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Standard molar enthalpies of formation of nickel(II) β-diketonates and monothio-β-diketonates

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Abstract

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of the crystalline diaquobis(dibenzoylmethanate)nickel(II), $\mathrm{Ni(DBM)_2(H_2O)_2}$, diaquobis(thenoyltrifluoroacetonate)nickel(II), $\mathrm{Ni(TTFA)_2(H_2O)_2}$ bis(monothiodibenzoylmethanate)nickel(II), $\mathrm{Ni(DBMS)_2}$ and bis(monothiothenoyltrifluoroacetonate)nickel(II), $\mathrm{Ni(HTTFAS)_2}$ were determined, at $T = 298.15$ K, by high precision solution-reaction calorimetry. The standard molar enthalpy of sublimation of the monothiothenoyltrifluoroacetone (HTTFAS) complex was measured by high-temperature Calvet microcalorimetry. From the standard molar enthalpies of formation of the complexes in the gaseous state, the mean nickel(II)-ligand molar dissociation enthalpies, $\langle D_\mathrm{m}\rangle$(Ni–L), were derived.

	$\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$
Diaquobis(dibenzoylmethanate)nickel(II), $\mathrm{Ni(DBM)_2(H_2O)_2}$	-993.3 ± 3.8
Diaquobis(thenoyltrifluoroacetonate)nickel(II), $\mathrm{Ni(TTFA)_2(H_2O)_2}$	-2452.0 ± 8.3
Bis(monothiodibenzoylmethanate)nickel(II), $\mathrm{Ni(DBMS)_2}$	-42.1 ± 5.9
Bis(monothiothenoyltrifluoroacetonate)nickel(II), $\mathrm{Ni(TTFAS)_2}$	-1473.5 ± 8.1

Keywords: Standard molar enthalpy of formation; Enthalpy of sublimation; High temperature Calvet microcalorimetry; Nickel(II) β-diketonates; Nickel(II) monothio-β-diketonates; Solution calorimetry; Ni(II)-ligand bond dissociation enthalpies; Bis(dibenzoylmethanate)nickel(II); Bis(thenoyltrifluoroacetonate)nickel(II); Bis(monothiodibenzoylmethanate)nickel(II); Bis(monothiothenoyltrifluoroacetonate)nickel(II); Diaquobis(dibenzoylmethanate)nickel(II); Diaquobis(thenoyltrifluoroacetonate)nickel(II)

1. Introduction

Nickel(II) complexes of β-diketones, monothio-β-diketones, dithio-β-diketones, and alkylthioureas are examples of crystalline inner chelates with O and/or S coordination that have been used as model compounds in physical-chemistry studies [1–9]. Nickel(II) acetylacetonate is a classic example of a complex in a trimmer form [10,11]. In tetra-coordinated complexes of Ni(II) with β-diketones and monothio-β-diketones, the coordination rings are generally square planar and, in the case of the monothio-β-diketonates the complexes are formed in the *cis* conformation [12,13].

Condensed phase thermochemistry of the nickel(II) β-diketonates has been investigated for few nickel(II) β-diketonates: the literature reports values of standard molar enthalpies of formation and standard molar enthalpies of sublimation for bis(acetylacetonate)nickel(II) [$\mathrm{Ni(ACAC)_2}$ and $\mathrm{\{Ni(ACAC)_2\}_3}$] [9,14], bis(dipivaloylmethanate)nickel(II) $\mathrm{Ni(DPM)_2}$ [14], bis(benzoylmethanate)nickel(II) [$\mathrm{Ni(BZAC)_2}$ and $\mathrm{\{Ni(BZAC)_2\}_3}$] [15], and diaquobis(hexafluoroacetylacet-

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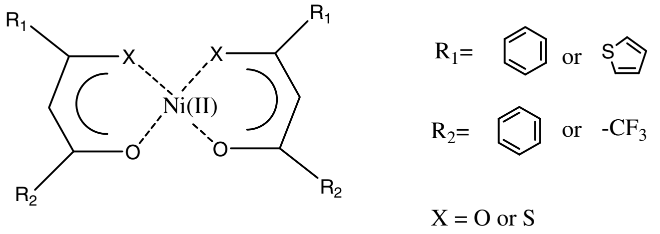

FIGURE 1. Schematic formulae for the β-diketonates (X = O) and monothio-β-diketonates (X = S) of nickel(II): R_1 and R_2-phenyl group, X = O: Diaquobis(dibenzoylmethanate)nickel(II), Ni(DBM)$_2$(H$_2$O)$_2$; X = S: Bis(monothiodibenzoylmethanate)nickel(II), Ni(DBMS)$_2$. R_1-thienyl group and R_2-trifluoromethyl group, X = O: Diaquobis(thenoyltrifluoroacetonate)nickel(II), Ni(TTFA)$_2$(H$_2$O)$_2$; X = S: Bis(monothiothenoyltrifluoroacetonate)nickel(II), Ni(TTFAS)$_2$.

onate)nickel(II) Ni(HFAC)$_2$(H_2O)$_2$ [16]. These values have been subject of some reviews [9,17].

Besides the extensive work done in the physical chemistry study involving monothio-β-diketonates complexes [2,5,8], so far, there is only one paper reporting the thermochemical study of the bis(monothiodipivaloylmethanate)-nickel(II), Ni(DPMS)$_2$ [18].

The aim of this work is to study the energetics of the Ni(II)-complexes of two β-diketonates and their analogous monothio-β-diketonates, in order to contribute to the understanding of the energetics of the metal-oxygen and metal-sulfur bonds.

The present work on the thermochemistry of Ni(DBM)$_2$(H$_2$O)$_2$, Ni(TTFA)$_2$(H$_2$O)$_2$, Ni(DBMS)$_2$, and Ni(TTFAS)$_2$, reports their standard molar enthalpies of formation in crystalline and gaseous phases (see figure 1).

From the standard molar enthalpies of formation of the complexes in the gaseous state, the mean molar bond dissociation enthalpies nickel(II)-ligand, $\langle D_m \rangle$(Ni–O + Ni–S), were derived.

2. Experimental

2.1. Syntheses

The β-diketones and monothio-β-diketones were prepared, purified and characterized as previously described [19,20].

Diaquobis(dibenzoylmethanate)nickel(II), Ni(DBM)$_2$(H$_2$O)$_2$: 2 mmol of ligand, dibenzoylmethane (HDBM) were dissolved in methanol (100 cm^3) and mildly heated; 1 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ in warm methanol (20 cm^3) was added, dropwise, under stirring. The mixture was kept refluxing during 1 h; after cooling down the mixture overnight, the formed crystals were filtered off and washed with ethanol. The precipitates were dried under reduced pressure, at $T = 330$ K, for 6 h. Light green crystals were obtained.

Diaquobis(thenoyltrifluoroacetonate)nickel (II), Ni(TTFA)$_2$(H$_2$O)$_2$: 2 mmol of ligand, thenoyltrifluoroacetone (HTTFA) were dissolved in methanol (50 cm^3) and mildly heated; 1 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ in of warm methanol (50 cm^3) was added, dropwise, under stirring. The mixture was kept under reflux during 1 h and the solvent was evaporated until a volume of 50 cm^3. After cooling down the mixture overnight, the formed light green crystals were filtered off and recrystallized from acetone. The precipitates were dried under reduced pressure, at $T = 330$ K, for 4 h.

Bis(monothiodibenzoylmethanate)nickel(II), Ni(DBMS)$_2$: 2 mmol of monothiodibenzoylmethane (HDBMS) were dissolved in methanol (100 cm^3) and mildly heated; 1 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ in warm ethanol (20 cm^3) was added, dropwise, under stirring. A dark brown precipitate was formed and the mixture was kept under reflux during 1 h. Brown crystals were filtered off, washed with ethanol and dried under reduced pressure, at $T = 330$ K, for 6 h.

Bis(monothiothenoyltrifluoroacetonate)nickel(II), Ni(TTFAS)$_2$: 2 mmol of monothiothenoyltrifluoroacetone (HTTFAS) were dissolved in methanol (50 cm^3) and mildly heated; 1 mmol of $Ni(CH_3COO)_2 \cdot 4H_2O$ in warm methanol (50 cm^3) was added, dropwise, under stirring. The mixture was kept under reflux for 30 min. After cooling down, the formed dark brown crystals were filtered off, washed with ethanol and dried under reduced pressure, at room temperature.

The purities of the samples were checked by elemental analysis; the mass fraction w of C, H, and S were as follows: for Ni(DBM)$_2$(H$_2$O)$_2$, $C_{30}H_{26}O_4Ni$, found $10^2w(C) = 66.5$, $10^2w(H) = 4.7$, calculated $10^2w(C) = 66.58$, $10^2w(H) = 4.84$; for Ni(DBMS)$_2$, $C_{30}H_{22}OSNi$, found $10^2w(C) = 67.1$, $10^2w(H) = 4.2$, $10^2w(S) = 11.9$, calculated $10^2w(C) = 67.07$, $10^2w(H) = 4.13$, $10^2w(S) = 11.93$; for Ni(TTFA)$_2$(H$_2$O)$_2$, $C_{16}H_{14}O_4F_3Ni$, found $10^2w(C) = 36.4$, $10^2w(H) = 2.1$, calculated $10^2w(C) = 36.58$, $10^2w(H) = 2.25$; for Ni(TTFAS)$_2$, $C_{16}H_{10}OF_3SNi$, found $10^2w(C) = 36.1$, $10^2w(H) = 1.5$, $10^2w(S) = 24.2$ calculated $10^2w(C) = 36.04$, $10^2w(H) = 1.59$, $10^2w(S) = 24.06$.

2.2. Nickel(II) salts and solvents

Nickel(II) chloride hexahydrate (Merck p.a.) and nickel (II) acetate tetrahydrate (Merck p.a.) were powdered, dried and stored over silica gel in a desiccator and their compositions confirmed by means of EDTA analysis [21] and found to be, respectively, $NiCl_2 \cdot 6.00H_2O$ and $Ni(CH_3COO)_2 \cdot 4.00H_2O$; periodic analyses showed no change in their compositions.

A solution of hydrochloric acid, 2.000 $mol \cdot dm^{-3}$, was prepared by dilution with distilled water of a Merck Titrisol solution, which corresponds to $HCl \cdot 26.65H_2O$. A solution of acetic acid, 2.000 $mol \cdot dm^{-3}$, was prepared by dilution with distilled water of a Merck Titrisol solution, which corresponds to $CH_3COOH \cdot 24.82H_2O$. Two independent constant boiling temperature hydrochloric acid solutions were prepared by dilution, with distilled water, of concentrate HCl (AnalaR B.D.H.). The concentrations of the HCl solutions were determined by titration against $Na_2B_4O_7 \cdot 10H_2O$: series of six independent determinations gave the results (4.162 ± 0.001) $mol \cdot dm^{-3}$, which corre-