Molecular thermochemical study of Ni(II), Cu(II) and Zn(II) complexes with *N,N′*-bis(salicylaldehydo)ethylenediamine

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Abstract

The standard ($p^0 = 0.1$ MPa) molar enthalpies of formation, at $T = 298.15$ K, of crystalline Ni(II), Cu(II) and Zn(II) complexes with *N,N′*-bis(salicylaldehydo)ethylenediamine (H$_2$salen) were determined by solution–reaction calorimetry measurements as, respectively, $\Delta_f H_m^\circ$ {[Ni(salen)], cr} $= -(226.1 \pm 3.9)$ kJ mol^{-1}, $\Delta_f H_m^\circ$ {[Cu(salen)], cr} $= -(139.0 \pm 3.9)$ kJ mol^{-1} and $\Delta_f H_m^\circ$ {[Zn(salen)], cr} $= -(281.3 \pm 4.6)$ kJ mol^{-1}. The standard molar enthalpies of sublimation of the same metal complexes, at $T = 298.15$ K, were obtained by effusion methods as $\Delta_{cr}^g H_m^\circ$ [Ni(salen)] $= (163.9 \pm 3.2)$ kJ mol^{-1}, $\Delta_{cr}^g H_m^\circ$ [Cu(salen)] $= (175.3 \pm 2.7)$ kJ mol^{-1} and $\Delta_{cr}^g H_m^\circ$ [Zn(salen)] $= (179.6 \pm 3.7)$ kJ mol^{-1}. The differences between the mean metal−ligand and hydrogen−ligand bond dissociation enthalpies were derived and discussed in terms of structure, in comparison with identical parameters for complexes of the same metals with other tetradentate Schiff bases involving a N$_2$O$_2$ donor set.
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1. Introduction

Metal complexes of Schiff bases derived from aromatic carbonyl compounds have been widely studied in connection with metalloprotein models and asymmetric catalysis, due to the versatility of their steric and electronic properties, which can be fine-tuned by choosing the appropriate amine precursors and ring substituents [1–4]. In fact, the Schiff bases derived from salicylaldehyde and diamines, as *N,N′*-bis(salicylaldehydo)ethylenediamine (H$_2$salen), constitute one of the most relevant synthetic ligand systems with importance in asymmetric catalysis. While providing an easier synthetic access, they appeared to be of importance as catalysts for a broad range of transition-metal catalysis reactions including epoxidation of olefins, hydroxylation, lactide polymerization and asymmetric ring opening of epoxides [2,5–7]. The value of these tetradentate N$_2$O$_2$ ligands

and their transition-metal complexes, as catalysts, has attracted significant attention, being relevant for their applications, particularly on the development of agrochemical and pharmaceutical industries. Also, due to the potential catalytic interest of these metal-salen chelates, a very rapid growth in their chemical study has been developed, in view of a good characterization of their properties. The recent use of salen complexes as catalytically active materials to develop surface-modified electrodes for sensing applications has stimulated the use of the cyclic voltammetry as a technique to study the structure–reactivity relationships for this class of compounds [8].

Detailed quantitative knowledge on the energetics of metal−ligand bonding in these tetradentate N$_2$O$_2$ Schiff base complexes is crucial to the understanding of stoichiometric and catalytic reactions. Indeed, a substantial interpretation of chemical processes involving these tetradentate N$_2$O$_2$ Schiff base complexes requires a good knowledge of the metal−ligand bond energies, which may eventually help in the design of new and improved processes.

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Besides investigating enthalpic and entropic stereo controlling factors in Mn-salen catalysed oxidations [9], there is a lack of reliable thermodynamic data in the literature. We have previously reported results for the energetic study of some Schiff bases [10–12] and some of their metallic complexes [13,14], being relevant in this context those reporting thermochemical studies for Schiff bases derived from ß-diketones and diamines, their Cu(II) and Ni(II) complexes [14], as well as for Schiff bases derived from salicylaldehyde and diamines [12]. We are now involved on a thermochemical study of the first row transition metal (Cu(II), Ni(II) and Zn(II)) complexes with H_2salen, in order to contribute to understand the relation of the metal–ligand bonding with the reactivity in complexes of tetradentate N_2O_2 Schiff bases shown in Fig. 1.
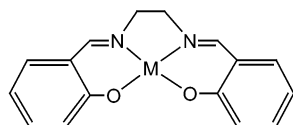
In this work we present the standard molar enthalpies of formation of these complexes, at $T = 298.15$ K, for the crystalline phase, derived from solution–reaction calorimetric measurements, and the corresponding enthalpies of sublimation, measured by the Knudsen effusion technique. These results yield the standard molar enthalpies of formation of the gaseous species, which are used to derive the total binding energy between metals and the ligand.

The determination of the gas phase enthalpies of formation for a metallic complex, ML, and one tetradentate N_2O_2 ligand, H_2L, allows to derive the mean metal–ligand bond dissociation enthalpy, $DH(M–L)$, or the metal/hydrogen mean exchange value, $DH(M–L) - 2\langle DH(H–L)\rangle$, if the value $\langle DH(H–L)\rangle$ is unknown.

2. Experimental

2.1. Synthesis and characterization of compounds

The ligand *N,N′*-bis(salicylaldehydo)ethylenediimine, $C_{16}H_{16}N_2O_2$ (H_2salen), was prepared according to previously published methods [15], by refluxing 0.05 mol of salicylaldehyde (Merck-Schuchard, purified by distillation) and 0.025 mol of ethylenediamine (Aldrich Chemie, 99%, purified by distillation) in 30 cm^3 of dried ethanol, for 30 min and cooling the reaction mixture. The Schiff base was separated as yellow needles and was recrystallized twice from methanol (yield 75–80%). The compound is stable at room temperature and has been characterized by IR spectroscopy and elemental analysis. The microanalytical results (Microanalytical Services of the University of Manchester) for the mass fractions w of C, H and N were as follows: for (H_2salen), $C_{16}H_{16}N_2O_2$, found $10^2 w(C) = 72.42$, $10^2 w(H) = 6.08$, $10^2 w(N) = 10.36$, calculated $10^2 w(C) = 71.62$, $10^2 w(H) = 6.01$, $10^2 w(N) = 10.44$. The ligand was studied by d.s.c. over the temperature range 323–413 K and no phase transitions were found before the melting temperature (melting point: 397.9 K).

The three complexes were prepared using a method described in literature by Batley and Graddon [16]. A solution of 0.012 mol of metal acetate (p.a. Merck) in 50 cm^3 of ethanol was added to 50 cm^3 of an ethanolic solution containing 0.012 mol of H_2salen and the mixture was refluxed for 2 h. After slowly cooling, small dark green crystals, brown/reddish crystals and yellow needles were formed, respectively for [Cu(salen)], [Ni(salen)] and [Zn(salen)]. The crystals were filtered, washed with cold ethanol and dried in an exsiccator, over phosphorous (V) oxide. The yields of preparation of the three complexes were: [Cu(salen)], 85%; [Ni(salen)], 80%; and [Zn(salen)], 90%.
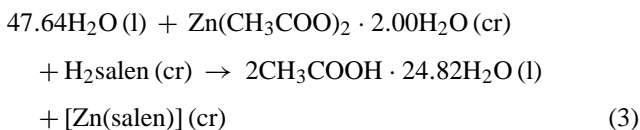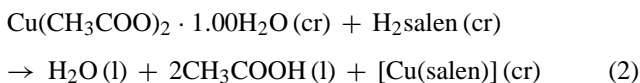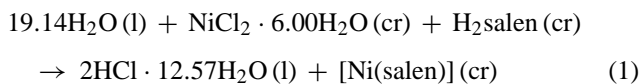
The purity of the samples was checked by IR spectroscopy and elemental analysis; the mass fractions w of C, H and N were as follows: for [Cu(salen)], $CuC_{16}H_{14}N_2O_2$, found $10^2 w(C) = 58.36$, $10^2 w(H) = 4.26$, $10^2 w(N) = 8.15$; calculated $10^2 w(C) = 58.26$, $10^2 w(H) = 4.28$, $10^2 w(N) = 8.49$. For [Ni(salen)], Ni $C_{16}H_{14}N_2O_2$, found $10^2 w(C) = 59.24$, $10^2 w(H) = 4.33$, $10^2 w(N) = 8.52$; calculated $10^2 w(C) = 59.13$, $10^2 w(H) = 4.34$, $10^2 w(N) = 8.62$. For [Zn(salen)], $ZnC_{16}H_{14}N_2O_2$, found $10^2 w(C) = 58.94$, $10^2 w(H) = 4.46$, $10^2 w(N) = 8.40$; calculated $10^2 w(C) = 57.94$, $10^2 w(H) = 4.25$, $10^2 w(N) = 8.45$. The three metal complexes were studied by d.s.c. over the temperature ranges 323–573 K and no phase transitions were found. The temperature range of the supplementary effusion measurements are shown to be below the melting ranges.

2.2. Solution–reaction calorimetry

The reaction and solution enthalpies were measured in a Dewar isoperibol solution–reaction calorimeter, whose basic auxiliary equipment and technique used has been previously described [17,18], although this calorimeter has been equipped with a newly designed all-glass reaction vessel [19,20], with capacity for 120.0 cm^3 of solvent. The vessel is equipped with a twin-bladed stirrer and an ampoule holder that allows the introduction of new ampoules into the reaction vessel without having to take the reaction vessel out of the thermostatic bath. The temperatures in the calorimeter were measured with a quartz thermometer (Hewlett Packard HP 2804-A) to 10^{-4} K, every 10 s; the thermometer was interfaced to a PC using the program LABTERMO [19] to control the system. The accuracy and performance of the calorimetric system were tested by measuring the molar enthalpy of solution of THAM, tris(hydroxymethyl)aminomethane (BDH, Thermochemical Standard) in 0.100 $mol\,dm^{-3}$ HCl (aq) at $T = 298$ K; six independent measurements

M = Cu(II), Ni(II); Zn(II)   ML = [Cu(salen)], [Ni(salen)] and [Zn(salen)]

Fig. 1. Molecular structure of metallic complexes with *N,N′*-bis(salicylaldehydo)ethylenediamine.

gave $\Delta_r H_m^\circ = -(29.763 \pm 0.016)\,kJ\,mol^{-1}$, in good agreement with the value reported by Kilday and Prosen, $-(29.77 \pm 0.31)\,kJ\,mol^{-1}$ [21].

The thermochemical reactions (1)–(3) were used for determining the enthalpies of formation of the [Ni(salen)], [Cu(salen)] and [Zn(salen)] complexes:

$$19.14H_2O\,(l) + NiCl_2 \cdot 6.00H_2O\,(cr) + H_2salen\,(cr)$$
$$\rightarrow 2HCl \cdot 12.57H_2O\,(l) + [Ni(salen)]\,(cr) \quad (1)$$

$$Cu(CH_3COO)_2 \cdot 1.00H_2O\,(cr) + H_2salen\,(cr)$$
$$\rightarrow H_2O\,(l) + 2CH_3COOH\,(l) + [Cu(salen)]\,(cr) \quad (2)$$

$$47.64H_2O\,(l) + Zn(CH_3COO)_2 \cdot 2.00H_2O\,(cr)$$
$$+ H_2salen\,(cr) \rightarrow 2CH_3COOH \cdot 24.82H_2O\,(l)$$
$$+ [Zn(salen)]\,(cr) \quad (3)$$

The standard molar enthalpy of each reaction, $\Delta_r H_m$, was determined by successively measuring the enthalpy of solution, $\Delta_i H_m$, of stoichiometric amounts of each reactant or product in the calorimetric solvent (for the study of the Ni(II) and Cu(II) complexes, the solvent used has been 1,4-dioxan/4.057 mol dm^{-3} HCl, 2:1, v/v; for the study of the Zn(II) complex, the solvent has been 1,4-dioxan/4.200 mol dm^{-3} HCl, 3:1, v/v) so that the final solution resulting from the dissolution of all the reactants had the same composition as that resulting from the dissolution of the products. The validity of this procedure has been tested by breaking ampoules of the final solution, resulting from the dissolution of the reactants, into the final solution of the dissolution of all the products in the calorimeter, and no enthalpy change has been detected.

2.3. Enthalpies of sublimation using a quartz crystal deposition system

The standard molar enthalpies of sublimation of [Ni(salen)], [Cu(salen)] and [Zn(salen)] were determined by the Knudsen effusion method using the apparatus as described by Burkinshaw and Mortimer [22], with the detailed modifications previously reported [23]. The equipment was tested with several compounds of known standard molar enthalpies of sublimation (benzanthrone, squaric acid, and 4-hydroxy-2-methylquinoline) and good agreement with the literature values was obtained. The vapour effusing from the Knudsen cell was allowed to condense on a quartz crystal positioned above the effusion hole; changes in the frequency Δf of oscillation of the quartz crystal were proportional to the mass condensed in its surface, $\Delta f = C_f \Delta m$, where C_f is a proportionally constant.

From the Knudsen equation:

$$p = \left(\frac{\Delta m}{\Delta t}\right) \cdot a^{-1} \cdot \left(\frac{2\pi RT}{M}\right)^{1/2} \quad (4)$$

where $(\Delta m/\Delta t)$ is the rate of mass loss, a the effective area of the effusion hole, and M the molar mass of the effusing vapour. As the measured rate of change of frequency of oscillation with time, $v = \Delta f/\Delta t$, is directly proportional to the rate of sublimed mass [24] of the crystalline sample, $v = C_f \Delta m/\Delta t$, the relation (5) is obtained.

$$p = v \cdot T^{1/2} \cdot \frac{(2\pi R/M)^{1/2}}{(a \cdot C_f)} \quad (5)$$

By applying the integrated form of the Clausius–Clapeyron equation, the enthalpy of sublimation, $\Delta_{cr}^g H_m^\circ$, may be derived from the slope (m) of $\ln(v \cdot T^{1/2})$ against T^{-1}. From at least five independent sets of experimental measurements of the frequency of the quartz oscillator for each complex, at convenient temperature intervals, the enthalpy of sublimation of each compound, referred to the mean temperature of the experimental range, was calculated.

3. Results and discussion

3.1. Solution–reaction calorimetry

The molar enthalpies of solution and reaction are listed in Table 1, and correspond to an average of at least six independent measurements for each enthalpy of solution; the uncertainties given are twice the standard deviation of the mean, in accordance with normal thermochemical practice.

Table 2 lists the standard molar enthalpies of the reactions (1)–(3) calculated, respectively, by means of Eqs. (6)–(8), in which $\Delta_i H_m$ are the molar enthalpies of solution and reaction of each chemical species, as defined in Table 1:

$$\Delta_r H_m[Ni(salen)] = 19.14\Delta_1 H_m + \Delta_2 H_m + \Delta_3 H_m$$
$$- 2\Delta_4 H_m - \Delta_5 H_m \quad (6)$$

$$\Delta_r H_m[Cu(salen)] = \Delta_{1a} H_m + \Delta_{2a} H_m - \Delta_{3a} H_m$$
$$- 2\Delta_{4a} H_m - \Delta_{5a} H_m \quad (7)$$

$$\Delta_r H_m[Zn(salen)] = 47.64\Delta_{1b} H_m + \Delta_{2b} H + \Delta_{3b} H_m$$
$$- 2\Delta_{4b} H_m - \Delta_{5b} H_m \quad (8)$$

The standard molar enthalpies of formation of the complexes in the crystalline state, also listed in Table 2, were derived by means of the following auxiliary quantities: $\Delta_f H_m^\circ$ (H$_2$O, l)/kJ mol^{-1} = $-(285.83 \pm 0.04)$ [25]; $\Delta_f H_m^\circ$ (HCl in 12.57H$_2$O, l)/kJ mol^{-1} = $-(162.34 \pm 0.01)$ [26]; $\Delta_f H_m^\circ$ (CH$_3$COOH, l)/kJ mol^{-1} = $-(484.5 \pm 0.2)$ [26]; $\Delta_f H_m^\circ$ (CH$_3$COOH in 24.82H$_2$O, l)/kJ mol^{-1} = $-(485.156 \pm 0.10)$ [26]; $\Delta_f H_m^\circ$ [NiCl$_2 \cdot$6.00H$_2$O, cr]/kJ mol^{-1} = $-(2103.17 \pm$

Table 1
Solution calorimetric results for the Ni(II), Cu(II) and Zn(II) complexes of H$_2$salen, at $T = 298.15$ K

i	Reactant	Solvent[a]	Solution formed	$\Delta_i H_m$ (kJ mol^{-1})
1	H$_2$O	Dioxan/HCl	A$_1$	-0.978 ± 0.032
1a	Cu(CH$_3$COO)$_2$·1.00H$_2$O	Dioxan/HCl	A$_{1a}$	$+16.07 \pm 0.32$
1b	H$_2$O	Dioxan/HCl	A$_{1b}$	-0.669 ± 0.040
2	NiCl$_2$·6.00H$_2$O	A$_1$	A$_2$	$+3.48 \pm 0.16$
2a	H$_2$salen	A$_{1a}$	A$_{2a}$	6.496 ± 0.091
2b	Zn(CH$_3$COO)$_2$·2.00H$_2$O	A$_{1b}$	A$_{2b}$	$+9.30 \pm 0.67$
3	H$_2$salen	A$_2$	A$_3$	$+6.58 \pm 0.80$
3a	H$_2$O	Dioxan/HCl	B$_{3a}$	-0.978 ± 0.032
3b	H$_2$salen	A$_{2b}$	A$_{3b}$	$+14.88 \pm 0.61$
4	HCl·12.57 H$_2$O	Dioxan/HCl	B$_4$	-19.26 ± 0.15
4a	CH$_3$COOH	B$_{3a}$	B$_{4a}$	-0.424 ± 0.012
4b	CH$_3$COOH·24.82 H$_2$O	Dioxan/HCl	B$_{4b}$	-15.90 ± 0.32
5	[Ni(salen)]	B$_4$	B$_5$	-18.94 ± 0.08
5a	[Cu(salen)]	B$_{4a}$	B$_{5a}$	$+17.29 \pm 0.46$
5b	[Zn(salen)]	B$_{4b}$	B$_{5b}$	-36.29 ± 0.70
6	A$_3$	B$_5$	A$_3$ = B$_5$	0.00 ± 0.02
6a	A$_{2a}$	A$_5$	A$_{2a}$ = B$_{5a}$	0.00 ± 0.02
6b	A$_{3b}$	B$_{5b}$	A$_{3b}$ = B$_{5a}$	0.00 ± 0.02

[a] Solvent 1,4-dioxan/4.057 mol dm^{-3} HCl, 2:1 (v/v) for Ni(II) and Cu(II) complexes, and 1,4-dioxan/4.200 mol dm^{-3} HCl, 3:1 (v/v) for Zn(II).

Table 2
Derived standard ($p^0 = 0.1$ MPa) molar values (kJ mol^{-1}) at $T = 298.15$ K

Compound	$\Delta_f H_m^\circ$	$\Delta_f H_m^\circ$ (cr)	$\Delta_f H_m^\circ$	$\Delta_f H_m^\circ$ (g)
[Ni(salen)]	$+48.80 \pm 0.80$	-226.1 ± 3.9	163.9 ± 3.2	-62.2 ± 5.0
[Cu(salen)]	$+7.10 \pm 4.12$	-139.0 ± 3.9	175.3 ± 2.7	$+36.3 \pm 4.7$
[Zn(salen)]	-60.40 ± 2.31	-281.3 ± 4.6	179.6 ± 3.7	-101.7 ± 5.9

0.21) [26]; $\Delta_f H_m^\circ$ [Cu(CH$_3$COO)$_2$·1.00H$_2$O, cr]/kJ mol^{-1} = $-(1189.1 \pm 0.5)$ [26]; $\Delta_f H_m^\circ$ [Zn(CH$_3$COO)$_2$·2.00H$_2$O, cr]/kJ mol^{-1} = $-(1672.3 \pm 0.17)$ [26]; $\Delta_f H_m^\circ$ (H$_2$salen, cr)/kJ mol^{-1} = $-(211.4 \pm 3.8)$ [12].

3.2. Sublimation

The results for the measurement of the standard molar enthalpies of sublimation of the Ni(II), Cu(II) and Zn(II) complexes with H$_2$salen, by the Knudsen effusion technique, are summarized in Tables 3–5, respectively, together with the mean temperatures, $\langle T \rangle$, of the experimental temperature intervals, typically of 10–18 K, and the standard molar enthalpies of sublimation at these mean temperatures, $\Delta_{cr}^g H_m^\circ(\langle T \rangle)$; the parameter of the Clausius–Clapeyron equation corresponding to the slope was obtained using a least square fitting of the experimental data. The value of $\Delta_{cr}^g H_m^\circ(\langle T \rangle)$ was corrected to $T = 298.15$ K assuming

$\Delta_{cr}^g C_{p,m}^\circ = -50$ J K^{-1} mol^{-1}, a value previously estimated for metal complexes [22], to yield $\langle \Delta_{cr}^g H_{cr}^\circ$ [M(salen)] $\rangle$, where the uncertainties assigned are twice the overall standard deviations of the mean.

Table 2 summarises also the standard molar enthalpies of sublimation, at $T = 298$ K, for the metal complexes studied in this work, as well as the corresponding standard molar enthalpies of formation in gaseous state.

The obtained results are a contribution to the study of metal–ligand bond enthalpies in metallic complexes of N,N'-bis(salicylaldehydo)ethylenediimine, following previous studies for other tetradentate Schiff bases, also involving a N$_2$O$_2$ donor atom set, derived from β-diketones and ethylenediamine, and their copper(II) and nickel(II) complexes [14].

The metal–ligand dissociation enthalpy DH(M–L) for these complexes, Msalen, involving one tetradentate N$_2$O$_2$ donor ligand, H$_2$salen, is defined as the enthalpy of the homolytic disruption reaction (9):

$$[M(salen)] (g) \rightarrow M (g) + salen (g) \qquad (9)$$
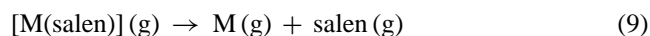
The dissociation enthalpy of the metal–ligand bond includes the energy associated with the difference in structure of the ligand when bound and free, i.e. the radical reorganization energy. The determination of the absolute metal–ligand bond

Table 3
Experimental and corrected standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation of [Ni(salen)]

Exp.	$\langle T \rangle$ (K)	$m \pm \sigma_m$ (K)	r	$\Delta_{cr}^g H_m^\circ(\langle T \rangle)$ (kJ mol^{-1})	$\Delta_{cr}^g H_m^\circ(T = 298.15$ K) (kJ mol^{-1})
1	477.2	18606 ± 331	0.9995	154.69 ± 2.75	163.6 ± 2.8
2	474.2	18656 ± 97	0.9999	155.11 ± 0.80	163.9 ± 0.8
3	475.6	18505 ± 150	0.9999	153.85 ± 1.24	162.7 ± 1.2
4	481.2	18118 ± 183	0.9998	150.63 ± 1.52	159.8 ± 1.5
5	472.6	19337 ± 199	0.9999	160.77 ± 1.65	169.5 ± 1.6

$\langle \Delta_{cr}^g H_m^\circ(T = 298.15$ K) $\rangle = 163.9 \pm 3.2$ kJ mol^{-1}.

Table 4
Experimental and corrected standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation of [Cu(salen)]

Exp.	$\langle T \rangle$ (K)	$m \pm \sigma_m$ (K)	r	$\Delta_{cr}^g H_m^\circ(\langle T \rangle)$ (kJ mol^{-1})	$\Delta_{cr}^g H_m^\circ(T = 298.15$ K) (kJ mol^{-1})
1	489.2	20549 ± 125	0.9999	170.86 ± 1.04	180.4 ± 1.0
2	489.2	19776 ± 341	0.9997	164.43 ± 2.84	174.0 ± 2.8
3	489.6	19471 ± 44	0.9999	161.89 ± 0.36	171.5 ± 0.4
4	488.6	19600 ± 275	0.9996	162.96 ± 2.29	172.5 ± 2.3
5	489.8	20207 ± 123	0.9999	168.01 ± 1.02	177.6 ± 1.0
6	481.6	20026 ± 212	0.9998	166.50 ± 1.76	175.7 ± 1.8

$\langle \Delta_{cr}^g H_m^\circ(T = 298.15$ K)$\rangle = 175.3 \pm 2.7$ kJ·mol^{-1}.

Table 5
Experimental and corrected standard ($p^0 = 0.1$ MPa) molar enthalpies of sublimation of [Zn(salen)]

Exp.	$\langle T \rangle$ (K)	$m \pm \sigma_m$ (K)	r	$\Delta_{cr}^g H_m^\circ(\langle T \rangle)$ (kJ mol^{-1})	$\Delta_{cr}^g H_m^\circ(T = 298.15$ K) (kJ mol^{-1})
1	517.2	20938 ± 715	0.9983	174.09 ± 5.94	185.0 ± 5.9
2	522.2	19458 ± 197	0.9998	161.78 ± 1.64	173.0 ± 1.6
3	524.5	20664 ± 344	0.9996	171.81 ± 2.86	183.1 ± 2.9
4	521.7	20436 ± 242	0.9997	169.91 ± 2.01	181.1 ± 2.0
5	521.7	20310 ± 1241	0.9944	168.87 ± 10.32	180.0 ± 10.3
6	525.2	19738 ± 676	0.9977	164.11 ± 5.62	175.5 ± 5.6

$\langle \Delta_{cr}^g H_m^\circ(T = 298.15$ K)$\rangle = 179.6 \pm 3.7$ kJ mol^{-1}.

dissociation enthalpies in the chelate system is not possible, since the experimental value for the enthalpy of formation of the radical salen is not known. However, the consideration of the average bond dissociation enthalpy of the hydrogen atoms to the ligand radical, $\langle DH(\text{H-salen})\rangle$, defined as one-half of the enthalpy of reaction for Eq. (10), enables to eliminate the effect of the reorganization energies. This is done by considering the dissociation enthalpy of the metal to the ligand, $\langle DH(\text{M-salen})\rangle$, in relation to the binding enthalpy of the hydrogens of the ligand, this is the value of the difference $DH(\text{M–L}) - 2\langle DH(\text{M–L})\rangle$, given by Eq. (11):

$$H_2\text{salen (g)} \rightarrow 2H\text{(g)} + \text{salen (g)} \tag{10}$$

$$
\begin{aligned}
DH(&\text{M–L}) - 2\langle DH(\text{H} - \text{L})\rangle \\
&= \Delta_f H_m^\circ(\text{M, g}) - \Delta_f H_m^\circ(\text{ML, g}) + \Delta_f H_m^\circ(\text{H}_2\text{L, g}) \\
&\quad - 2\Delta_f H_m^\circ(\text{H, g})
\end{aligned} \tag{11}
$$

Using the following auxiliary data for $\Delta_f H_m^\circ$ (H, g) $= (217.998 \pm 0.006)$ kJ mol^{-1} [25], $\Delta_f H_m^\circ$ (Ni, g) $=$

Table 6
Values of $DH(\text{M–L}) - 2\langle DH(\text{H–L})\rangle$ values for metallic complexes with N$_2$O$_2$ systems, at $T = 298.15$ K

Compound	$DH(\text{M–L}) - 22\langle DH(\text{H–L})\rangle$ (kJ mol^{-1})
[Ni(salen)]	−14.2 ± 7.2[a]
[Ni(acacen)]	−22.5 ± 4.7[b]
[Ni(bzacen)]	−20.3 ± 9.4[b]
[Cu(salen)]	−206.1 ± 8.2[a]
[Cu(acacen)]	−200.6 ± 4.7[b]
[Cu(bzacen)]	−205.1 ± 9.5[b]
[Zn(salen)]	−274.0 ± 8.0[a]

[a] This work
[b] Ref. [14].

(429.7 ± 1.2) kJ mol^{-1} [26], $\Delta_f H_m^\circ$ (Cu, g) $= (337.4 \pm 1.2)$ kJ mol^{-1} [25], $\Delta_f H_m^\circ$ (Zn, g) $= (130.40 \pm 0.40)$ kJ mol^{-1} [25] and $\Delta_f H_m^\circ$ (H$_2$salen, g) $= -(70.1 \pm 5.0)$ kJ mol^{-1} [12], the values obtained for $DH(\text{M–L}) - 2\langle DH(\text{H–L})\rangle$ are reported in Table 6. From previous studies, the corresponding data for two copper(II) complexes and two nickel(II) complexes with the N,N'-bridged tetradentate ligands, derived from acetylacetone or benzoylacetone with ethylenediamine, respectively H$_2$acacen and H$_2$bzacen are known [14]. Table 6 reports also the energetic values for the binding of copper and nickel complexes with H$_2$acacen and H$_2$bzacen, so the comparison of the corresponding metal–ligand bond strengths is possible.

4. Conclusions

The values in Table 6 confirm previous studies [27,28] showing that for the same metal bound to a similar type of ligand, there is a constancy for the difference between enthalpies of binding of the radical ligand to the metal and to the hydrogen atom, this is the difference $DH(\text{M–L}) - 2\langle DH(\text{H–L})\rangle$ is constant. Indeed, the values of this difference for [Cu(salen)], [Cu(acacen)] and [Cu(bzacen)] are the same, within the uncertainties ascribed to them; similar considerations can be done for the complexes [Ni(salen)], [Ni(acacen)] and [Ni(bzacen)]. So it is possible to say that for one type of N,N'-bridged tetradentate Schiff base, with the same N$_2$O$_2$ boundary, the effects influencing $\langle DH(\text{M–L})\rangle$ are compensated in $\langle DH(\text{M–L})\rangle$. From Table 6, the comparison of the $DH(\text{M-salen}) - 2\langle DH(\text{H-salen})\rangle$ values for the three different metals, reveals the same thermochemical tendency of the dissociation enthalpy of the metal–ligand bond reported for other N$_2$O$_2$ and S$_2$O$_2$

systems [28]:

$$DH(\text{Ni-salen}) > DH(\text{Cu-salen}) > DH(\text{Zn-salen})$$
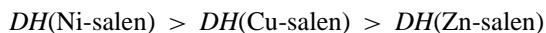
Since many reactions of transition-metal coordination compounds proceed by dissociation pathway, the fact that the mean bond enthalpies decrease along the first row transition metals, from Ni to Cu to Zn, mean that the complexes become less inert with respect to substitution reactions. The stronger metal−ligand bonding makes their coordination complexes more stereochemically rigid, i.e., the energies between alternative coordination geometries become larger and, therefore, rearrangements in which these alternative geometries participate as intermediates or transition states require more energy.

The present experimental study represents a contribution to the interpretation of chemical processes involving tetradentate N_2O_2 Schiff base complexes, trying to explain the influence on the metal−ligand bond of different boundaries of the N_2O_2 set. This brief account emphasizes the value of metal−ligand enthalpy information for better understanding metal−ligand bonding and for aiding in the design of new types of transformations.

Current investigations in asymmetric catalysis has been utilizing the Hard-Soft-Lewis-Acid-Base (HSAB) concept in predictions on the driving force of a catalytic reaction, using bond energy data, thus showing the applicability of thermodynamic data for a better understanding of phenomena like enantioselectivity [29]. The experimental thermochemical data reported reveal confidence, and further thermochemical studies with different *N,N'*-bridged systems, going under way, will help, eventually, to obtain a better description of the energetics for the binding on these type of coordination compounds, providing tools for the improvement of the applied and industrial processes in which these systems are involved.

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