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ENTHALPY OF FORMATION OF TRIS[BIS(BENZOYLACETONATO)-NICKEL(II)] AND THE MEAN NICKEL(II)-OXYGEN BOND DISSOCIATION ENTHALPIES

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ABSTRACT

The standard enthalpy of formation of crystalline tris[bis(benzoylacetonato)nickel(II)] has been determined at 298.15 K by solution calorimetry as -1895.3 ± 17.5 kJ mole^{-1}. The enthalpies of sublimation of both the trimeric and monomeric forms of the complex were estimated. From the enthalpies of formation of the gaseous forms, the average bond dissociation enthalpies of 203 kJ mole^{-1} and 107 kJ mole^{-1} were derived for the non-bridging and the bridging Ni–O bonds, respectively.

INTRODUCTION

Complexes of β-diketones with Ni(II) tend to polymerize. To give the nickel atom a coordination number of six and an octahedral configuration of ligands, trimeric molecules are formed in the solid. Thermochemical studies of the trimeric [1,2] bis(acetylacetonato)nickel(II) and the monomeric [3] bis(dipivaloylmetanato)-nickel(II) have been reported [4] and an estimation of both bridging and non-bridging Ni–O bond dissociation enthalpies was made. This paper extends this study to the trimeric [5,6] bis(benzoylacetonato) nickel(II) *.

EXPERIMENTAL

The solution calorimeter

The isoperibol LKB 8700 reaction-and-solution precision calorimeter was used. The operation and calculation methods have been described [4,7] and the same symbols are used here.

Thermochemical functions refer to the isothermal process at 298.15 K. The uncertainty interval is twice the standard deviation of the mean. The accuracy of the

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* Benzoylacetone, abbreviated as Hbzac, is 1-phenylbutane-1,3-dione.

calorimeter was checked by measuring the enthalpy of solution of tris[(hydroxymethyl)amino]methane (tham) in 0.1 mole dm^{-3} hydrochloric acid: -29.78 ± 0.02 kJ mole^{-1} is in agreement with the literature value (-29.79 ± 0.03 kJ mole^{-1}) [8].

The complex was decomposed into metal ion and free ligand by dissolving in a mixture of 75% 1,4-dioxan and 25% "constant-boiling" hydrochloric acid.

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 $NiCl_2 \cdot 6.00\ H_2O$.

Constant boiling hydrochloric acid of composition 4.37 mole dm^{-3} ($HCl \cdot 11.91\ H_2O$) was used. 1,4-Dioxan was purified according to references [9,10].

Benzoylacetone (Koch-Light Laboratories Ltd.) was recrystallized from ethanol/water and twice sublimed (Found: C = 73.87%, H = 6.26%; calcd. for $C_{10}H_{10}O_2$: C = 74.06%, H = 6.22%).

Tris[bis(benzoylacetonato)nickel(II)] was prepared by dissolving Analar nickel(II) chloride hexahydrate (1.5 g) in water (20 cm^3), adding methanol (5 cm^3), heating and adding slowly, with stirring, a solution of benzoylacetone (2 g) in methanol (20 cm^3); ammonia (4 mole dm^{-3}) was added dropwise to the hot solution until pH = 8–9. The nickel complex was filtered off, washed with water and dried in air. The complex was twice recrystallised from methanol. The green crystals of $Ni(bzac)_2 \cdot 2\ CH_3OH$ [5] were dried under vacuum (water pump), at 135–140°C for 4 h, yielding the trimer $[Ni(bzac)_2]_3$ [11]. The complex was stored in a desiccator over phosphorus pentoxide. M.p. = 139–140°C. (Found: C = 63.15%, H = 4.71%, Ni = 14.39%; calcd. for $C_{60}H_{54}O_{12}Ni_3$: C = 63.04%, H = 4.76%, Ni = 14.41%).

All carbon and hydrogen analyses were carried out by the Microanalytical Service of the University of Surrey; nickel was analysed by the ethylenediaminetetraacetic acid method [12].

RESULTS AND DISCUSSION

The standard enthalpy of formation of tris[bis(benzoylacetonato)nickel(II)] $[Ni(bzac)_2]_3$ was determined from the thermochemical reaction

$$53.46\ H_2O(l) + 6\ Hbzac(c) + 3\ NiCl_2 \cdot 6\ H_2O(c) \xrightarrow{\Delta H_R}$$

$$\xrightarrow{\Delta H_R} 6\ HCl \cdot 11.91\ H_2O(l) + [Ni(bzac)_2]_3(c) \tag{1}$$

The difference between the enthalpies of solution of the products and reactants in the correct stoichiometric ratio gives the required enthalpy of reaction provided equilibrium is reached from either side within the period of the experiment.

To the calorimetric solvent (100.0 cm^3), ampoules containing water, ligand and

$$\begin{tikzcd}
53.46\ H_2O(l) \arrow[d, "\Delta H_1"] & +6\ Hbzac(c) \arrow[d, "\Delta H_2"] & +3\ NiCl_2\cdot 6\ H_2O(c) \arrow[d, "\Delta H_3"] \arrow[r, "\Delta H_R"] & 6\ HCl\cdot 11.91\ H_2O(l) \arrow[d, "\Delta H_4"] & +[Ni(bzac)_2]_3(c) \arrow[d, "\Delta H_5"] \\
\text{Solvent (75\% dioxan/25\% HCl 4.3 mole dm}^{-3}\text{)} & & & \text{Solvent(75\% dioxan/25\% HCl 4.3 mole dm}^{-3}\text{)} & \\
\text{Solution } A_3 \arrow[rrr, "\Delta H_6=0"] & & & \text{Solution } B_2 &
\end{tikzcd}$$

$$\text{Solvent} + H_2O \xrightarrow{\Delta H_1} \text{Solution } A_1 \qquad \text{Solvent} + HCl\cdot 11.91\ H_2O \xrightarrow{\Delta H_4} \text{Solution } B_1$$

$$\text{Solution } A_1 + \text{Hbzac} \xrightarrow{\Delta H_2} \text{Solution } A_2 \qquad \text{Solution } B_1 + [Ni(bzac)_2]_3 \longrightarrow \text{Solution } B_2$$

$$\text{Solution } A_2 + NiCl_2\cdot 6\ H_2O \xrightarrow{\Delta H_3} \text{Solution } A_3$$

$$\Delta H_R = 53.46\ \Delta H_1 + 6\ \Delta H_2 + 3\ \Delta H_3 - 6\ \Delta H_4 - \Delta H_5 + \Delta H_6$$

Scheme 1.

$NiCl_2\cdot 6\ H_2O$ were added consecutively and ΔH_1, ΔH_2 and ΔH_3, respectively, were measured. To a second portion of the same solvent (100.0 cm^3), ampoules containing $HCl\cdot 11.91\ H_2O$ and $[Ni(bzac)_2]_3$ were added consecutively and ΔH_4 and ΔH_5, respectively, were measured. The thermochemical cycle and the general procedure is given in Scheme 1. The quantities of reactants in a particular series of experiments were determined by the amount of nickel chloride hexahydrate in a particular ampoule so that control of the stoichiometry was maintained for each series.

With this procedure, the value calculated for ΔH_R refers to the reaction indicated in the first line of the scheme, provided that solutions A_3 and B_2 are identical so that ΔH_6 is zero. To check the validity of this assumption, ampoules of solution B_2 were broken into solution A_3 in the calorimeter; no enthalpy change was detected.

The results for the measurements are listed in Tables 1–5 and they lead to $\Delta H_R = +324.29 \pm 4.9$ kJ mole^{-1}.

TABLE 1

Addition of H_2O to solvent (75% dioxan/25% HCl 4.3 mole dm^{-3})

H_2O 10^3 amount/mole	$10^4\ \Delta R/Rm$	ϵ	ΔH/kJ mole^{-1}
4.2690	6.2165	6527.9	−0.9506
4.2587	6.1692	6564.7	−0.9510
4.2748	5.8238	6550.5	−0.8924
4.1541	5.9556	6537.1	−0.9372
4.1510	5.9209	6570.6	−0.9372
Mean	$\Delta H_1 = -0.934 \pm 0.025$ kJ mole^{-1}		

TABLE 2

Addition of benzoylacetone to solution A_1

Hbzac 10^4 amount/mole	10^5 $\Delta R/Rm$	ϵ	ΔH/kJ mole^{-1}
5.0046	2.0179	6559.3	+26.448
5.0583	2.0686	6590.6	+26.952
5.0348	2.0417	6596.5	+26.750
4.9824	2.0318	6546.3	+26.696
4.9676	2.0275	6561.3	+26.780
Mean	$\Delta H_2 = +26.73 \pm 0.17$ kJ mole^{-1}		

The standard enthalpy of formation of the crystalline tris[bis(benzoylacetonato) nickel(II)] is derived from the above enthalpy of reaction and the auxiliary data $\Delta H_f^0(H_2O, l) = -285.83 \pm 0.04$ kJ mole^{-1} [13], ΔH_f^0(Hbzac,c) $= -335.1 \pm 2.8$ kJ mole^{-1} [14], ΔH_f^0 ($NiCl_2 \cdot 6\ H_2O$, c) $= -2103.17$ kJ mole^{-1} [15], and $\Delta H_f^0(HCl \cdot 11.91\ H_2O, l) = -3563.5$ kJ mole^{-1} [16] as $\Delta H_f^0\{[Ni(bzac)_2]_3, c\} = -1895.3 \pm 17.5$ kJ mole^{-1}.

Kakołowicz and Giera [17] gave for the enthalpy of formation of the pseudo monomer of crystalline bis(benzoylacetonato)nickel(II) -658.6 ± 4.2 kJ mole^{-1}, which is different by 80.5 kJ mole^{-1} from the one reported here. They used 4.36 mole dm^{-3} HCl as the calorimetric solvent and as benzoylacetone is insoluble in that solvent, they assumed $\Delta H_2 = 0$. We attempted to measure the enthalpy of solution of benzoylacetone in 4.36 mole dm^{-3} HCl and found the enthalpy of solution to be negligible because most of this compound did not dissolve. On solution of bis(benzoylacetonato)nickel(II) in the same solvent, an exothermic enthalpy change was observed in agreement with Kakołowicz's result, but no precipitate of benzoylacetone was formed. The final solutions, resulting from dissolution of the reactants and that from the products, were not equivalent when 4.36 mole dm^{-3} HCl was used as

TABLE 3

Addition of $NiCl_2 \cdot 6\ H_2O$ to solution A_2

$NiCl_2 \cdot 6\ H_2O$ 10^4 amount/mole	10^5 $\Delta R/Rm$	ϵ	ΔH/kJ mole^{-1}
2.3930	3.1846	6546.7	−0.8712
2.4680	5.0981	6333.3	−1.3083
2.5306	4.5518	5976.0	−1.0749
2.5620	4.2009	6777.7	−1.1113
2.4450	4.4591	6780.2	−1.2365
Mean	$\Delta H_3 = -1.120 \pm 0.142$ kJ mole^{-1}		

TABLE 4

Addition of $HCl \cdot 11.91\ H_2O$ to solvent (75% dioxan/25% HCl 4.3 mole dm^{-3})

$HCl \cdot 11.91\ H_2O$ 10^4 amount/mole	$10^3\ \Delta R/Rm$	ϵ	ΔH/kJ $mole^{-1}$
5.0276	1.6365	6605.7	−21.502
5.0874	1.6225	6573.9	−20.966
5.0734	1.5491	6608.6	−20.179
4.9838	1.6014	6538.3	−21.009
5.0881	1.6271	6485.2	−20.738
Mean	$\Delta H_4 = -20.88 \pm 0.42$ kJ $mole^{-1}$		

the solvent, and this could account for the discrepancy between our value and that of Kakołowicz's.

As with the nickel(II) complex with acetylacetone, that with benzoylacetone is a trimer in the crystalline state as shown by spectrophotometric analysis and molecular weight determinations [5,6]. It has been reported that metal(II)-β-diketonates are monomeric in the gaseous state [18,19].

There is no measured value available for the enthalpy of sublimation of tris[bis(benzoylacetonato)nickel(II)]. Using as base for estimation the value [4] of 117.2 ± 8.4 kJ $mole^{-1}$ for eqn. (2)

$$\tfrac{1}{3}[Ni(acac)_2]_3(c) \rightarrow [Ni(acac)_2](g) \qquad (2)$$

and an estimate [4] of 21 kJ $mole^{-1}$ for the enthalpy of trimerisation in the crystalline state per Ni atom, this gives for the sublimation

$$[Ni(acac)_2](c) \rightarrow [Ni(acac)_2]\ (g) \qquad (3)$$

95.8 kJ $mole^{-1}$. Generally, the enthalpies of sublimation of metal complexes of benzoylacetone are ca. 30 kJ $mole^{-1}$ greater than for metal complexes of acetylacetone [20]. Hence we estimate for

$$[Ni(bzac)_2](c) \rightarrow [Ni(bzac)_2](g) \qquad (4)$$

TABLE 5

Addition of $\{[Ni(bzac)_2]_3\}$ to solution B_1

$\{[Ni(bzac)_2]_3\}$ 10^5 amount/mole	$10^3\ \Delta R/Rm$	ϵ	ΔH/kJ $mole^{-1}$
8.4820	1.1811	6542.1	−91.097
8.5843	1.2415	6444.2	−93.199
8.3403	1.1562	6568.9	−91.063
8.2977	1.1618	6512.0	−91.178
8.5303	1.1901	6670.1	−93.058
Mean	$\Delta H_5 = -91.92 \pm 1.00$ kJ $mole^{-1}$		

125 kJ mole^{-1} and assuming the same enthalpy of trimerisation in the solid state, that for

$$\tfrac{1}{3}[\mathrm{Ni(bzac)_2}]_3(\mathrm{c}) \rightarrow [\mathrm{Ni(bzac)_2}](\mathrm{g}) \tag{5}$$

$\Delta H = 146 \pm 20$ kJ mole^{-1}.

This leads to the enthalpy of formation of the monomeric gaseous complex, $\Delta H_f^0\{[\mathrm{Ni(bzac)_2}], \mathrm{g}\} = -486 \pm 22$ kJ mole^{-1}.

From the enthalpy of dissociation of the gaseous molecule into metal atoms and ligand radicals (eqn. (6)) the metal–oxygen mean bond dissociation enthalpy can be derived.

$$[\mathrm{Ni(bzac)_2}](\mathrm{g}) \xrightarrow{\Delta H_{\mathrm{f.r.}}} \mathrm{Ni(g)} + 2\ \mathrm{bza\dot{c}(g)} \tag{6}$$

Since the oxygen atoms in β-diketonates are equivalent [21], the mean nickel(II)–oxygen homolytic bond enthalpy, $\bar{E}$(Ni–O), is $\Delta H_{\mathrm{f.r.}}/4$.

$$\begin{aligned}\Delta H_{\mathrm{f.r.}} = {} & \Delta H_f^0(\mathrm{Ni, g}) - 2\,\Delta H_f^0(\mathrm{Hbzac, g}) - 2\,\Delta H_f^0(\mathrm{H, g}) \\ & - \Delta H_f^0\{[\mathrm{Ni(bzac)_2}], \mathrm{g}\} + 2\,\bar{D}(\mathrm{H\text{-}bzac})\end{aligned} \tag{7}$$

where $\bar{D}$(H-bzac) corresponds to the enthalpy of dissociation of eqn. (8)

$$\mathrm{Hbzac(g)} \rightarrow \mathrm{H(g)} + \mathrm{bza\dot{c}(g)} \tag{8}$$

and from previous work [22–24] this is taken to be $\bar{D}$(H-bzac) = 418 ± 20 kJ mole^{-1}. Hence, with ΔH_f^0(Hbzac,c) = −335.1 ± 2.8 kJ mole^{-1} [14] and $\Delta H^0_{\mathrm{subl.}}$(Hbzac,c) = 83.8 ± 0.8 kJ mole^{-1} [25] one calculates ΔH_f^0(Hbzac,g) = 251.3 ± 2.9 kJ mole^{-1}, and using ΔH_f^0(H, g) = 218.00 ± 0.01 kJ mole^{-1} [16] and ΔH_f^0(Ni, g) = 429.7 kJ mole^{-1} [15], then $\Delta H_{\mathrm{f.r}} = 813 \pm 30$ kJ mole^{-1} leading to $\bar{E}$(Ni–O) = 203.3 ± 7.5 kJ mole^{-1}.

The previous reported values [4] for the (Ni–O) bonds in the nickel(II) complexes of acetylacetone and dipivaloylmethane are, respectively, 205.0 ± 8.4 kJ mole^{-1} and 209.2 ± 8.4 kJ mole^{-1} and so there are no significant differences in the values for the nickel(II)–oxygen bonds in these three nickel(II)-β-diketonates. This was also observed for beryllium [26], aluminium [23] and copper [7,22] β-diketone type complexes.

The enthalpy of the hypothetical sublimation reaction (9)

$$[\mathrm{Ni(bzac)_2}]_3(\mathrm{c}) \rightarrow [\mathrm{Ni(bzac)_2}]_3(\mathrm{g}) \tag{9}$$

is three times that of the process (5), minus the trimerization energy (3 × 21 = 63 kJ per mole of trimer), i.e. 375 kJ per mole of trimer, and this gives $\Delta H_f^0\{[\mathrm{Ni(bzac)_2}]_3, \mathrm{g}\} = -1520 \pm 25$ kJ mole^{-1}.

There is no X-ray structure determination of $\{[\mathrm{Ni(bzac)_2}]_3\}$ but its trimeric nature is known in the crystal state. Assuming that its structure is similar to that of $\{[\mathrm{Ni(acac)_2}]_3\}$ [1,2] there will be six non-bridging (Ni–O) bonds and twelve bridging (Ni–O) bonds. If the average bond enthalpy of 203 kJ is assigned to each of the six non-bridging bonds, the residual binding enthalpy can be shared among the 12 equivalent bridging bonds. The resulting bridging (Ni–O) bond enthalpy of 107 kJ is close to half that of the non-bridging (Ni–O) bonds. This was also found [4] for the corresponding (Ni–O) bonds in the nickel(II) complex of acetylacetone.

These bond enthalpies refer to the hypothetical trimer molecule in the gaseous state, but intermolecular interactions in the solid may influence the relative magnitude for the two types of (Ni–O) bonds.

It should be noted that both the non-bridging and bridging (Ni–O) bond enthalpies have almost the same values as the corresponding (Co–O) bonds [27] but, of course, the same proviso with respect to lattice forces must be taken into account.

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REFERENCES

1 G.J. Bullen, R. Mason and P. Pauling, Nature (London), 189 (1961) 291.
2 G.J. Bullen, R. Mason and P. Pauling, Inorg. Chem., 4 (1965) 456.
3 F.A. Cotton and J.J. Wise, Inorg. Chem., 5 (1966) 1200.
4 R.J. Irving and M.A.V. Ribeiro da Silva, J. Chem. Soc. Dalton Trans., (1978) 399.
5 A. Choplin-Gast and R. Hugel, Bull. Soc. Chim. Fr., (1970) 1244.
6 A. Choplin-Gast and R. Hugel, J. Inorg. Nucl. Chem., 34 (1972) 2595.
7 M.A.V. Ribeiro da Silva and R.J. Irving, Bull. Chem. Soc. Jpn., 50 (1977) 734.
8 E.J. Prosen and M.V. Kilday, J. Res. Natl. Bur. Stand. Sect. A, 77 (1973) 581.
9 J.O. Hill and R.J. Irving, J. Chem. Soc. A, (1966) 971.
10 D.D. Perrin, W.L. Armarego and R.D. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1966, p. 148.
11 A. Choplin-Gast and R. Hugel, Bull. Soc. Chim. Fr., (1970) 2840.
12 H.A. Flaschka, EDTA Titrations, Pergamon Press, London, 1959, p. 79.
13 CODATA, J. Chem. Thermodyn., 10 (1978) 903.
14 M.L.C.C.H. Ferrão, M.A.V. Ribeiro da Silva, S. Suradi, G. Pilcher and H.A. Skinner, J. Chem. Thermodyn., 13 (1981) 567.
15 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, Natl. Bur. Stand. (U.S.), Washington, 1969.
16 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 270-3, Natl. Bur. Stand. (U.S.), Washington, 1968.
17 W. Kakołowicz and E. Giera, Thermochim. Acta, 32 (1979) 19.
18 D.P. Graddon, Coord. Chem. Rev., 4 (1969) 1, and references therein.
19 C. Reichert and J.B. Westmore, Inorg. Chem., 8 (1969) 1012 and references therein.
20 M.A.V. Ribeiro da Silva, unpublished work.
21 E.C. Lingafelter and R.L. Braun, J. Am. Chem. Soc., 88 (1966) 2951.
22 M.A.V. Ribeiro da Silva and A.M.M.V. Reis, Bull. Chem. Soc. Jpn., 52 (1979) 3080.

23 R.J. Irving and M.A.V. Ribeiro da Silva, J. Chem. Soc., Dalton Trans., (1976) 1940.
24 C.A. Coulson, personal communication, 1973.
25 A. Aihara, Bull. Chem. Soc. Jpn., 32 (1959) 1242.
26 R.J. Irving and M.A.V. Ribeiro da Silva, J.C. Chem. Soc. Dalton Trans. (1977) 143.
27 R.J. Irving and M.A.V. Ribeiro da Silva, J. Chem. Soc. Dalton Trans. (1981) 99.