bar{D}'$(Ni–S), is calcuated from ΔF_{fi}, the gas-phase enthalpy change corresponding to the formation of gaseous bis(diethyldithiocarbamato)nickel(II) from gaseous nickel cations and gaseous diethyldithiocarbamate anions in the lowest energy state [equation (6)], $\Delta H_{fi} = -4\bar{D}'$(Ni–S). The

$$Ni^{2+}(g) + 2Et_2NCS_2^-(g) \xrightarrow{\Delta H_{fi}} [Ni(S_2CNEt_2)_2](g) \quad (6)$$

$$\bar{D}'(Ni\text{–}S) = \bar{D}(Ni\text{–}S) + \tfrac{1}{4}\sum_{i=1}^{i=2} I_i + \tfrac{5}{4}RT - \tfrac{1}{2}E_L \quad (7)$$

two parameters are related by equation (7) where I_i is the *i*th ionisation potential of nickel and E_L is the

TABLE 1

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

Calorimetric reaction	No. of determinations	$\Delta H^{\ominus}$/kJ mol^{-1} (298 K)
Solvent + $[Ni(C_5H_7O_2)_2]$ (c) ⟶ Solution S_1	5	$\Delta H_{S_1}^{\ominus}$ 14.21 ± 0.38
S_1 + $[NEt_2H_2][S_2CNEt_2]$ (c) ⟶ Solution S	5	$\Delta H_{S_2}^{\ominus}$ 62.22 ± 0.47
Solvent + $[Ni(S_2CNEt_2)]$ (c) ⟶ Solution S_2	5	$\Delta H_{S_3}^{\ominus}$ 42.0 ± 1.1
S_2 + NEt_2H(l) ⟶ Solution S_3	6	$\Delta H_{S_4}^{\ominus}$ −15.26 ±0.68
S_3 + $C_5H_8O_2$(l) ⟶ Solution S′	3	$\Delta H_{S_5}^{\ominus}$ 2.14 ± 0.04
S ⟶ S′	1	$\Delta H_{R}'^{\ominus}$ 0.0

electron affinity of the dithiocarbamate radical. The resonance-stabilised diethyldithiocarbamate radical is formed by removal of the thiolic hydrogen atom from the parent dithiocarbamic acid; the S–H bond dissociation energy, $\bar{D}(Et_2NCS_2\text{–}H)$, is derived from equation (8).

$$Et_2NC({=}S)\text{–}S\text{–}H(g) \longrightarrow Et_2NCS_2^{\bullet}(g) + H^{\bullet}(g)$$

$$\bar{D}(Et_2NCS_2\text{–}H) = \Delta H_f(\text{radical}) + \Delta H_f(H) - \Delta H_f(\text{acid, g}) \quad (8)$$

The enthalpy of formation of $H^{\bullet}(g)$ (298 K) = 217.99 ± 0.25 kJ mol^{-1}.[31] The enthalpy of formation of gaseous diethyldithiocarbamic acid ΔH_f(acid, g) is unknown, but may be calculated using the Allen bond-energy scheme.[32] The following total effective bond-energy terms are adopted: B(C–H) = −187.02; B(C–C) = 55.31; B(C–N) = 192.05; B(C–S) = 43.01; and B(S–H) = −9.37 kJ. The total interaction energy terms for adjacent bond pairs, Γ(CCN) = −34.31 and Γ(CNC) = −53.97 kJ, are also assumed and the interaction energy term for the CCC non-bonded trio Δ^{N}_{CCC} is taken as +6.82 kJ. Values of B(C=S), Γ(NCS), $\Gamma(NC_dS_d)$, $\Gamma(S_dC_dS)$, and $\Delta^{C(d)}_{NSS(d)}$ [(d) indicates that the atom is involved in double-bond formation] are unavailable but may be estimated as a composite-group contribution by reference to 1,3-dithiane-2-thione as a comparison molecule. The $S{=}CS_2$ group of this molecule approximates to the S=CSN group of diethyldithiocarbamic acid and the heat of formation of gaseous 1,3-dithiane-2-thione = 78.66 ± 2.93 kJ mol^{-1}.[31] Thus, the S=CSN composite-group energy contribution is estimated as 22.59 kJ and hence ΔH_f(acid,g) = 35.13 kJ mol^{-1}. The S–H bond-dissociation energy $\bar{D}$(S–H) for diethyldithiocarbamic acid is estimated by comparison of $\bar{D}$(O–H) for water, and $\bar{D}$(O–H) for carboxylic acids, with $\bar{D}$(S–H) for hydrogen sulphide. The value of $\bar{D}$(O–H) for water is 498.3 kJ,[33] and that of acetic acid is 468.6 kJ.[33] Thus, in the absence of more realistic data for comparison, $\bar{D}$(S–H) for diethyldithiocarbamic acid is estimated as 30 kJ less than $\bar{D}$(S–H) for H_2S. Since the latter value is 376.6 kJ,[34] $\bar{D}$(S–H) for Et_2NCS_2H is 346.6 ± 25 kJ * and ΔH_f(radical) = 163.8 ± 25 kJ mol^{-1}. The value of ΔH_{fr} is calculated from equation (9)

$$\Delta H_{fr} = \Delta H_f^{\ominus}[Ni(S_2CNEt_2)_2,g] - 2\Delta H_f(\text{radical}) - \Delta H_{sub}(Ni) \quad (9)$$

assuming that ΔH_{sub} for Ni is 430.12 kJ mol^{-1}.[31] Thus ΔH_{fr} = 773.6 ± 51 kJ mol^{-1} and $\bar{D}$(Ni–S) = 193.4 ± 13 kJ. E_L, the electron affinity of the diethyldithiocarbamate radical, is assumed to be equal to the electron affinity of atomic sulphur for one electron, 2.07 eV † ≡ 200 kJ mol^{-1}.[34] Thus, from equation (7) $\bar{D}$(Ni–S) = 718 ± 13 kJ and ΔH_{fi} = −2 872 ± 52 kJ mol^{-1}. Using the spectroscopic data for bis(diethyldithiocarbamato)-nickel(II) reported by Dingle,[35] the crystal-field stabilisation energy δH for this complex is calculated as 206 kJ mol^{-1} yielding corrected ΔH_{fi} and $\bar{D}'$(Ni–S) values of −2 666 ± 52 kJ and 666 ± 13 kJ mol^{-1}.

Bernard and Borel [14] have reported the standard heat of formation of three metal dithiocarbamates, $[M(S_2CNH_2)_2]$ (M = Pb^{II}, Zn^{II}, or Cd^{II}), $\Delta H_f^{\ominus}$ = −100.5, −190.4, and −144.9 kJ mol^{-1}, respectively. $\bar{D}$(M–S) and $\bar{D}'$(M–S) may be calculated for these complexes if the enthalpy of sublimation for each complex is estimated as 115 ± 15 kJ mol^{-1}. The data are recorded in Table 2.

TABLE 2

Bond-energy parameters for metal dithiocarbamate complexes

Complex	$-\Delta H_{fr}$/ kJ mol^{-1}	$\bar{D}$(M–S)/ kJ	$-\Delta H_{fi}$/ kJ mol^{-1}	$\bar{D}'$(M–S)/ kJ
$[Pb(S_2CNH_2)_2]$	617	154	2 396	599
$[Zn(S_2CNH_2)_2]$	642	161	2 887	722
$[Cd(S_2CNH_2)_2]$	578	145	2 683	671

The bond-energy parameters for the zinc and cadmium complexes probably represent maximum values since it is known that in these complexes the metal is weakly five-co-ordinate.[2] Assuming that the thermochemical influence of the R groups attached to the dithiocarbamate moiety is small, the calculated bond-energy parameters for $[Zn(S_2CNH_2)_2]$ and $[Cd(S_2CNH_2)_2]$ compare favourably with the corresponding values for $[Ni(S_2CNEt_2)_2]$. Thus, it appears, from the very limited thermodynamic data available for metal dithiocarbamates, that a primary trend is recognisable between the ionic radius of the metal cation and the corrected enthalpy change for the gas-phase formation of the complex from the constituent ions.[36] The value of ΔH_{fi} for bis(diethyldithiocarbamato)copper(II) is required to establish this trend more succinctly.

To exemplify the significance of the present thermochemical bond-energy data, it is relevant and appropriate to review all other published nickel–sulphur bond-energy data. Ashcroft [37] has reported reaction calorimetric data for a series of transition-metal thiourea (tu) chloride complexes, $[M(tu)_4Cl_2]$ (M = Mn, Fe, Co, Ni, Zn, Cd, or Hg). Within the first transition series, the 'uncorrected' $\bar{D}$(M–S) values (298 K) range from 126 kJ (M = Mn) to 127 kJ (M = Zn) with M = Ni at the maximum of 148 kJ. For the octahedral complex $[Ni(tu)_6]Br_2$, $\bar{D}$(Ni–S), uncorrected for ligand-field stabilisation energy, is calculated as 363.4 kJ.[38] Apart from the present work, the only square planar nickel(II) complex containing nickel–sulphur bonds that has been studied calorimetrically is bis(5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato-*S*)nickel(II),[39] and $\bar{D}$(Ni–S) is reported as 232 ± 15 kJ. These data indicate that the thermochemical nickel–oxygen and nickel–sulphur coordinate bond energies are approximately equal and thus for square-planar nickel complexes it may be inferred that the groups NiS_2O_2 and NiS_4 are thermochemically equivalent and thus $\bar{D}$(Ni–S) for the heptenonato-complex should be approximately equal to $\bar{D}$(Ni–S) for bis(diethyldithiocarbamato)nickel(II). Considering all

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* The standard deviation of ±25 kJ mol^{-1} reflects the range in $\bar{D}$(O–H) values for a variety of organic compounds containing the hydroxyl group and it is assumed that $\bar{D}$(S–H) values span a similar range.

† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

the assumptions associated with such calculations, the two derived $\bar{D}$(Ni–S) values compare favourably.

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