

## Note

### THE MEAN ZINC–OXYGEN BOND ENTHALPY IN BIS(2,4-PENTANEDIONATO)ZINC(II)

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Coordination compounds involving  $\beta$ -diketonates are widely covered in the literature and the appearance of significant reviews [1–4] certainly reflects the increasing importance of this field. The great ability of this class of ligand in coordinating metals is illustrated by the number of compounds studied [4]. In particular, our interest is mainly driven to 2,4-pentanedione (acacH) and zinc group elements. The reaction of this ligand with zinc salts produces monoaquobis(acetylacetonato)zinc(II) [5], where the coordinated water can be easily replaced by heterocyclic bases and amines, forming 1 : 1 adducts [6–8]. The derivative compounds of heterocyclic ligands dissociate in benzene solution, probably giving a metal with a coordination number of five [6].

Some thermochemical data of the anhydrous chelate were reported in a recent publication [9], which was extracted from an international conference [10]. Taking into consideration the thermochemistry of the zinc group elements, we decided to restudy this system using a different approach, by the use of a calorimetric replacement reaction, taking into account the previous results obtained with bis(diethyldithiocarbamato)zinc(II) chelate [11].

#### EXPERIMENTAL

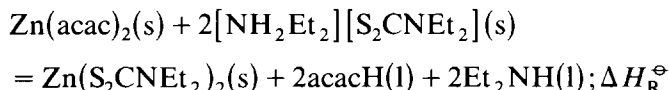
All chemicals were of analytical reagent grade, which were rigorously purified for the preparations and calorimetric determinations.

The monohydrated chelate,  $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$ , was prepared as before, and became anhydrous after subliming in vacuo, with a melting point of 128°C [5]. Bis(diethyldithiocarbamato)zinc(II) was obtained by reacting zinc chloride with diethylammonium diethyldithiocarbamate in ethanol [11].

A precision calorimeter system (LKB 8700-1) was used for all solution reactions [12]. For each enthalpy determination a series of ampoules containing ca.  $10^{-4}$  mol of reactant was broken into a glass reaction vessel at  $298.15 \pm 0.02$  K, charged with 100 cm<sup>3</sup> of calorimetric solvent. A dry-box was used for preparing ampoules of air-sensitive compounds.

## RESULTS AND DISCUSSION

The determination of the standard enthalpy of formation of bis (acetylacetonato)zinc(II) was based on the following calorimetric replacement reaction



The standard enthalpy change,  $\Delta H_{\text{R}}^{\ominus}$ , for this reaction was made in acetone due to its ability to dissolve the five components of the reaction. For this determination a calorimetric sequence of reactions is presented below, and the results are summarized in Table 1

$\text{Zn}(\text{acac})_2(\text{s}) + \text{acetone} = \text{solution A}$	$\Delta H_1^{\ominus}$
$\text{Solution A} + 2[\text{Et}_2\text{NH}_2][\text{S}_2\text{CNEt}_2](\text{s}) = \text{solution B}$	$\Delta H_2^{\ominus}$
$\text{Zn}(\text{S}_2\text{CNEt}_2)_2(\text{s}) + \text{acetone} = \text{solution C}$	$\Delta H_3^{\ominus}$
$\text{Solution C} + 2[\text{Et}_2\text{NH}](\text{l}) = \text{solution D}$	$\Delta H_4^{\ominus}$
$\text{Solution D} + 2\text{acacH}(\text{l}) = \text{solution E}$	$\Delta H_5^{\ominus}$
$\text{Solution B} = \text{solution E}$	$\Delta H_6^{\ominus}$

For this series of reactions a strict control of the stoichiometry of the individual reactions was made throughout the cycle, to give a zero  $\Delta H_6^{\ominus}$  value. The application of the first law of thermodynamics to the cycle gave:  $\Delta H_{\text{R}}^{\ominus} = \Delta H_1^{\ominus} + \Delta H_2^{\ominus} - \Delta H_3^{\ominus} - \Delta H_4^{\ominus} - \Delta H_5^{\ominus}$ , which from the data listed in Table 1 produced  $\Delta H_{\text{R}}^{\ominus} = +49.46 \pm 1.05 \text{ kJ mol}^{-1}$ .

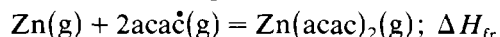
The standard enthalpy of formation of the solid chelate was calculated through the expression:  $\Delta H_{\text{f}}^{\ominus} [\text{Zn}(\text{acac})_2, \text{s}] = \Delta H_{\text{R}}^{\ominus} - \Delta H_{\text{f}}^{\ominus} [\text{acacH}, \text{l}] + 2\Delta H_{\text{f}}^{\ominus} ([\text{NH}_2\text{Et}_2][\text{S}_2\text{CNEt}_2], \text{s})$ . By the use of the values  $-289.65 \pm 4.9$ ,  $-101.29 \pm 0.37$ ,  $-425.5 \pm 1.0$  and  $-248.9 \pm 2.1 \text{ kJ mol}^{-1}$ , for bis(diethyldithiocarbamato)zinc(II) [11], diethylamine [13], acetylacetonone [14] and dieth-

TABLE 1  
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	No. of experiments	<i>i</i>	$\Delta H_i^{\ominus} (\text{kJ mol}^{-1})$
$\text{Zn}(\text{acac})_2(\text{s})$	Acetone	5	1	$+29.41 \pm 0.42$
$[\text{NH}_2\text{Et}_2][\text{S}_2\text{CNEt}_2](\text{s})$	$\text{Zn}(\text{acac})_2$ -acetone	5	2	$+46.94 \pm 0.89$
$\text{Zn}(\text{S}_2\text{CNEt}_2)_2(\text{s})$	Acetone	6	3	$+35.03 \pm 0.22$
$\text{Et}_2\text{NH}(\text{l})$	$\text{Zn}(\text{S}_2\text{CNEt}_2)_2$ -acetone	5	4	$-9.73 \pm 0.28$
$\text{acacH}(\text{l})$	$\text{Zn}(\text{S}_2\text{CNEt}_2)_2$ - $\text{Et}_2\text{NH}$ -acetone	4	5	$+1.59 \pm 0.02$

ylammonium diethyldithiocarbamate [15], respectively, the value  $\Delta H_f^\ominus [\text{Zn}(\text{acac})_2, \text{s}] = -849.89 \pm 6.88 \text{ kJ mol}^{-1}$  was found which, combined with its enthalpy of sublimation [16] ( $\Delta H_{\text{sub}} [\text{Zn}(\text{acac})_2] = 117 \pm 3 \text{ kJ mol}^{-1}$ ) gave  $\Delta H_f^\ominus [\text{Zn}(\text{acac}), \text{g}] = 777.9 \pm 7.5 \text{ kJ mol}^{-1}$ .

The enthalpy of the zinc-oxygen bond must refer to the breaking of the chelate molecule in the gaseous phase. The homolytic parameter [17] can be related to the equation



As the coordination sites are equivalent, the mean zinc-oxygen bond enthalpy is equated to one-quarter of the enthalpy of the above equation. Thus,  $\bar{D}(\text{Zn}-\text{O}) = -1/4\Delta H_{\text{fr}}$ . By using the enthalpy of sublimation of zinc [18] and the enthalpy of the radical in the gaseous phase [19] ( $130.73$  and  $-182.42 \pm 21.34 \text{ kJ mol}^{-1}$ , respectively)  $\bar{D}(\text{Zn}-\text{O}) = 136 \pm 11 \text{ kJ mol}^{-1}$  is derived.

In comparing our result with that available from the literature [9] ( $138 \pm 4 \text{ kJ mol}^{-1}$ ) a close agreement can be noted between them, but they clearly differ in the uncertainty. The calculation in the uncertainty used by the authors of ref. 10 is unknown; however, our result has a large uncertainty attached to  $\bar{D}(\text{Zn}-\text{O})$ , which comes from the enthalpy of formation of the radical.

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