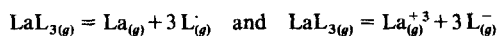


THERMOCHEMICAL PROPERTIES OF SOME f-ELECTRON ELEMENT β -DIKETONATES, AND METAL-OXYGEN BOND ENERGIES. LANTHANUM(III) β -DIKETONATES

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The standard molar enthalpies of formation of the crystalline lanthanum(III) chelate complexes with pentane-2,4-dione (acetylacetone, Hacac) and 1-phenylbutane-1,3-dione (benzoylacetone, Hbzac) were determined by the solution calorimetry method. The following values of $\Delta H_{f(s)}^{\circ}$ (kJ mol^{-1}) were obtained: $\text{La}(\text{acac})_3$, -1916.2 ± 7.0 ; $\text{La}(\text{bzac})_3 \cdot 2\text{H}_2\text{O}$, -2099.1 ± 9.7 . The enthalpies of the hypothetical complex dissociation reactions in the gaseous phase:



were calculated as a measure of the mean bond dissociation energy, $\langle D \rangle(\text{La-O})$, and the mean coordinate bond dissociation energy, $\langle D_{\text{CB}} \rangle(\text{La-O})$, respectively.

The interest in the lanthanum(III) β -diketonate complexes as well as in chelates of the other rare earth elements is great, because of their unusual physicochemical properties: laser activity, performance as shift reagents, volatility and solubility in non-aqueous solvents. The latter feature allows isotopic separations (gas chromatography, solvent extraction). However, the lack of complete thermodynamic characterization of these compounds makes it difficult to rationalize these processes. The standard enthalpies of formation of some lanthanum(III) β -diketonate complexes are presented here.

Experimental

The solution isoperibol calorimeter has been described elsewhere [1].

Materials

Acetylacetone (Schuchardt) was purified by drying over anhydrous sodium sulphate, followed by distillation. The fraction with boiling point 407-408 K was

*John Wiley & Sons, Limited, Chichester
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used for measurements. Benzoylacetone (Fluka AG) was repeatedly recrystallized from ethanol.

$\text{HCl} \cdot 11.618 \text{H}_2\text{O}$ was prepared by dilution of the concentrated acid and analyzed alkalimetrically. 1,4-Dioxane was purified by the routine method described elsewhere [2]. Hydrated lanthanum(III) chloride was obtained by dissolving spectrally pure La_2O_3 (Ubichem Ltd, England) in the stoichiometric amount of hydrochloric acid. The substrate was repeatedly recrystallized from water. It was stored under the experimental conditions and was analyzed before each experiment, because of the variable content of water molecules in the hydrate. The composition of the hydrate was found to be: $\text{LaCl}_3 \cdot 3.41 \text{H}_2\text{O}$.

Chelates

Lanthanum(III) acetylacetonate: La_2O_3 was dissolved in the stoichiometric amount of hydrochloric acid. Next, a 50% excess of an aqueous solution of ammonium acetylacetonate was added dropwise with continuous stirring. The solution was stirred for 12 h; the pH of the reaction mixture did not exceed 7.2. The white crystalline precipitate of the hydrated complex was filtered off, washed with water and dried in the air. It was dehydrated by careful heating under vacuum at 340–360 K for a few days [3]. The IR spectrum showed no presence of water. The results of the elemental analysis were as follows. Found: La, 31.72; C, 41.13; H, 4.80. Calculated: La, 31.84; C, 41.30; H, 4.85 mass %.

Lanthanum(III) benzoylacetate dihydrate: To an aqueous solution of sodium benzoylacetate, obtained through the reaction between benzoylacetate and the stoichiometric amount of sodium in *p*-xylene at 343 K, an aqueous solution of lanthanum chloride was added dropwise with continuous stirring. The yellow, flocculent precipitate was filtered off, washed with water and dried in vacuo at room temperature for 10 h. Attempts at dehydration failed. The results of the elemental analysis were as follows. Found: La, 20.93; C, 54.52; H, 4.82. Calculated: La, 21.09; C, 54.72; H, 4.74 mass %.

Results and discussion

The standard molar enthalpies of formation of the complexes were evaluated from the formal thermochemical reactions:

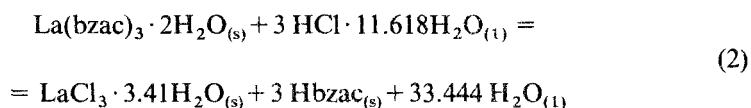
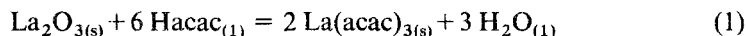


Table 1 Results of calorimetric measurements at 298.15 K

<i>i</i>	Reactant	Solvent	Solution	ΔH_f^\ddagger (kJ mol ⁻¹)
1	La ₂ O _{3(s)}	4.36 M HCl	A ₁	-438.16 ± 3.67
2	Hacac ₍₁₎	A ₁	A ₂	- 1.397 ± 0.023
3	La(acac) _{3(s)}	4.36 M HCl	B ₁	- 50.74 ± 0.3
4	H ₂ O ₍₁₎	B ₁	B ₂	- 0.344 ± 0.004
5	La(bzac) ₃ · 2H ₂ O _(s)	HCl-dioxane	C ₁	- 38.09 ± 0.13
6	HCl · 11.618H ₂ O ₍₁₎	C ₁	C ₂	- 20.14 ± 0.02
7	LaCl ₃ · 3.41H ₂ O _(s)	HCl-dioxane	D ₁	- 55.60 ± 0.52
8	Hbzac _(s)	D ₁	D ₂	27.94 ± 0.09
9	H ₂ O ₍₁₎	D ₂	D ₃	- 0.911 ± 0.009

* The mean values from five measurements, together with the standard deviation of the mean.

Their enthalpies, $\Delta H(1)$ and $\Delta H(2)$, were calculated from the calorimetrically measured enthalpies of the successive dissolution of stoichiometric amounts of the reaction substrates and products in the appropriate solvents, following the scheme in Table 1.

At the strictly preserved stoichiometry of reactions (1) and (2), solutions A₂ and B₂ as well as C₂ and D₃ are respectively thermodynamically equivalent, and hence

$$\Delta H(1) = \Delta H_1 + 6\Delta H_2 - 2\Delta H_3 - 3\Delta H_4 = -343.7 \pm 3.7 \text{ kJ mol}^{-1}$$

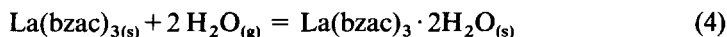
$$\Delta H(2) = \Delta H_5 + 3\Delta H_6 - \Delta H_7 - 3\Delta H_8 - 33.444\Delta H_9 = -96.3 \pm 0.7 \text{ kJ mol}^{-1}$$

The calculations of the standard molar enthalpies of formation of the complexes were based on the following literature data for ΔH_f° (kJ mol⁻¹): La₂O_{3(s)}: -1793.3 [4]; Hacac₍₁₎: -425.5 ± 1.0 [5]; H₂O₍₁₎: -285.83 ± 0.04 [6]; HCl · 11.618H₂O₍₁₎: -3482.79 ± 0.01 [6]; Hbzac_(s): -335.1 ± 2.8 [7]. $\Delta H_f^\circ(\text{LaCl}_3 \cdot 3.41\text{H}_2\text{O}_{(s)})$ was determined from measurement of the heat of the reaction:



and was found to be -2079.1 ± 4.6 kJ mol⁻¹. The results are presented in Table 2.

The standard enthalpy of formation of anhydrous lanthanum benzoylacetate was calculated by assuming the hydration enthalpy value for the reaction:



to be equal to that for lanthanum sulphate and chloride, i.e. -60 kJ mol⁻¹ per water molecule [8, 9], and taking $\Delta H_f^\circ(\text{H}_2\text{O}_{(g)}) = -241.82 \text{ kJ mol}^{-1}$ [6].

So far, only the heats of sublimation of La(III) hexafluoroacetylacetonate and dipivaloylmethanate have been determined experimentally, as 88.3 [10] and 143.6 [11] kJ mol⁻¹, respectively. The thermal properties of β -diketonates and their

Table 2 Thermochemical properties of La(III) β -diketonates (values in kJ mol⁻¹)

Complex	$-\Delta H_f^0(\text{g})$	$\Delta H(5)$	$\langle D \rangle(\text{La-O})$	$\Delta H(6)$	$\langle D_{\text{CB}} \rangle(\text{La-O})$
La(acac) ₃	1916.2 ± 7.0	1675 ± 64	279 ± 11	5050 ± 64	842 ± 11
La(bzac) ₃ · 2H ₂ O	2099.1 ± 9.7				
La(bzac) ₃	1495 ± 14	1653 ± 65	276 ± 11	5028 ± 65	838 ± 11

fluoro derivatives revealed the higher volatility of the latter. Moreover, comparison with the data for the other metal β -diketonates showed the values of the sublimation enthalpies of the acetylacetonates to be lower than for the dipivaloyl-methanates of the other metals. On this basis, $\Delta H_{\text{sub}} = 120 \pm 20$ kJ mol⁻¹ was assumed for the complexes studied. This leads to $\Delta H_f^0(\text{La}(\text{acac})_3(\text{g})) = -1796 \pm 21$ and $\Delta H_f^0(\text{La}(\text{bzac})_3(\text{g})) = -1375 \pm 24$ kJ mol⁻¹.

The mean bond dissociation energy, $\langle D \rangle(\text{La-O})$, and mean coordinate bond dissociation energy, $\langle D_{\text{CB}} \rangle(\text{La-O})$, corresponding to the gas-phase reactions:



were calculated from the relations:

$$\langle D \rangle(\text{La-O}) = 1/6 \Delta H_f^0 \text{La}(\text{g}) + 1/2 \Delta H_f^0 \text{L}(\text{g}) - 1/6 \Delta H_f^0 \text{LaL}_3(\text{g})$$

$$\langle D_{\text{CB}} \rangle(\text{La-O}) = 1/6 \Delta H_f^0 \text{La}(\text{g})^{+3} + 1/2 \Delta H_f^0 \text{L}(\text{g})^{-} - 1/6 \Delta H_f^0 \text{LaL}_3(\text{g})$$

The O—H bond dissociation energies in the enol form of the β -diketonates for the reaction: $\text{HL}_{\text{enol}}(\text{g}) = \text{H}(\text{g}) + \text{L}(\text{g})$ were assumed to be equal to the $D(\text{O—H})$ in alcohols, i.e. 418 ± 20 kJ mol⁻¹ [1]. This value and the following literature data on ΔH_f^0 (kJ mol⁻¹): $\text{H}(\text{g})$: 218 ± 0.04 [12]; $\text{Hacac}_{\text{enol}}(\text{g})$: -384.4 ± 1.3 [5]; $\text{Hbzac}_{\text{enol}}(\text{g})$: -251.3 ± 2.9 [7], lead to $\Delta H_f^0 \text{acac}(\text{g}) = -184 \pm 20$ and $\Delta H_f^0 \text{bzac}(\text{g}) = -51 \pm 20$ kJ mol⁻¹. The enthalpies of formation of the ions were calculated from the electron affinity, determined as 33 kJ mol⁻¹ [13]. This leads to $\Delta H_f^0 \text{acac}(\text{g}) = -217 \pm 20$ and $\Delta H_f^0 \text{bzac}(\text{g}) = -84 \pm 20$ kJ mol⁻¹. From these values, together with $\Delta H_f^0 \text{La}(\text{g}) = 431.0$ [14] and $\Delta H_f^0 \text{La}(\text{g})^{+3} = 3905.1$ kJ mol⁻¹ [15], the mean La—O bond dissociation energies were calculated (Table 2).

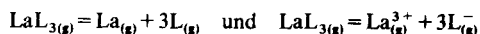
The present paper reports our preliminary studies on the thermochemical properties of lanthanide β -diketonates. For this reason, the general conclusions about the effects of substituents in the chelate ring of a complex and the electronic structure of the metal on the energy value should be formulated only after studies of other lanthanide β -diketonates. However, the present results allowed the statement that the structure of the ligand has no effect (within the limits of error) on the

$\langle D \rangle(\text{La-O})$ value. The same applies for the first series of transition metal β -diketonates [1, 16]. Finally, it should be emphasized that the obtained $\langle D \rangle(\text{La-O})$ values are close to $\langle D \rangle(\text{Be-O}) = 277 \text{ kJ mol}^{-1}$ [17] for Be(II) β -diketonates, and greatly exceed the M-O bond energy values ($166\text{--}218 \text{ kJ mol}^{-1}$) [17] for the β -diketonates of 3d-electron metals in the +2 and +3 oxidation states.

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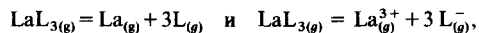
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Zusammenfassung — Die molaren Standardbildungsenthalpien $\Delta H_{f(\text{s})}^0$ der kristallinen Chelate von Lanthan(III) mit Pentandion(2,4) (Acetylaceton, Hacac) und 1-Phenylbutandion(1,3) (Benzoylaceton, Hbzac) wurden lösungskalorimetrisch bestimmt zu: $\text{La}(\text{acac})_3$: $\Delta H_{f(\text{s})}^0 = (-1916.2 \pm 7.0) \text{ kJ mol}^{-1}$ $\text{La}(\text{bzac})_3 \cdot 2\text{H}_2\text{O}$: $\Delta H_{f(\text{s})}^0 = -2099,1 \pm 9,7) \text{ kJ mol}^{-1}$. Die Enthalpien der hypothetischen Dissoziationsreaktionen in der Gasphase



als Maß für die mittlere Dissoziationsenergie $\langle D \rangle(\text{La-O})$ bzw. der mittleren Dissoziationsenergie der koordinativen Bindung $\langle D_{\text{CB}} \rangle(\text{La-O})$ wurden berechnet.

Резюме — Методом калориметрии в растворе определены стандартные молярные энтальпии образования кристаллических хелатных комплексов трехвалентного лантана с пентан-2,4-дионом (ацетилацетон, Насас) и 1-фенилбутан-1,3-дионом (бензоилацетон, Нбзас). Получены следующие значения $\Delta H_{f(s)}^0$ (кдж·моль⁻¹) для La(асас)₃: $-1916,2 \pm 7,0$; для La(бзас)₃·2H₂O: $-2099,1 \pm 9,7$. Вычислены энтальпии гипотетических реакций диссоциации комплексов в газовой фазе:



являющиеся мерой средней энергии диссоциации связи $\langle D \rangle(\text{La}-\text{O})$ и мерой средней энергии диссоциации координационной связи $\langle D_{\text{св}} \rangle(\text{La}-\text{O})$.