Thermochemical Study of the Nickel–Sulphur Bond Energy in Bis(5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato-*S*)nickel(II)

By **Roger J. Irving** * and **Trevor N. Lockyer**, Department of Chemistry, The University of Surrey, Guildford GU2 5XH

The standard enthalpy of formation of the title complex has been determined at 298.15 K by solution calorimetry. The gas-phase enthalpy of formation has been calculated and a value for the Ni–S bond energy has been derived.

MONOTHIO-β-DIKETONE complexes of a wide range of transition metals have been investigated in recent years. Articles by Cox [1] and Livingstone [2] review this work. Such metal complexes are generally formed under similar conditions to those used for simple β-diketone compounds, since the free thio-ligands have a similar intramolecular hydrogen-bonded enol structure in the liquid or crystalline state.[3] Differences in the properties of the metal complexes can be rationalised in terms of the alteration in ligand-field strength resulting from a change in co-ordination environment from MO_4 or MO_6 to MO_2S_2 or MO_3S_3, respectively, for metal(II) or metal(III) ions. For example, the nickel complexes are generally quite different to the corresponding β-diketone complexes

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[1] M. Cox and J. Darken, *Co-ordination Chem. Rev.*, 1971, **7**, 29.

[2] S. E. Livingstone, *Co-ordination Chem. Rev.*, 1971, **7**, 59.

[3] S. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**, 673.

in that they are square-planar diamagnetic monomers,[3] soluble in organic solvents, rather than octahedral paramagnetic polymers such as [{Ni(pd)$_2$}$_3$] (pd = pentane-2,4-dionate anion).

Irving and his co-workers [4,5] have published precise thermochemical data on pentane-2,4-dione complexes of a variety of metals, obtained from direct calorimetric methods, and reliable estimates of the metal–oxygen bond energies in these complexes have been made. Few similar measurements have been carried out on thio-complexes. Ashcroft [6] investigated thiourea complexes of the type [M(tu)$_4$Cl$_2$] (tu = thiourea and M = bivalent Mn, Fe, Co, Ni, Zn, Cd, and Hg) by calorimetric methods and values in the range 115—145 kJ were found for $\bar{D}$(M–S), the metal–sulphur bond energy. In particular, the nickel–sulphur bond energy in [Ni(tu)$_4$Cl$_2$] was given as 147.7 kJ. However, in a later communication [7] Ashcroft determined $\bar{D}$(Ni-S) in the related complex [Ni(tu)$_6$]Br$_2$ as 363.4 kJ. It is difficult to see why, for a change in co-ordination from NiS$_4$Cl$_2$ to NiS$_6$, there should be such a dramatic change in $\bar{D}$(Ni–S). It is likely that assumptions concerning the values for $\bar{D}$(Ni–Cl) in [Ni(tu)$_4$Cl$_2$] and for the lattice energy of [Ni(tu)$_6$]Br$_2$ may be responsible for the variance in the values for $\bar{D}$(Ni–S). In general, compounds exhibiting MS$_4$ or MS$_6$ co-ordination are not amenable to study. For example, dithio-β-diketone ligands cannot be isolated in the free state, and in systems such as dithiocarbamate, dithiophosphate, dithiocarbonate, or dithiocarboxylate important thermochemical parameters such as ΔH_f or ΔH_v for the ligand or ΔH_v for a metal complex are either (*a*) not known, (*b*) not readily measured, or (*c*) not obtainable by reliable estimation.

However, in the case of the monothio-β-diketone complexes, these parameters can be estimated or calculated with some degree of confidence, and it would appear possible to obtain an estimate of the metal–sulphur bond energy in this case. Ideally, a compound of monothiopentane-2,4-dione would be the best choice for such an investigation, since the data on Hpd complexes are now well established. However, the free ligand is not very stable and calorimetric measurements involving it would be suspect. A more suitable thio-β-diketone is 2,2,6,6-tetramethyl-5-thioxoheptan-3-one (HL) since it is more stable, and thermochemical data are available on its parent β-diketone, dipivaloylmethane (HL′). Furthermore the nickel complex of HL′ has been recently investigated [8] *via* solution calorimetry. Since it is one of the very few nickel β-diketone complexes which are square and diamagnetic, it thus provides a more valid comparison with the corresponding monothio-complex. In any other nickel β-diketone complex the differences in stereochemistry and spin state would preclude valid comparison or estimation of some thermochemical data.

In moderate to strong acid conditions nickel complexes of monothio-β-diketones decompose, as do their oxygen analogues, to yield solvated nickel ions and protonated ligand. In the present work, use is made of this reaction to determine the heat of formation of bis(5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato-*S*)nickel(II), [NiL$_2$], and to calculate the nickel–sulphur bond energy.

EXPERIMENTAL

The LKB 8 700 precision calorimeter was used for all the reactions. Its operation and calibration have been described previously.[4]

The molar enthalpy of reaction was obtained from the equation (*i*) where $\Delta R_r = R_i - R_f$, $R_{mr} = (R_i + R_f)/2$, n is the

$$\Delta H = \varepsilon \Delta R_r / n R_{mr}\ \mathrm{J} \qquad (i)$$

number of moles of reactant, and R_i and R_f are the initial and final thermistor resistances determined by the Dickinson treatment.[9] The energy equivalent of the system is defined as $\varepsilon = Q_c R_{mc}/\Delta R_c$ J K^{-1}, where Q_c is an accurate amount of heat supplied from the calibration heater such that $Q_c = R_h I^2 t$ J where R_h is the calibration heater resistance (50.183 Ω), I is the calibration current, t is the heating time, and R_{mc} and ΔR_c correspond, for a calibration experiment, to R_{mr} and ΔR_r as defined above. The relation $\Delta R_r/R_{mr}$ is directly proportional to the temperature change. The value of ε was remarkably constant throughout all the measurements in the calorimetric solvent and its value, as determined from 25 determinations, was taken as 5 607 ± 8. This result was used in all subsequent calculations of ΔH.

Thermochemical results are expressed in terms of Joules. They refer to the isothermal process at 25 °C. The uncertainty intervals as quoted are twice the mean standard deviation.

Materials.—*Nickel*(II) *perchlorate hexahydrate.* The B.D.H. laboratory reagent was twice recrystallised from water and dried in air (Found: Ni, 16.1. Calc. for Ni[ClO$_4$]$_2$·6H$_2$O: Ni, 16.05%).

2,2,6,6-*Tetramethyl*-5-*thioxoheptan*-3-*one.* This compound was prepared from its parent β-diketone, dipivaloylmethane, as described by Chaston *et al.*[3] After solvent extraction and evaporation the residual oil was dissolved in ethanol and treated with excess of lead acetate dissolved in aqueous ethanol. The yellow lead complex precipitated quickly and the mixture was allowed to stand overnight. The complex was filtered off, washed with hot water, and recrystallised from ethanol to give the pure yellow complex. The dry material was suspended in anhydrous diethyl ether and dry H$_2$S gas was passed into the suspension for 10 min. The precipitated lead sulphide was filtered off and the filtrate was evaporated *in vacuo* to yield the monothio-β-diketone as an orange oil (Found: C, 65.4; H, 10.2. Calc. for C$_{11}$H$_{20}$OS: C, 65.9; H, 10.1%).

Bis(5-*mercapto*-2,2,6,6-*tetramethylhept*-4-*en*-3-*onato*-S)-*nickel*(II). The brown nickel complex was prepared as described by Chaston *et al.*[3] It was recrystallised twice from acetone (Found: C, 57.9, 57.7; H, 8.5, 8.6. Calc. for C$_{22}$H$_{38}$NiO$_2$S$_2$: C, 57.8; H, 8.4%). The crystalline material was finely ground prior to weighing to ensure fast reaction in the calorimeter.

Butan-2-*one.* The B.D.H. laboratory reagent was boiled under reflux over solid K[MnO$_4$], dried with anhydrous

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[4] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1968, 3116.

[5] R. J. Irving and G. W. Walter, *J. Chem. Soc.* (*A*), 1969, 2690.

[6] S. J. Ashcroft, *J. Chem. Soc.* (*A*), 1970, 1020.

[7] S. J. Ashcroft, *J. Inorg. Nuclear Chem.*, 1971, **33**, 603.

[8] R. J. Irving and M. A. V. Ribeiro da Silva, unpublished work.

[9] H. C. Dickinson, *Bull. Nat. Bur. Stand.* (*U.S.*), 1915, **11**, 189.

sodium sulphate, and twice distilled. The material boiling in the range 79—80 °C was collected and used.

Perchloric acid. AnalaR grade perchloric acid (72%) was diluted carefully to 65%. The density was 1.591 g cm^{-3} which corresponds [10] to a concentration of 64.8% $HClO_4$ equivalent to $HClO_4 \cdot 3.03\ H_2O$.

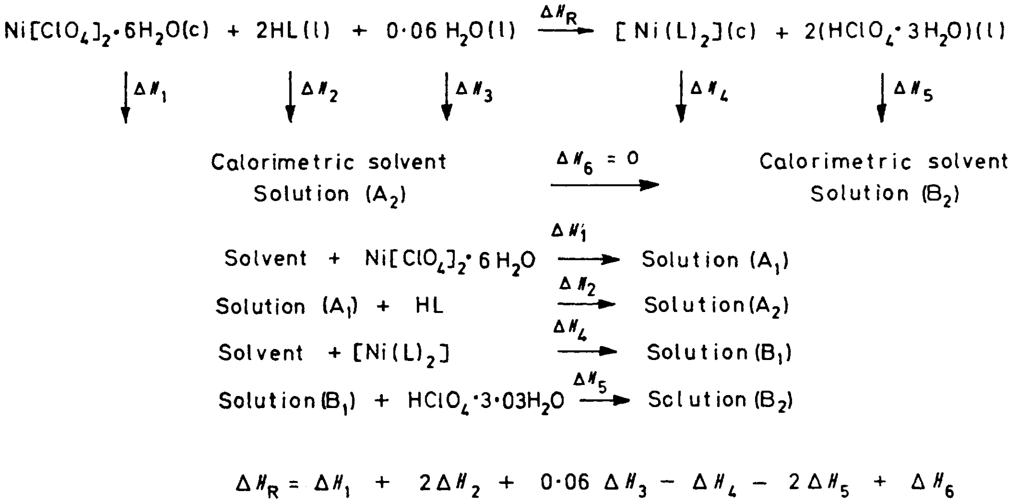
The calorimetric solvent. A butan-2-one–$HClO_4 \cdot 3.03\ H_2O$ (9 : 1) mixture was found to be suitable. In this mixture, solution of the complex was fast and decomposition was complete within 5 min. The solvent mixture was made up separately for each series of calorimetric measurements and used immediately, since over 24 h it develops a distinct yellow colouration.

RESULTS AND DISCUSSION

The standard enthalpy of formation of crystalline $[NiL_2]$ may be determined from reaction (1). The

$$Ni[ClO_4]_2 \cdot 6H_2O(c) + 2HL(l) \xrightarrow{\Delta H_R} [NiL_2](c) + 2HClO_4 \cdot 3H_2O(l) \quad (1)$$

difference between the enthalpies of solution of products and reactants, in the correct stoicheiometric ratios, measured separately in the calorimetric solvent, gives the required ΔH_R value provided equilibrium is attained on dissolution of both products and reactants. That is, the final solutions obtained from both the reactant and product sides of equation (1) must be thermodynamically equivalent.



SCHEME

To 100.0 cm^3 of solvent, ampoules of nickel(II) perchlorate and the ligand HL were added consecutively to give ΔH_1 and ΔH_2. To a second portion (100.0 cm^3) of the same solvent were added consecutively ampoules of $[NiL_2]$ and $HClO_4 \cdot 3.03H_2O$, to give ΔH_4 and ΔH_5. This procedure and the related thermochemical cycle is summarised in the Scheme. The quantities of reactants used in any series of experiments were determined by the amount of nickel(II) perchlorate weighed out for that particular series, and correct stoicheiometry was thus maintained through each series. In this way, ΔH_R will be valid for the Scheme reaction, provided that $\Delta H_6 = 0$. In order to check this, solution (B_2) was added to (A_2) in the calorimeter; no detectable heat change occurred.

The experimental data are given in the Table. In order to evaluate ΔH_R, ΔH_3 must be obtained from the published [11] data on the heat of dilution of perchloric acid. In this case, the value so calculated for 0.06 ΔH_3 is so small that it may be neglected and calculation of ΔH_R gives 5.52 ± 1.17 kJ mol^{-1}. The heat of vaporisation of HL′ has been recently determined [12] as 59.54 ± 0.13 kJ mol^{-1}. Measurements of heats of vaporisation of several esters and their thio-analogues have shown [13] that the thio-esters have ΔH_v values which are 4.85 kJ greater than the corresponding esters. Applying a similar correction in the present case yields a value for ΔH_v(HL) of 64.4 ± 0.4 kJ mol^{-1}. The heat of vaporisation of $[NiL_2]$ was measured by the Knudsen method [8] and a value $\Delta H_v\{[NiL_2]\} = 117.7 \pm 8.0$ kJ mol^{-1} was thus obtained. It is apparent that the introduction of the thio-group in this complex causes no marked change in the value of ΔH_v, when compared to values for other β-diketone complexes which vary between 105 and 125 kJ mol^{-1}.

Using the literature values [14] $\Delta H_f^{\ominus}\{Ni[ClO_4]_2 \cdot 6H_2O(c)\} = -2\,035.9$ kJ mol^{-1} and $\Delta H_f^{\ominus}[HClO_4 \cdot 3.03\ H_2O(l)] = -974.8$ kJ mol^{-1} and ΔH_R, then $2\Delta H_f^{\ominus}[HL(l)] - \Delta H_f^{\ominus}\{[NiL_2](c)\} = 80.8$ kJ and $2\Delta H_f^{\ominus}[HL(g)] - \Delta H_f^{\ominus}\{[NiL_2](g)\} = 91.9$ kJ. The heat of formation of the ligand radical can be derived from the dissociation energy of the ligand (ΔH_d) according to

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[10] J. Timmermans, ' The Physico-Chemical Constants of Binary Systems in Concentrated Solutions,' Interscience, New York, 1960, vol. 4, p. 495.

[11] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, ' Selected Values of Chemical Thermodynamic Properties,' Technical Note 270–3, U.S. National Bureau of Standards, Washington, 1968.

[12] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1975, 798.

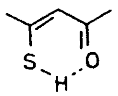
[13] I. Wadsö, *Acta Chem. Scand.*, 1966, **20**, 544.

[14] U. S. National Bureau of Standards, Circular 500, U.S. Govt. Printing Office, Washington D.C., 1952.

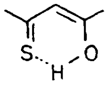
reaction (2). In simple β-diketones, a value for ΔH_d of 418 ± 20 kJ mol^{-1} is used.[15] It is a matter of conjecture whether the structure of liquid monothio-β-diketones

$$\mathrm{HL(g)} \xrightarrow{\Delta H_d} \mathrm{H^{\bullet}(g)} + \mathrm{L^{\bullet}(g)} \qquad (2)$$

shows the predominance of either of the two possible intramolecular hydrogen-bonded forms, *i.e.* keto–thioenol (1) or thioketo–enol (2). Cox and Darken[1] summarised evidence from n.m.r. and i.r. studies and pointed out that this is quite conflicting, and that a valid case for the predominance of either tautomeric isomer can be put forward. In HL the intramolecular hydrogen-bonded structure of the liquid would almost certainly persist in the gas phase. In this case we are presented with the problem of whether the dissociation is best represented by $\bar{D}$(O–H) (418 ± 20 kJ mol^{-1}) or by $\bar{D}$(S–H) (377 ± 20 kJ mol^{-1})[16] or by some intermediate value. As these values do not differ greatly and are each subject to a fairly large uncertainty we feel justified in using the value for ΔH_d of 398 ± 20 kJ mol^{-1}. This leads to $\Delta H_f[\mathrm{L^{\bullet}(g)}] - \Delta H_f[\mathrm{HL(g)}] = 180$ kJ and for $[\mathrm{NiL_2}](\mathrm{g}) \longrightarrow \mathrm{Ni(g)} + 2\mathrm{L^{\bullet}(g)}$, $\Delta H_{\mathrm{f.r.}} = \Delta H_f^{\ominus}\{[\mathrm{NiL_2}](\mathrm{g})\} - 2\Delta H_f^{\ominus}[\mathrm{L^{\bullet}(g)}] - \Delta H_f^{\ominus}[\mathrm{Ni(g)}] = -882 \pm 46$ kJ mol^{-1}. The Ni–O contribution to this bond energy may be taken as 209 ± 17 kJ for each Ni–O bond as determined for [NiL′$_2$].[8] The residual 464 kJ represents two Ni–S bonds, thus giving $\bar{D}$(Ni–S) = 232 ± 15 kJ mol^{-1}.



(1)



(2)

Enthalpy of formation of [NiL$_2$]

(*a*) Addition of Ni[ClO$_4$]$_2$·6H$_2$O to the calorimetric solvent

Amount of Ni[ClO$_4$]$_2$·6H$_2$O (mmol)	$10^3\Delta R/R_m$	ΔH / kJ mol^{-1}
0.250 29	1.033 3	−23.14
0.250 20	1.020 1	−22.84
0.249 90	0.976 9	−21.92
0.249 74	1.000 0	−22.47
0.249 11	0.965 5	−21.71

Mean $\Delta H_1 = -22.42 \pm 0.54$ kJ mol^{-1}

(*b*) Addition of HL to solution (A$_1$)

Amount of HL (mmol)	$10^3\Delta R/R_m$	ΔH / kJ mol^{-1}
0.502 67	0.419 8	4.69
0.501 17	0.415 9	4.64
0.498 43	0.402 1	4.52
0.497 93	0.397 7	4.48
0.494 53	0.386 4	4.44

Mean $\Delta H_2 = 4.55 \pm 0.09$ kJ mol^{-1}

(*c*) Addition of [NiL$_2$] to the calorimetric solvent

Amount of [NiL$_2$] (mmol)	$10^3\Delta R/R_m$	ΔH / kJ mol^{-1}
0.250 46	2.139 2	47.91
0.250 09	2.114 8	47.40
0.249 65	2.099 6	47.15
0.249 37	2.070 0	46.53
0.249 20	2.084 4	46.90

Mean $\Delta H_4 = 47.18 \pm 0.46$ kJ mol^{-1}

(*d*) Addition of HClO$_4$·3.03H$_2$O to solution (B$_1$)

Amount of HClO$_4$·3.03H$_2$O (mol)	$10^3\Delta R/R_m$	ΔH / kJ mol^{-1}
0.501 94	2.989 8	−33.39
0.500 77	2.949 8	−33.01
0.500 00	2.999 7	−33.64
0.498 77	2.893 1	−32.51
0.496 45	2.879 0	−32.51

Mean $\Delta H_5 = -33.01 \pm 0.46$ kJ mol^{-1}

A value of ε = 5 607 was used in all the calculations of ΔH.

Mass-spectrometric investigations of nickel complexes of other monothio-β-diketones show that (*a*) the Ni–O bond ruptures prior to Ni–S,[17] and (*b*) paramagnetic adducts of the type bis(monothio-β-diketone)(2,2′:6′,2″-terpyridine)nickel are six-co-ordinate with one unidentate thio-β-diketone residue bound only through the sulphur, as shown by the presence of a band attributable to ν(C=O) in the i.r. spectra.[18] However, it is apparent that, within the error limits of the present study, the nickel–oxygen and –sulphur bond energies are equal. The extensive electron delocalisation through the metal–chelate ring system may act such as to minimise the differences in the individual bond energies, and indeed the difference between Ni–O and Ni–S will be less than 30 kJ mol^{-1}.

Comparison of the above Ni–S bond-energy value with those obtained by Ashcroft[6,7] in the thiourea complexes shows a marked difference, and indeed the present value corresponds approximately to the mean of those values. However, it would be unwise to compare nickel–sulphur bond energies in two systems which differ so much in bond type, ligand charge, and stereochemistry. It is usually assumed that the Ni–S bond energy in a chelated monothio-β-diketone will be substantially greater than that in a simple thioketone–nickel co-ordinate bond. The results presented in this paper do not support this and we do not know of any other determinations of $\bar{D}$(Ni–S) in complexes similar to ours which would provide a more valid comparison.

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[15] J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 971.

[16] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[17] S. E. Livingstone, personal communication.

[18] S. H. Chaston, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1966, **19**, 1401; R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *ibid.*, 1968, **21**, 103.