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Thermochimica Acta 307 (1997) 107–115

thermochimica acta

Standard enthalpies of formation and metal-ligand bond dissociation enthalpies of some lead(II) β-diketonates

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Received 10 January 1996; received in revised form 10 June 1997; accepted 30 June 1997

Abstract

The standard enthalpies of formation of some lead(II) β-diketonates: $Pb(aa)_2$; $Pb(dpm)_2$; $Pb(zis)_2$; $Pb(pta)_2$; and $Pb(hfa)_2$ (where aa = pentane-2,4-dionate, dpm = 2,2,6,6-tetramethylheptane-3,5-dionate, zis = 2-methoxy-2,6,6-trimethylheptane-3,5-dionate, pta = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate, and hfa = 1,1,1,6,6,6-hexafluoropentane-2,4-dionate) were determined by solution-reaction calorimetry measurements. The corresponding sublimation enthalpies of the complexes were derived from measurements of saturated vapour pressure by means of the flow method. The homolytic $\langle DH_R\rangle$(Pb–O) and heterolytic $\langle DH_I\rangle$(Pb–O) bond dissociation enthalpies were hence derived. © 1997 Elsevier Science B.V.

Keywords: Lead(II) β-diketonates; Metal-ligand bond dissociation enthalpies; Solution calorimetry; Standard formation enthalpies; Sublimation enthalpies

1. Introduction

The thermochemistry of metal β-diketonates has been investigated extensively and is well known. A typical thermodynamic investigation of such complexes is to determine the enthalpies of formation and sublimation and hence to estimate the metal-ligand bonding enthalpies. Several reviews [1–4] present extensive data on the thermochemistry of β-diketones and metal β-diketonates, but there has been no information about thermodynamic characteristics for lead β-diketonates.

Lead is known to be a key component of optical, ferroelectric and superconducting materials obtained by chemical vapour deposition (CVD), using metal β-diketonate precursors. Since the metal-ligand bonding energy determines the mechanism of thermal decomposition of metal β-diketonates and the composition of films formed in CVD processes, the importance of thermodynamic investigation of these compounds is obvious. We have already reported the preliminary values of standard formation enthalpies obtained by combustion calorimetry and the sublimation enthalpies derived by the Langmuir method for lead(II) complexes of pentane-2,4-dione (Haa) and dipivaloylmethane (Hdpm) [5]. For comparison, we have determined the temperature dependence of saturated vapour pressure by the flow method and the standard enthalpies of formation by solution calorimetry for $Pb(aa)_2$, $Pb(dpm)_2$ and for $Pb(zis)_2$, $Pb(pta)_2$, $Pb(hfa)_2$, where zis = 2-methoxy-2,6,6-trimethylhep-

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PII S0040-6031(97)00287-6

tane-3,5-dionate, pta = 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate, hfa = 1,1,1,6,6,6-hexafluoropentane-2,4-dionate.

2. Experimental

2.1. Materials

Synthesis of lead(II) β-diketonates is described in Ref. [6]. The complexes were purified by double sublimation in vacuum. Microanalysis results are given in Table 1.

Nitric acid solutions of selected concentrations ($HNO_3*16.973H_2O$, $HNO_3*10.539H_2O$, $HNO_3*12.147H_2O$) were prepared from commercially available pure concentrated nitric acid.

Pentane-2,4-dione (Haa) was purified by fractional distillation. Ligands Hdpm and Hzis were recrystallized from melts.

$Pb(NO_3)_2$ was twice recrystallized from double-distilled water followed by drying in vacuo over P_2O_5.

2.2. Solution-reaction calorimeter

A precision solution-reaction calorimeter with isothermal jacket was employed. The calorimeter was developed and made at the Institute of Chemical Physics of RAS (Moscow). The calorimeter consists of the following units: measuring block (general scheme is presented in Fig. 1), electronic block of temperature control and block of calibration. The isothermal jacket (1) of the calorimeter is a cylinder made of Ni-plated brass. Swinged measuring sleeve (2) is placed in a cavity of the jacket. The calorimetric cell (3) made of stainless steel is inserted into the sleeve. Thermistors for measurement and control of the cell temperature are built in the measuring sleeve. Inside the cell there are a calibration heater (4), sylphon (5) for breaking the glass ampoule (6) with the substance under investigation. The volume of the calorimetric cell is 100 ml. The jacket is placed in the liquid thermostat (7), filled with the distilled water. Inside the thermostat there is a turbine (8) providing intensive circulation of water in the whole volume. Cooler water is pumped in pipeline (9) throughout the thermostat. Temperature of the thermostat is adjusted by an automatic system controlling the resistance heater which is built in the jacket.

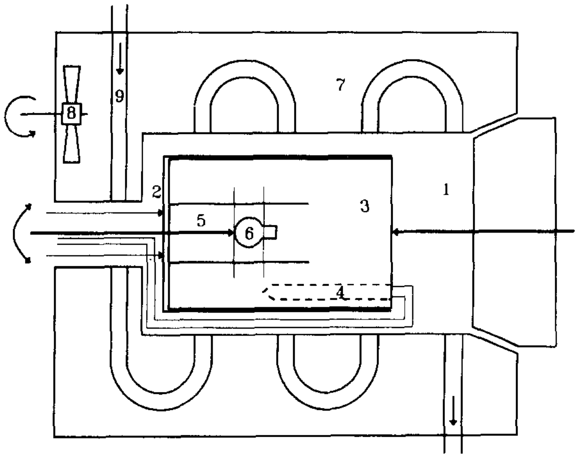

Fig. 1. A general scheme of the calorimeter measuring block: (1) isothermal jacket, (2) measuring sleeve, (3) calorimetric cell, (4) calibration heater, (5) sylphon, (6) ampoule with a compound, (7) thermostat, (8) turbine, (9) coil pipe.

The accuracy of temperature measurement was no worse than 1.5×10^{-5} K/division. Time of passing the current during calibration was measured at an

Table 1
Mass percentage analyses of the complexes

Compound	Found			Expected				
	C	H	F	Pb	C	H	F	Pb
$Pb(aa)_2$	29.5	3.4		51.3	29.6	3.5		51.4
$Pb(dpm)_2$	45.2	6.6		36.2	46.0	6.7		36.1
$Pb(zis)_2$	43.5	6.5		34.1	43.6	6.3		34.2
$Pb(pta)_2$	33.2	3.6	19.3	34.5	33.2	3.3	19.1	34.7
$Pb(hfa)_2$	19.9	0.3	36.8	33.7	19.6	0.3	36.6	33.7

accuracy of 10^{-3} s. The accuracy of temperature maintenance at 25°C was 10^{-3} K. The measurement procedure is standard and similar to that described in Ref. [7].

The accuracy of the calorimeter was tested by measuring the enthalpy of dissolving of KCl samples (ca. 0.5 mmol) in twice distilled water (100 g). The result $\Delta_{sol}H^0 = 17.539 \pm 0.0047$ kJ mol^{-1} is in agreement with the value 17.564 ± 0.042 kJ mol^{-1} [8].

2.3. Flow method

For the determination of saturated vapour pressure of the compounds, a flow (or transpiration) method was used [9,10]. The measurement consists of passing a stream of dry gas-carrier (He) through the tube cell with the sample at known rate and constant temperature. The amount of the compounds vapourized and condensed in the cool part of the cell under quasi-equilibrium conditions (the pressure values were independent of the flow rate within $0.5 \div 5$ l/h) were determined by weighting the cool part of the cell. The saturated vapour pressure was calculated from the formula $p^0 = P{\cdot}n/(n+N)$, where n is the number of moles of the substance transported by N moles of helium carrier gas under temperature T at different flow rates, and P the total pressure in the system.

In our experiments, the influence of vapour diffusion was negligible. The temperature fluctuation was ±0.5 K. The error of the flow measurement was ±2%. Previously the calibration experiments were carried out using NH_4Cl and iodine. The error of the method was not more than ±5%.

3. Results

3.1. Saturated vapour pressure measurement

The values of saturated vapour pressure of lead(II) β-diketonates were determined from the density of their vapours assuming that only monomolecular gases were formed under the experimental conditions. Initial compound and condensate obtained in the cool zone of the tube cell were composed of the same crystal phases. Thermodynamic parameters are calculated from $\ln(P) = -\Delta H/RT + \Delta S/R$ and listed in Table 2.

3.2. Solution-reaction calorimetry

Lead(II) β-diketonates decompose in nitric acid according to the reaction:

$$PbL_{2(s)} + 2HNO_{3(solv)} \rightarrow Pb^{2+}_{(solv)} + 2NO^{-}_{3(solv)} + 2HL_{solv} \quad (1)$$

The general thermochemical reaction for determining the standard formation enthalpies of the PbL_2 complexes was:

$$PbL_{2(s)} + 2(HNO_3 * xH_2O)_{(l)} \xrightarrow{\Delta_r H^0} 2HL_{(l)} + Pb(NO_3)_{2(s)} + 2xH_2O_{(l)} \quad (2)$$

The standard enthalpy $\Delta_r H^0$ of this reaction was determined by measuring the enthalpy of stepwise dissolution of each reactant or product in the calorimetric solvent, so that the final solution resulting from the dissolution of the reactants was of the same composition as that resulting from the dissolution of the products:

Table 2
Thermodynamic parameters of the lead(II) β-diketonates evapouration processes

PbL_2	Process	Temperature range (°C)	Number of points	$\Delta H^0(\langle T\rangle)$ (kJ mol^{-1})	$\Delta S^0(\langle T\rangle)$ (J mol^{-1} K^{-1})
$Pb(aa)_2$	Sublimation	120–150	5	102.4 ± 5.0	176.7 ± 12.4
$Pb(dpm)_2$	Sublimation	100–125	5	117.5 ± 2.8	218.8 ± 7.3
$Pb(dpm)_2$	Vapourization	130–210	8	87.4 ± 0.7	143.1 ± 1.6
$Pb(zis)_2$	Vapourization	120–230	11	93.5 ± 0.8	146.4 ± 1.8
$Pb(pta)_2$	Sublimation	120–190	7	134.4 ± 1.4	246.9 ± 3.2
$Pb(hfa)_2$	Sublimation	95–140	10	111.7 ± 1.3	211.8 ± 3.2
$Pb(hfa)_2$	Vapourization	150–190	9	90.5 ± 3.6	160.6 ± 8.3

Table 3
Molar enthalpies of dissolution at 25°C

i	Sample	Solvent	Solution	Number of experiments	Δ_iH (kJ mol^{-1})
1	H_2O	$HNO_3*16.973H_2O$	A_1	4	-0.06 ± 0.01
2	$Pb(NO_3)_2$	A_1	A_2	5	16.96 ± 0.15
3	Haa	A_2	A_3	5	-0.32 ± 0.07
3	Hhfa	A_2	A_3	5	-52.53 ± 0.94
4	$HNO_3*16.973H_2O$	$HNO_3*16.973H_2O$	B_1	0	0
5	$Pb(aa)_2$	B_1	B_2	5	-27.04 ± 0.14
5	$Pb(hfa)_2$	B_1	B_2	7	-97.72 ± 0.85
1	H_2O	$HNO_3*10.539H_2O + C_2H_5OH$ (v/v = 1 : 1)	A_1	3	-0.625 ± 0.008
2	$Pb(NO_3)_2$	A_1	A_2	5	21.97 ± 0.24
3	Hdpm	A_2	A_3	5	11.97 ± 0.13
4	$HNO_3*10.539H_2O$	$HNO_3*10.539H_2O + C_2H_5OH$ (v/v = 1 : 1)	B_1	5	-3.87 ± 0.08
5	$Pb(dpm)_2$	B_1	B_2	5	-23.13 ± 0.18
1	H_2O	$HNO_3*12{,}147H_2O + CH_3COCH_3$ (v/v = 1 : 1)	A_1	5	-0.578 ± 0.007
2	$Pb(NO_3)_2$	A_1	A_2	5	17.08 ± 0.31
3	Hzis	A_2	A_3	5	10.93 ± 0.07
3	Hpta	A_2	A_3	5	2.63 ± 0.06
4	$HNO_3*12{,}147H_2O$	$HNO_3*12{,}147H_2O + CH_3COCH_3$ (v/v = 1 : 1)	B_1	5	-8.55 ± 0.08
5	$Pb(zis)_2$	B_1	B_2	5	-7.63 ± 0.09
5	$Pb(pta)_2$	B_1	B_2	5	12.46 ± 0.08

solution A = calorimetric solvent

$$H_2O + \text{solution A} \overset{\Delta_1 H}{\longrightarrow} \text{solution } A_1 \quad (3)$$

$$Pb(NO_3)_2 + \text{solution } A_1 \overset{\Delta_2 H}{\longrightarrow} \text{solution } A_2 \quad (4)$$

$$HL + \text{solution } A_2 \overset{\Delta_3 H}{\longrightarrow} \text{solution } A_3 \quad (5)$$

$$HNO_3 * xH_2O + \text{solution A} \overset{\Delta_4 H}{\longrightarrow} \text{solution } B_1 \quad (6)$$

$$PbL_2 + \text{solution } B_1 \overset{\Delta_5 H}{\longrightarrow} \text{solution } B_2 \quad (7)$$

$$\text{solution } A_3 \overset{\Delta_6 H = 0}{\longrightarrow} \text{solution } B_2 \quad (8)$$

The following solutions were selected as calorimetric solvents: $HNO_3*16.973H_2O$ for $Pb(aa)_2$ and $Pb(hfa)_2$, $HNO_3*10.539H_2O + C_2H_5OH$ (v/v = 1 : 1) for $Pb(dpm)_2$ and $HNO_3*12.147H_2O + CH_3COCH_3$ (v/v = 1 : 1) for $Pb(zis)_2$ and $Pb(pta)_2$.

Testing of solutions A_3 and B_2 showed that the value of $\Delta_6 H$ lies below the sensitivity of the calorimeter. The error of the measurements for the 95% confidence interval was estimated according to the equation $\varepsilon = \pm t_{dn}\bar{S}_{\Delta H}$. Here $\bar{S}_{\Delta H}$ is the mean-square error of the evolved heat value, which was obtained by averaging the partial mean-square errors for each reaction from the sequence. The molar dissolution enthalpies for each reactant and product are listed in Table 3.

The standard formation enthalpies of the complexes are calculated from:

$$\Delta_r H^0 = \sum \Delta_f H^0_{(\text{products})} - \sum \Delta_f H^0_{(\text{reactants})},$$

where $\Delta_r H^0$ is a sum of dissolution enthalpies ($\Delta_i H$). Thus,

$$\begin{aligned} \Delta_r H^0 &= 2x\Delta_1 H + \Delta_2 H + 2\Delta_3 H - 2\Delta_4 H \\ &\quad - \Delta_5 H + \Delta_6 H = \Delta_f H^0(PbL_{2(s)}) \\ &\quad + 2\Delta_f H^0(HNO_3 * xH_2O_{(\text{solution})}) \\ &\quad - \Delta_f H^0(Pb(NO_3)_{2(s)}) - 2\Delta_f H^0(HL_{(l)}) \end{aligned} \quad (9)$$

from where $\Delta_f H^0(PbL_{2(s)}) = \Delta_r H^0 - 2\Delta_f H^0$ ($HNO_3 * xH_2O_{(\text{solution})}$) + $\Delta_f H^0(Pb(NO_3)_{2(s)}) + 2\Delta_f H^0(HL_{(l)})$. Hence, for $Pb(aa)_2$: $\Delta_r H^0 = 41.19 \pm 0.22$, for $Pb(dpm)_2$: $\Delta_r H^0 = 63.61 \pm 0.23$, for $Pb(zis)_2$: $\Delta_r H^0 = 49.68 \pm 0.23$, for $Pb(pta)_2$: $\Delta_r H^0 = 12.94 \pm 0.30$ and for $Pb(hfa)_2$: $\Delta_r H^0 = 7.44 \pm 1.23$ kJ mol^{-1}. The standard formation enthalpies of the complexes in crystalline and gas state (Table 4) were derived from

Table 4
The standard formation enthalpies of lead(II) β-diketonates

Compound	$Pb(aa)_2$	$Pb(dpm)_2$	$Pb(zis)_2$	$Pb(pta)_2$	$Pb(hta)_2$
$-\Delta_f H^0_{(s)}$ (kJ mol^{-1})	848.3 ± 2.6 904.6 ± 4.0 [a]	1151.8 ± 3.1 1206.3 ± 4.8 [a]	1174.7 ± 4.2	2271.6 ± 6.2	3303.8 ± 6.4
$-\Delta_f H^0_{((g))}$ (kJ mol^{-1})	745.9 ± 5.6	1034.3 ± 4.2	1060.0 ± 5.9	2137.2 ± 6.3	3192.1 ± 6.5

[a] Data obtained by combustion calorimetry [5].

the data obtained and the following literature data (in kJ mol^{-1}) (Eqs. (9e) and (9f): see Ref. [1], Eqs. (9a), (9b) and (9c): see Ref. [11], Eq. (9d): see Ref. [12], Eqs. (9g) and (9h): see Ref. [13]):

$$\Delta_f H^0(HNO_3 * 12.147H_2O) = -206.17 \pm 0.42 \quad (9a)$$

$$\Delta_f H^0(HNO_3 * 16.973H_2O) = -206.61 \pm 0.42 \quad (9b)$$

$$\Delta_f H^0(HNO_3 * 10.539H_2O) = -205.86 \pm 0.42 \quad (9c)$$

$$\Delta_f H^0(Pb(NO_3)_{2(s)}) = -451.74 \pm 1.17 \quad (9d)$$

$$\Delta_f H^0(Haa_{(l)}) = -425.5 \pm 1.1 \quad (9e)$$

$$\Delta_f H^0(Hdpm_{(l)}) = -587.7 \pm 3.8, \quad (9f)$$

$$\Delta_f H^0(Hpta_{(l)}) = -1122.6 \pm 4.2, \quad (9g)$$

$$\Delta_f H^0(Hhfa_{(l)}) = -1636.4 \pm 1.7. \quad (9h)$$

Any data on the measurements of the standard formation enthalpy for the ligand 2-methoxy-2,6,6-trimethyl-3,5-heptanedione (Hzis) are absent from the literature. Because of this, in the present work we estimated the value of $\Delta_f H^0(Hzis_{(l)})$ according to the following equation:

$$\Delta_f H^0(Hzis_{(l)}, \text{enole}) = \Delta_f H^0(Hzis_{(g)}, \text{ketone}) + \Delta H^0(\text{g, enolization}) - \Delta H_V.$$

The value of $\Delta_f H^0(Hzis_{(g)}$, ketone) was calculated using the method of group contributions [14] and was found to be -533.6 ± 1.4 kJ mol^{-1}. The value of ΔH^0(g, enolization) was taken equal to that for Haa [15]. The standard vapourization enthalpy of Hzis was calculated using the boiling temperature of Hzis (216°C) from the equation $\Delta H_V = 20.9 + 0.172t$ which was obtained from the experimental data for β-diketones [16]: $\Delta H_V(Hzis) = -59.3 \pm 0.8$ kJ mol^{-1}. So, the standard formation enthalpy for $Hzis_{(l)}$ calculated on the basis of these data is -592.5 ± 2.2 kJ mol^{-1}.

In the present work, $\Delta_f H^0(PbL_{2(g)})$ was calculated using the most simple approximation $\Delta_{subl}H(\langle T \rangle) = \Delta_{subl}H$ (298.15 K). We did not succeed in measuring sublimation enthalpy for $Pb(zis)_2$ because of its very low vapour pressure at a temperature below the melting point; so, in order to estimate the required value, we measured the enthalpy of melting for this compound with the help of DSC 111G 'Setaram' scanning calorimeter. The obtained value was 21.2 kJ mol^{-1}. Sublimation enthalpy of $Pb(zis)_2$ estimated using the values of vapourization and melting enthalpies was 114.7 ± 4.2 kJ mol^{-1}:

3.3. Bond dissociation enthalpies

The calculation of the homolytic and heterolytic bond dissociation enthalpies of the investigated compounds is based on a consideration of hypothetical gas-phase reactions:

$$PbL_{2(g)} \overset{\Delta_R H}{\rightarrow} Pb_{(g)} + 2L^{\bullet}_{(g)} \quad (10)$$

$$PbL_{2(g)} \overset{\Delta_I H}{\rightarrow} Pb^{2+}_{(g)} + 2L^{-}_{(g)} \quad (11)$$

Since all the oxygen atoms in metal β-diketonates are equivalent, the mean metal-ligand bond dissociation enthalpies may be presented as:

$$\langle DH_{R,I} \rangle (Pb - O) = \Delta_{R,I}H/4,$$

where

$$\Delta_R H = \Delta_f H^0 Pb_{(g)} + 2\Delta_f H^0 L^{\bullet}_{(g)} - \Delta_f H^0 PbL_{2(g)},$$

$$\Delta_I H = \Delta_f H^0 Pb^{2+}_{(g)} + 2\Delta_f H^0 L^{-}_{(g)} - \Delta_f H^0 PbL_{2(g)},$$

$$\Delta_f H^0 PbL_{2(g)} = \Delta_f H^0 PbL_{2(s)} + \Delta_{subl} HPbL_2,$$

$$\Delta_f H^0 HL_{(g)} = \Delta_f H^0 HL_{(l)} + \Delta_v H^0 HL.$$

Table 5
Homolytic and heterolytic bond dissociation enthalpies of lead(II) β-diketonates (in kJ mol^{-1})

Compound	$Pb(aa)_2$	$Pb(dpm)_2$	$Pb(zis)_2$	$Pb(pta)_2$	$Pb(hfa)_2$
$\langle DH_R\rangle$(Pb–O)	97.1 ± 5.9	105.2 ± 5.0	109.1 ± 6.1	131.3 ± 6.4	132.0 ± 6.8
$\langle DH_I\rangle$(Pb–O)	509.6 ± 5.9	509.2 ± 5.0	513.0 ± 6.1	433.1 ± 6.6	400.3 ± 7.2

Calculation of $\Delta_f H^0 L^{\cdot}$ and $\Delta_f H^0 L^-$ follows the reactions:

$$HL_{(g)} \overset{\Delta_R H(\text{RO}-\text{H})}{\rightarrow} H_{(g)} + L^{\bullet}_{(g)} \qquad (12)$$

$$HL_{(g)} \overset{\Delta_I H(\text{RO}-\text{H})}{\rightarrow} H^+_{(g)} + L^-_{(g)} \qquad (13)$$

producing:

$$\Delta_f H^0 L^{\bullet}_{(g)} = \Delta_R H(\text{RO}-\text{H}) - \Delta_f H^0 H_{(g)} + \Delta_f H^0 HL_{(g)}$$

and

$$\Delta_f H^0 L^-_{(g)} = \Delta_I H(\text{RO}-\text{H}) - \Delta_f H^0 H^+_{(g)} + \Delta_f H^0 HL_{(g)}.$$

$\langle DH_{R,I}\rangle$(Pb–O) was calculated from the obtained data (Table 4) and the following auxiliary data (in kJ mol^{-1}): $\Delta_f H^0 Pb_{(g)} = 195.8 \pm 0.8$ [12], $\Delta_f H^0 Pb^{2}_{(g)}$ $+ = 2361.6 \pm 4.3$ [12], $\Delta_f H^0 H_{(g)} = 218.3 \pm 2.1$ [12], $\Delta_f H^0 H^+_{(g)} = 1536.2 \pm 4.3$ [12], $\Delta_f H^0 Haa_{(g)} = -384.4 \pm 1.3$ [1], $\Delta_f H^0 Hdpm_{(g)} = -528.4 \pm 3.9$ [1], $\Delta_f H^0 Hzis_{(g)} = -533.6 \pm 3.2$ [14–16], $\Delta_f H^0 Hpta_{(g)} = -1077.2 \pm 4.2$ [13], $\Delta_f H^0 Hhta_{(g)} = -1605.0 \pm 7.1$ [13], for Hpta $\Delta_R H(\text{RO–H}) = 392 \pm 2$, $\Delta_I H(\text{RO–H}) = 1276 \pm 4$; for Hhfa $\Delta_R H(\text{RO–H}) = 393 \pm 2$, $\Delta_I H(\text{RO–H}) = 1165 \pm 2$; for Haa $\Delta_R H(\text{RO–H}) = 326 \pm 2$, $\Delta_I H(\text{RO–H}) = 1386 \pm 2$; for Hdpm and Hzis $\Delta_R H(\text{RO–H}) = 342 \pm 2$, $\Delta_I H(\text{RO–H}) = 1385 \pm 2$ [13]. For Hzis, we assumed $\Delta_{R,I} H(\text{RO–H})$ to be equal to that for Hdpm since these ligands are similar in structure, physical and chemical properties [17]. The results of the calculation are presented in Table 5.

4. Discussion

The standard enthalpies of formation in the solid state obtained in the present work for $Pb(aa)_2$ and $Pb(dpm)_2$ differ from the values presented in Ref. [5] by the same quantity ~55 kJ mol^{-1} (see Table 2). The reason of this difference should be sought in the most probable sources of errors in calorimetric methods used. In Ref. [5], the standard equipment and techniques of combustion calorimetric measurements have been used. The accuracy of measurement of combustion heat was sufficiently high (~0.02% by benzoic acid). Among the solid products of combustion there were PbO, PbO_2 and soot in different proportions in every experiment. It seems likely that incomplete identification of combustion products and hence improper corrections contributed the main uncertainty in the calculation in Ref. [5]. In the present study, we verified thermodynamic identity of A_3 and B_2 solutions and used the unique thermochemical cycle with individual calorimetric solvent for each complex. Thus, we are inclined to believe that $\Delta_f H^0$ values determined by solution-reaction calorimetry measurements are more reliable.

It was found earlier [13,18,19] that for standard enthalpies of complex and ligand formation in the gas phase, the following equations are true at high accuracy:

$$\Delta_f H^0 ML_{2(g)} = a + b \cdot \Delta_f H^0 HL_{(g)},$$

$$\Delta_f H^0 ML_{2(s)} = c + d \cdot \Delta_f H^0 HL_{(l)},$$

In the case under consideration, on the basis of the obtained results, a similar dependence of standard formation enthalpies of lead(II) β-diketonates was obtained using standard enthalpies of ligand formation in the gas phase (Fig. 2):

$$\Delta_f H^0 PbL_{2(g)} = 18 + 2.00 * \Delta_f H^0 HL_{2(g)} \pm 8\,\text{kJ mol}^{-1} (R = 0.99998). \qquad (14)$$

A similar dependence is also observed for thermodynamic parameters of the complexes and ligands in the condensed state (Fig. 3):

$$\Delta_f H^0 PbL_{2(s)} = 31 + 2.04 * \Delta_f H^0 HL_{2(g)} \pm 13\,\text{kJ mol}^{-1} (R = 0.99993). \qquad (15)$$

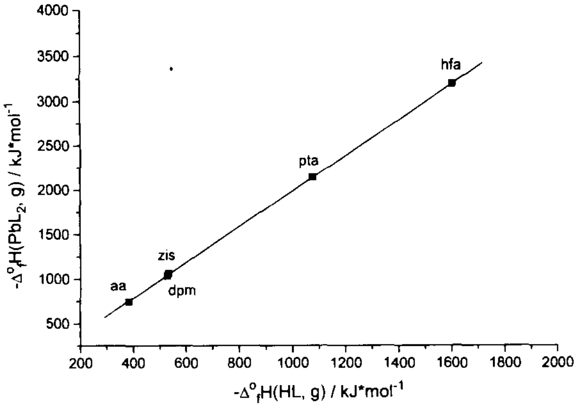

Fig. 2. Variation of standard molar enthalpies of formation of the gaseous lead(II) β-diketonates with the standard molar enthalpies of formation of the β-diketone ligands in the gaseous state.

The obtained equations can be used to estimate standard formation enthalpies of lead(II) complexes with other β-diketonate ligands. The whole set of the obtained linear dependences can serve as a reliability criterion of the results obtained using all the reference values. If the literature data used in Eq. (9) are true, the reliability of new $\Delta_fH^0PbL_{2(s)}$ and Δ_rH^0 values, obtained experimentally by solution calorimetry techniques, can be estimated with the help of Eq. (15).

For the enthalpies of sublimation, two values are known for Pb(dpm)$_2$ (in kJ mol^{-1}): 74.1 measured by Knudsen method [20] and 87.0 measured by Langmuir method [5]. For Pb(aa)$_2$ only the value 66.9 kJ mol^{-1} measured by Langmuir method was reported [5]. Comparing these values with literature data for other metal β-diketonates [1–4], we believe that the values derived from the mentioned methods are strongly understated for the reason of relatively low thermal stability of lead(II) β-diketonates in the solid state [6]. The value 87.0 kJ mol^{-1} for Pb(dpm)$_2$ in Ref. [5] is likely to be assigned to vapourization process (Table 2). Since the flow method is known to be a more suitable method for substances with low thermal stability in solid state, we believe that the data obtained by means of this method are more acceptable.

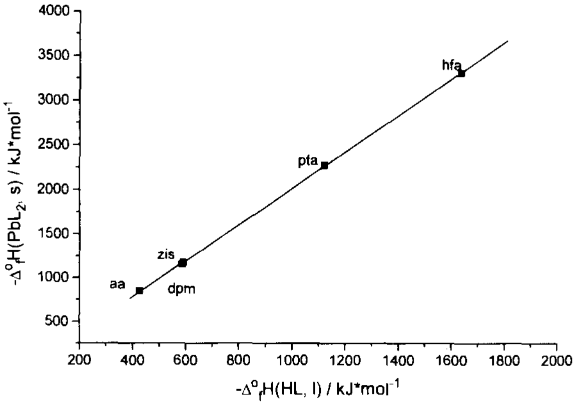

Fig. 3. Variation of standard molar enthalpies of formation of the solid lead(II) β-diketonates with the standard molar enthalpies of formation of liquid β-diketone ligands.

Thus, all the data obtained in the present work for lead(II) complexes were used for the calculation of metal-ligand dissociation enthalpies. For ΔH_R(RO–H), we used the values estimated by quantum-chemical method MINDO/3 [13] because this method takes into consideration the nature of substituents in β-diketones. To correlate $\langle DH \rangle$(Pb–O) values with data for other metal β-diketonates, we applied the idea of Ribeiro da Silva [1] that metal-oxygen bonds in acetylacetonate complexes have similarities with the corresponding bonds in the metal oxides in which the metal atom has the same coordination number as in M(aa)$_2$. From the molar enthalpy of the decomposition:

$$PbO_{(s)} \xrightarrow{\Delta_{dec}H^0} Pb_{(g)} + O_{(g)}$$

using $\Delta_fH^0(O_{(g)}) = 249.17 \pm 0.1$ kJ mol^{-1} [21] and $\Delta_fH^0(PbO_{(s)}$, red) $= 219.5 \pm 0.4$ kJ mol^{-1} [12], we obtained $\langle DH_R \rangle$(Pb–O, oxide, s)$=\Delta_{dec}H^0/4 = 166.5$ kJ mol^{-1}. The correlation between $\langle DH_R \rangle$(M–O, complex, g) in M(aa)$_2$ and $\langle DH_R \rangle$(M–O, oxide, s) [1] shown in Fig. 4 is excellent. Here, the values for other metals are plotted after recalculation of data from Ref. [21], assuming the new Δ_RH(RO–H) value for pentane-2,4-dione [13]. It is apparent that the value reported in this paper for $\langle DH_R \rangle$ (Pb–O, complex, g) in Pb(aa)$_2$ fits well in this correlation.

As to the comparison of $\langle DH_R \rangle$(Pb–O) for the lead(II) complexes, it appears that $-C(CH_3)_3$, $-C(CH_3)_2OCH_3$ and $-CF_3$ substituents of the ligand increase the strength of the metal-ligand

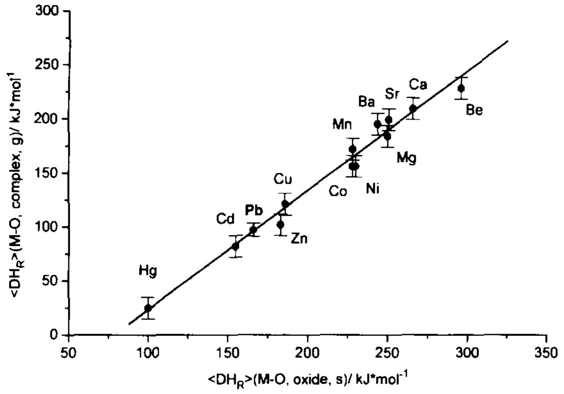

Fig. 4. Correlation between $\langle DH_R\langle(M–O, complex, g) in $M(aa)_2$ and $\langle DH_R\rangle$(M–O, oxide, s).

bond. Moreover, the general tendency known for the wide range of metal β-diketonates complexes is as follows: stronger the H-ligand bond stronger the metal-ligand bond in the complex [13]. This is also true for the lead(II) complexes under consideration.

The calculation of $\langle DH_I\rangle$(Pb–O) showed that the energy of heterolytic dissociation of metal-ligand bond in the lead(II) complexes is independent of the type of aliphatic substituent in the β-diketonate ligand within the error of measurements, indicating that in the gas phase the Pb–O bond length in such lead(II) β-diketonates is almost constant. But introduction of fluorine-containing groups into the ligand decreases the Pb–O bond strength under heterolytic dissociation.

It is shown in the review [18] that the value of $(DH(L-H) - DH(M-L))_{(g)}$ is practically constant for the complexes of one and the same metal with a series of organic ligands including β-diketonates. Subtracting reaction Eq. (10) from Eq. (12) and taking account of the stoichiometry, we obtain the following gas-phase reaction for lead:

$$2HL_{(g)} + Pb_{(g)} \xrightarrow{\Delta_g H} PbL_{(g)} + 2H^{\bullet}_{(g)} \qquad (16)$$

Here $\Delta_g H = 2\Delta H_R$(RO–H) $- 4\langle DH_R\rangle$(Pb–O, complex, g) $= \Delta_f H^0 PbL_{2(g)} + 2\Delta_f H^0 H^{\bullet}_{(g)} - 2\Delta_f H^0 HL_{(g)} - \Delta_f H^0 Pb_{(g)}$. So, $\Delta_f H^0 PbL_{2(g)} = \Delta_g H - 2\Delta_f H^0 H^{\bullet}_{(g)} + \Delta_f H^0 Pb_{(g)} + 2\Delta_f H^0 HL_{(g)}$. Comparing the obtained value of $\Delta_f H^0 PbL_{2(g)}$ with Eq. (14), one can state that $\Delta_g H$ is independent of the ligand type. This means that the value of $(\Delta_R H$(RO–H) $- 2\langle DH_R\rangle$(Pb–O, complex, g)$)_{HL}$ is practically the same. Finally, we obtain $\Delta_R H$(RO–H) $-$ DH_R(Pb–L, g) $= 131 \pm 4$ for the studied lead(II) β-diketonates. Similarly, it can be shown that $(\Delta H_I$(RO–H) $- 2\langle DH_I\rangle$(Pb–O, complex, g)$)_{HL} \approx$ const. This result obtained for lead(II) β-diketonates can mean the following: isocharge substitution of hydrogen with metal in reaction (16) either proceeds without any noticeable change of the ligand structure or this change, if any, is constant for all the HL under consideration.

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