Standard Enthalpies of Formation of Tris[bis(pentane-2,4-dionato)nickel(II)] and Bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II) and an Estimation of Nickel–Oxygen Bond Energies

By **Roger J. Irving** and **Manuel A. V. Ribeiro da Silva**,* Department of Home Economics, University of Surrey, Guildford GU2 5XH and Department of Chemistry, Faculty of Sciences, University of Oporto, Portugal

Standard enthalpies of formation of the title complexes have been determined from hydrolyses in acid solution by solution calorimetry at 298.15 K as −624.0 ± 2.2 and −299.2 ± 2.0 kcal mol^{-1} respectively. Estimates of gas-phase enthalpies of the monomeric forms of both complexes yield an average homolytic Ni–O bond energy of 50 ± 2 kcal mol^{-1}, but in the pentane-2,4-dionate trimer the bridging oxygens have Ni–O bond energies of approximately half those of the terminal Ni–O bonds.

IN its complex compounds Ni^{II} commonly has a co-ordination number of six: nickel(II) acetylacetonate (acetylacetonate = pentane-2,4-dionate), whose empirical formulae suggests a co-ordination number of 4, achieves the octahedral arrangement in the solid through the formation of a trimeric molecule [1,2] with oxygen-donor atoms forming three bridges between each pair of nickel atoms. This trimeric structure persists in solution in non-donor solvents,[3,4] but solvents such as water and pyridine break the oxygen bridges to give monomeric molecules,[5] [Ni(acac)$_2$L$_2$]. In the vapour state at 25 °C nickel(II) acetylacetonate exists as a planar monomer.[6] If the ligand is sufficiently bulky, steric hindrance can prevent the formation of trimers; thus 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane) [7] forms the stable monomeric planar compound [Ni(dpm)$_2$] which will not react with two molecules of pyridine.

In an attempt to determine the relative strengths of the bonds formed by β-diketones in their normal function as bidentate ligands and in their much less usual function as bridging groups, we have made a thermochemical study of [{Ni(acac)$_2$}$_3$] and [Ni(dpm)$_2$].

EXPERIMENTAL

The Solution Calorimeter.—The isoperibol LKB 8700 reaction-and-solution precision calorimeter was used for all the solution reactions.

The molar enthalpy of reaction was calculated from the relation $\Delta H = \varepsilon \Delta R_r/nR_{mr}$, where $\Delta R_r = R_i - R_f$, $R_{mr} = (R_i + R_f)/2$, n = number of moles of reactant, and R_i and R_f are the initial and final thermistor resistances in ohms as determined by the Dickinson treatment.[8] The energy constant, ε, of the calorimetric system is given by $\varepsilon = Q_cR_{mc}/\Delta R_c$, where Q_c is an accurately defined quantity of heat supplied electrically *via* the built-in heater, $Q_c = R_hI^2t/4.184$ cal (R_h is the resistance of the calibrating heater = 50.183 Ω, I is the calibration current in A, and t is the heating time in s), and R_{mc} and ΔR_c have the same significance in a calibration experiment as R_{mr} and ΔR_r have in a reaction. The quotient $\Delta R_r/R_{mr}$ is directly proportional to the temperature change.

Thermochemical functions are expressed in terms of 'the thermo-chemical calorie' (= 4.184 J) and refer to the isothermal process at 298.15 K and the true mass. The uncertainty interval is twice the standard deviation of the mean. A check on the accuracy of the calorimeter was carried out by determining the heat of dissolution of tris-[(hydroxymethyl)amino]methane (tham) in dilute hydrochloric acid. The result, −7.118 ± 0.006 kcal mol^{-1}, is in agreement with other work [9] (−7.120 ± 0.007 kcal mol^{-1}).

Decomposition of the complexes into metal ion and free ligand was extremely slow in dilute acid solution but satisfactory results could be obtained using 1 mol dm^{-3} sulphuric acid as solvent for the acetylacetonate complex and a solution of 75% 1,4-dioxan and 25% 'constant-boiling' hydrochloric acid for the dipivaloylmethanate complex.

Materials.—AnalaR grade nickel(II) chloride hydrate was powdered and stored in a desiccator *in vacuo* over sodium hydroxide. Periodic analyses of the nickel content showed that its composition remained constant at $NiCl_2 \cdot 6.00H_2O$. Nickel(II) sulphate hexahydrate was obtained from the corresponding AnalaR heptahydrate by dehydration in a vacuum desiccator. The compound was thoroughly mixed and stored in air-tight bottles for 2 weeks. Further analysis

---

[1] G. J. Bullen, R. Mason, and P. Pauling, *Nature*, 1961, **189**, 291.

[2] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

[3] D. P. Graddon and E. C. Watton, *Nature*, 1961, **190**, 906.

[4] F. A. Cotton and J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 2818.

[5] J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 24.

[6] S. Shibata, *Bull. Chem. Soc. Japan*, 1957, **30**, 753.

[7] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 1966, **5**, 1200.

[8] H. C. Dickinson, *Bull. Nat. Bur. Stand.*, 1915, **11**, 189.

[9] E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand., Sect. A.*, 1973, **77**, 581.

showed no change in composition. Constant boiling hydrochloric acid was found by titration to be 4.37 mol dm^{-3} ($HCl \cdot 11.60H_2O$). A 1 mol dm^{-3} solution of molar sulphuric acid was made from a B.D.H. AnalaR grade concentrated volumetric solution and checked by titration. It corresponded to the composition $H_2SO_4 \cdot 53.44(1)H_2O$. 1,4-Dioxan was purified according to ref. 10. 2,2,6,6-Tetramethylheptane-3,5-dione(Hdpm) was prepared and purified as described previously.[11] No impurities were detected by g.l.c. (Found: C, 71.65; H, 11.05. Calc. for $C_{11}H_{20}O_2$: C, 71.7; H, 10.95%). AnalaR grade B.D.H. acetylacetone (Hacac) was purified by successive fractional distillations (b.p. 140 °C at 760 mmHg),* and then stored under nitrogen in the dark. No impurities were detected by g.l.c. (Found: C, 60.1; H, 8.00. Calc. for $C_5H_8O_2$: C, 60.0; H, 8.05%).

Bis(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)*nickel*(II), [Ni(dpm)$_2$].—This complex was prepared by a modification of the method of Hammond *et al.*[12] A solution of AnalaR $NiCl_2 \cdot 6H_2O$ (7.2 g) in water (100 cm^3) was buffered with sodium acetate (10 g). A solution of Hdpm (9.8 g) in ethanol (15 cm^3) was added slowly with continuous stirring, and the light green precipitate was filtered off, washed with water, and dried in air. The green complex was twice recrystallized from light petroleum (b.p. 60—80 °C) and dried *in vacuo* at 94 °C, over P_4O_{10}, for 4 h. The colour changed from green to pinkish red, which corresponds to conversion of the dihydrate to the anhydrous form.[12] The complex was further purified by sublimation *in vacuo*, m.p. 225 °C (lit.,[12] 225 °C) (Found: C, 62.1; H, 9.10; Ni, 13.75. Calc. for $C_{22}H_{38}NiO_4$: C, 62.15; H, 9.00; Ni, 13.8%).

Tris[*bis*(*pentane*-2,4-*dionato*)*nickel*(II)], [{Ni(acac)$_2$}$_3$].—This complex was prepared in a similar manner from AnalaR $NiCl_2 \cdot 6H_2O$ and Hacac. The product was recrystallized three times from ethanol, and dried *in vacuo* at 90 °C, in the presence of P_4O_{10} for 6 h, to convert it into the anhydrous trimer. The complex was further purified by three sublimations *in vacuo*, m.p. 230 °C (lit.,[13] 230 °C) (Found: C, 46.75; H, 5.50; Ni, 22.9. Calc. for $C_{10}H_{14}NiO_4$: C, 46.75; H, 5.50; Ni, 22.85%).

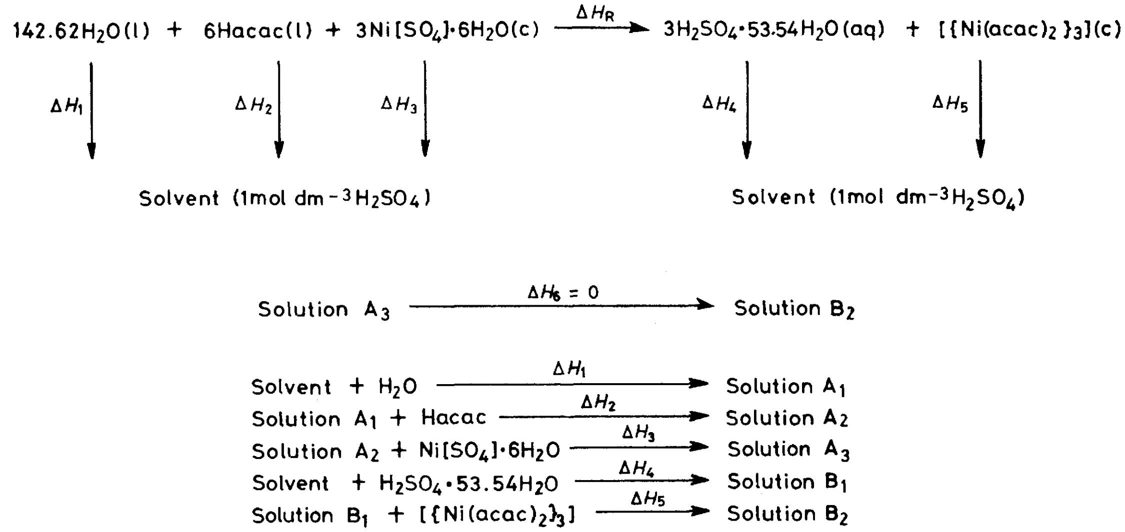
All the carbon and hydrogen analyses were carried out by the Microanalytical Service of the University of Surrey; nickel was analyzed by the ethylenediaminetetra-acetic acid method.[14]

RESULTS AND DISCUSSION

The standard enthalpies of formation of the nickel(II) β-diketonates can be determined from the reactions between the ligands and the nickel salts, *i.e.* for the acetylacetone complex as in (1). For the monomeric

$$6Hacac(l) + 3Ni[SO_4] \cdot 6H_2O(c) \xrightarrow{\Delta H_R} 3H_2SO_4 \cdot 6H_2O(l) + [\{Ni(acac)_2\}_3](c) \quad (1)$$

dipivaloylmethane complex a similar reaction was used, with $NiCl_2 \cdot 6H_2O$ as the nickel salt and $HCl \cdot 3H_2O$ on the right-hand side of the equation instead of $H_2SO_4 \cdot 6H_2O$. The difference between the enthalpies of solution of the products and reactants in the same stoicheiometric ratio gives the required enthalpy of formation, provided equilibrium is reached from either side within the period of the experiment.



SCHEME $\Delta H_R = 142.62\ \Delta H_1 + 6\ \Delta H_2 + 3\ \Delta H_3 - 3\Delta H_4 - \Delta H_5 + \Delta H_6$

To the calorimetric solvent (100.0 cm^3), ampoules of water, ligand, and the appropriate nickel(II) salt were added consecutively and ΔH_1, ΔH_2, and ΔH_3 were measured. To a second portion of the same solvent (100.0 cm^3), ampoules of the appropriate acid and nickel complex were added consecutively, and ΔH_4 and ΔH_5 were measured. The thermochemical cycle and the general procedure for the acetylacetonate complex is given in the Scheme. The quantities of reactants in a

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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

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

[12] G. S. Hammond, D. C. Nonhebel, and C. H. S. Wu, *Inorg. Chem.*, 1963, **2**, 73.

[13] E. W. Berg and J. T. Truemper, *J. Phys. Chem.*, 1960, **64**, 487.

[14] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1964.

particular series of experiments were determined by the amount of nickel hexahydrate salt in a particular ampoule; strict control of stoicheiometry was kept throughout each series.

If this procedure is used, the value calculated for ΔH_R will refer to the reaction indicated in the first line of the Scheme, provided that solutions A_3 and B_2 are identical and that the value of ΔH_6 is zero. As a check of the validity of this, ampoules of solution B_2 were broken into solution A_3 in the calorimeter; no heat change was detected.

For [{Ni(acac)$_2$}$_3$].*—(*a*) *Addition of water to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). The heat change was calculated from published data [15] as $\Delta H_1 = -0.029$ kcal mol^{-1}.

(*b*) *Addition of* Hacac(l) *to solution* A_1. $\Delta H_2 = 1.48 \pm 0.05$ kcal mol^{-1} (mean of five experiments). In a typical experiment, a solution of $9.838\,1 \times 10^{-4}$ mol of Hacac(l) in 100.0 cm^3 of solution A_1 gave $\Delta R/R_m = 5.602\,6 \times 10^{-4}$; taking $\varepsilon = 2\,574.3$ cal, this leads to $\Delta H = 1.466$ kcal mol^{-1}.

(*c*) *Addition of* Ni[SO$_4$]·6H$_2$O(c) *to solution* A_2. $\Delta H_3 = 5.18 \pm 0.03$ kcal mol^{-1} (mean of five experiments). In a typical experiment, a solution of $4.927\,1 \times 10^{-4}$ mol of Ni[SO$_4$]·6H$_2$O(c) in 100.0 cm^3 of solution A_2 gave $\Delta R/R_m = 9.913\,5 \times 10^{-3}$; taking $\varepsilon = 2\,568.0$ cal, this leads to $\Delta H = 5.167$ kcal mol^{-1}.

(*d*) *Addition of* $H_2SO_4 \cdot 53.54H_2O$(aq) *to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). This heat change was calculated from published data [15] as $\Delta H = 0.000$ kcal mol^{-1}.

(*e*) *Addition of* [{Ni(acac)$_2$}$_3$](c) *to solution* B_1. $\Delta H_5 = -30.59 \pm 0.07$ kcal mol^{-1} (mean of five experiments). In a typical experiment, a solution of $1.653\,2 \times 10^{-4}$ mol of [{Ni(acac)$_2$}$_3$](c) in 100.0 cm^3 of solution B_1 gave $\Delta R/R_m = 1.966\,2 \times 10^{-2}$; taking $\varepsilon = 2\,573.8$ cal, this leads to $\Delta H = -30.611$ kcal mol^{-1}.

The above results lead to $\Delta H_R = 50.88 \pm 0.24$ kcal mol^{-1} for the formation reaction of [{Ni(acac)$_2$}$_3$](c).

For [Ni(dpm)$_2$].—(*a*) *Addition of water to* 100.0 cm^3 *of solvent* (dioxan–HCl). This heat change has been measured in a previous study [16] as $\Delta H_1 = -0.22 \pm 0.02$ kcal mol^{-1}.

(*b*) *Addition of* Hdpm(l) *to solution* A_1. $\Delta H_2 = 2.74 \pm 0.04$ kcal mol^{-1} (mean of five experiments). In a typical experiment, a solution of $5.000\,5 \times 10^{-4}$ mol of Hdpm(l) in 100.0 cm^3 of solution A_1 gave $\Delta R/R_m = 8.383\,5 \times 10^{-4}$; taking $\varepsilon = 1\,640.6$ cal, this leads to $\Delta H = 2.750$ kcal mol^{-1}.

(*c*) *Addition of* NiCl$_2$·6H$_2$O(c) *to solution* A_2. $\Delta H_3 = -0.46 \pm 0.04$ kcal mol^{-1} (mean of five experiments). In a typical experiment, a solution of $2.503\,0 \times 10^{-4}$ mol of NiCl$_2$·6H$_2$O(c) in 100.0 cm^3 of solution A_2 gave $\Delta R/R_m = 6.928\,8 \times 10^{-5}$; taking $\varepsilon = 1\,652.0$ cal, this leads to $\Delta H = -0.457$ kcal mol^{-1}.

(*d*) *Addition of* HCl·11.60H$_2$O(l) *to* 100.0 cm^3 *of solvent* (dioxan–HCl). $\Delta H_4 = -4.92 \pm 0.04$ kcal mol^{-1}. In a typical experiment, a solution of $5.004\,3 \times 10^{-4}$ mol of HCl·11.60H$_2$O(l) in 100.0 cm^3 of solvent gave $\Delta R/R_m = 15.297\,0 \times 10^{-4}$; taking $\varepsilon = 1\,610.1$ cal, this leads to $\Delta H = -4.922$ kcal mol^{-1}.

(*e*) *Addition of* [Ni(dpm)$_2$](c) *to solution* B_1. $\Delta H_5 = -3.92 \pm 0.08$ kcal mol^{-1}. In a typical experiment, a solution of $2.511\,9 \times 10^{-4}$ mol of [Ni(dpm)$_2$](c) in 100.0 cm^3 of solution B_1 gave $\Delta R/R_m = 6.034\,9 \times 10^{-4}$; taking $\varepsilon = 1\,627.5$ cal, this leads to $\Delta H = -3.910$ kcal mol^{-1}.

The above results lead to $\Delta H_R = 15.00 \pm 0.37$ kcal mol^{-1} for the formation reaction of [Ni(dpm)$_2$](c).

The following data (kcal mol^{-1}) were used to calculate the enthalpies of formation of the crystalline complexes: $\Delta H_f^\ominus$(Ni[SO$_4$]·6H$_2$O, c) $= -641.21$; [17] $\Delta H_f^\ominus$(NiCl$_2$·6H$_2$O, c) $= -502.67$; [17] $\Delta H_f^\ominus$(H_2SO_4·6H$_2$O, l) $= -618.834$; [15] $\Delta H_f^\ominus$(HCl·3H$_2$O, l) $= -204.44$; [15] $\Delta H_f^\ominus$(Hacac, l) $= -101.29 \pm 0.37$; [18,19] $\Delta H_f^\ominus$(Hdpm, l) $= -146.2 \pm 1.0$.[11,16,20] The results are as follows: $\Delta H_f^\ominus$[{Ni(acac)$_2$}$_3$, c] $= -624.0 \pm 2.2$ and $\Delta H_f^\ominus$[Ni(dpm)$_2$, c] $= -299.2 \pm 2.0$ kcal mol^{-1}.

Wood and Jones [21] determined the heat of combustion of [Ni(acac)$_2$] and from this calculated the heat of formation of the solid complex. Although not stated specifically in their paper, the result presumably relates to the monomer, so that the true value of $\Delta H_f^\ominus$ would be 3×-413.18 kcal mol^{-1}, *i.e.* almost twice that which we have obtained. Recently Cavell and Pilcher [22] commented on possible sources of error in bomb-combustion studies of metal complexes which could explain the differences between the two techniques.

The enthalpy of sublimation of [Ni(dpm)$_2$] measured by the Knudsen effusion technique [23] is 34.7 ± 2.4 kcal mol^{-1}.

In the vapour state [Ni(acac)$_2$] is monomeric and, since the enthalpy of sublimation is derived from the variation of vapour pressure with temperature, the value obtained (22.9 ± 0.7 kcal mol^{-1}) [23] must refer to process (2). The enthalpy of reaction (3) has been determined

$$[\mathrm{Ni(acac)_2}]\ (\mathrm{c}) \longrightarrow [\mathrm{Ni(acac)_2}]\ (\mathrm{g}) \qquad (2)$$

$$\tfrac{1}{3}[\{\mathrm{Ni(acac)_2}\}_3]\ (\mathrm{c}) \longrightarrow [\mathrm{Ni(acac)_2}]\ (\mathrm{c}) \qquad (3)$$

---

* Further details of the calorimetric data for both complexes are available as Supplementary Publication No. SUP 22207 (5 pp.). See Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[15] 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. Nat. Bur. Standards, Washington, 1968.

[16] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1976, 1940.

[17] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values on Chemical Thermodynamic Properties,' Technical Note 270–4, U.S. Nat. Bur. Standards, Washington, 1969.

[18] G. R. Nicholsen, *J. Chem. Soc.*, 1957, 2431.

[19] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970.

[20] M. A. V. Ribeiro da Silva, Ph. D. Thesis, University of Surrey, 1973.

[21] J. J. Wood and M. M. Jones, *J. Phys. Chem.*, 1963, **67**, 1049.

[22] K. J. Cavell and G. Pilcher, *J.C.S. Faraday I*, 1977, 1590.

[23] R. J. Irving, R. A. Schulz, and H. Naghihi, unpublished work.

from equilibrium studies but the published value (-15 kcal)[24] is probably subject to a large uncertainty. For the corresponding system with 2,6-dimethylheptane-3,5-dione as ligand, 2 ± 2 kcal has been reported.[25]

In chloroform solution, nickel acetylacetonate is monomeric and, on the assumption that the net energy needed to break the bridging bond is comparable to, but cannot be greater than, the energy associated with the specific interaction between metal acetylacetonate and chloroform (5 kcal per Ni),[26] this value has been chosen for the energy needed to convert a third of the trimer into monomer. Accordingly, for process (4)

$$\tfrac{1}{3}[\{\mathrm{Ni(acac)_2}\}_3]\ (\mathrm{c}) \longrightarrow [\mathrm{Ni(acac)_2}]\ (\mathrm{g}) \qquad (4)$$

$\Delta H_{\mathrm{subl.}} = 28 \pm 2$ kcal mol^{-1}. The enthalpies of formation of the gaseous molecules are $\Delta H_f^{\ominus}[\mathrm{Ni(acac)_2, g}] = -180 \pm 2$ and $\Delta H_f^{\ominus}[\mathrm{Ni(dpm)_2, g}] = -265 \pm 2$ kcal mol^{-1}. Using the values $\Delta H_f^{\ominus}(\mathrm{H^{\bullet}, g}) = 52.1$,[15] $\Delta H_f^{\ominus}(\mathrm{acac^{\bullet}, g}) = -43.6 \pm 5.1$,[16] $\Delta H_f^{\ominus}(\mathrm{dmp^{\bullet}, g}) = -84.1 \pm 5.1$,[16] and $\Delta H_f^{\ominus}(\mathrm{Ni, g}) = 1\,027$ kcal mol^{-1},[17] the enthalpy change, $\Delta H_{\mathrm{f.r.}}$, can be found for the radical reaction (5), *i.e.*

$$\mathrm{Ni\ (g) + 2\ acac^{\bullet}\ (g)} \longrightarrow [\mathrm{Ni(acac)_2}]\ (\mathrm{g}) \qquad (5)$$

-196 ± 8 kcal mol^{-1}, and for the corresponding $[\mathrm{Ni(dpm)_2}]$ reaction $\Delta H_{\mathrm{f.r.}} = -199 \pm 8$ kcal mol^{-1}.

The average homolytic bond energies $\bar{E}$(Ni–O) derived from these values are 49 ± 2 kcal for $[\mathrm{Ni(acac)_2}]$ and 50 ± 2 kcal for $[\mathrm{Ni(dpm)_2}]$. A value of 71.8 kcal has been reported[21] for the Ni–O bond in nickel acetylacetonate. Using the published heat of combustion data, Ashcroft and Mortimer[27] recalculated this bond energy and found a value of 103 kcal. This seems far too high when it is considered that the bond-dissociation energy in NiO, a 'double' bond, is less than 99 kcal,[28,29] and suggests that the original heat of combustion data must be in error.

There is no significant difference in the strengths of bonds formed by acetylacetone and dipivaloylmethane with nickel. This was also found for the beryllium complexes[30] where $\bar{E} = 67 \pm 3$ kcal for both ligands, and aluminium[16] where $\bar{E} = 58 \pm 3$ for acetylacetone and 61 ± 3 for dipivaloylmethane. The enthalpy of the hypothetical sublimation reaction (6) is three times that

$$[\{\mathrm{Ni(acac)_2}\}_3]\ (\mathrm{c}) \longrightarrow [\{\mathrm{Ni(acac)_2}\}_3]\ (\mathrm{g}) \qquad (6)$$

for process (2) (minus the trimerization energy), *i.e.* 68.7 kcal per mol of trimer, and this gives $\Delta H_f^{\ominus}[\{\mathrm{Ni(acac)_2}\}_3, \mathrm{g}] = -555 \pm 4$ kcal mol^{-1}. For reaction (7)

$$3\ \mathrm{Ni\ (g)} + 6\ \mathrm{acac^{\bullet}\ (g)} \longrightarrow [\{\mathrm{Ni(acac)_2}\}_3]\ (\mathrm{g}) \qquad (7)$$

$\Delta H_{\mathrm{f.r.}} = -602 \pm 12$ kcal, representing the sum of the 18 Ni–O bonds in the trimer.

The *X*-ray structure determination[2] of $[\{\mathrm{Ni(acac)_2}\}_3]$ shows a Ni–O distance of 2.01 Å for the terminal (non-bridging) oxygens, and 2.12 Å for the bridging oxygens. If an average bond strength of 49 kcal is assigned to each of the six terminal bonds, then the residual bond energy can be shared equally among the 12 equivalent bridging oxygens. The resulting Ni–O bond energy of 26 kcal is close to half that of the terminal Ni–O bonds.

These bond energies refer to the hypothetical trimer molecule in the vapour state, but intermolecular forces in the solid might well influence the relative magnitude of the two types of Ni–O bond. Unfortunately, the relatively large errors inherent in this type of study do not permit a resolution in bond energy of less than 4 kcal so that in the vapour state both acetylacetone and dipivaloylmethane form bonds of equal strength; interatomic distances in the solid suggest that dipivaloylmethane (Ni–O 1.84 Å)[7] forms stronger bonds than does acetylacetone (Ni–O 2.01 Å),[2] but again the position is not really clarified as there is no quantitative relation between bond strength and bond length.

One of us (M. A. V. R. S.) thanks the Calouste Gulbenkian Foundation, Lisbon, for support for part of this work, the Instituto de Alta Cultura, Lisbon, for the award of a research grant, and the Chemistry Department of the Faculty of Sciences, Oporto University, for leave of absence.

[7/1195 *Received*, *7th July*, 1977]

---

[24] L. T. Ang and D. P. Graddon, *Austral. J. Chem.*, 1973, **26**, 1901.

[25] D. P. Graddon and T. T. Nyein, *Austral. J. Chem.*, 1974, **27**, 407.

[26] R. J. Irving and R. A. Schulz, *J.C.S. Dalton*, 1973, 2414.

[27] S. J. Ashcroft and C. T. Mortimer, 'Thermochemistry of Transition Metal Complexes,' Academic Press, London, 1970.

[28] L. Brewer and D. F. Mastick, *J. Chem. Phys.*, 1951, **19**, 834.

[29] T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

[30] R. J. Irving and M. A. V. Ribeiro da Silva, *J.C.S. Dalton*, 1977, 413.