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Thermochimica Acta 247 (1994) 245–263

thermochimica  
acta

## Standard enthalpies of formation and sublimation of some crystalline bis(8-hydroxyquinolate) metal complexes

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Received 24 January 1994; accepted 24 May 1994

### Abstract

Resulting from a collaboration among three departments, the standard enthalpies of formation of some crystalline bis(8-hydroxyquinolate) metal complexes were determined by reaction-solution calorimetry. Enthalpies of hydrolysis were measured for several samples of each complex using various acidic solvents. 8-hydroxyquinoline is written as Hox. At 298.15 K,  $\Delta_f H_m^\circ(M(\text{ox})_2, \text{cr})/(\text{kJ mol}^{-1})$  values are: Mg(ox)<sub>2</sub>,  $-516.0 \pm 4.0$ ; Ca(ox)<sub>2</sub>,  $-607.7 \pm 4.4$ ; Sr(ox)<sub>2</sub>,  $-585.9 \pm 4.1$ ; Ba(ox)<sub>2</sub>,  $-573.4 \pm 4.5$ ; Cu(ox)<sub>2</sub>,  $-103.3 \pm 3.3$ ; Zn(ox)<sub>2</sub>,  $-271.5 \pm 3.6$ ; Cd(ox)<sub>2</sub>,  $-179.6 \pm 4.3$ ; Pb(ox)<sub>2</sub>,  $-145.3 \pm 3.8$ ; Mn(ox)<sub>2</sub>,  $-307.1 \pm 3.7$ ; Fe(ox)<sub>2</sub>,  $-219.7 \pm 4.5$ ; Co(ox)<sub>2</sub>,  $-160.4 \pm 4.2$ ; Ni(ox)<sub>2</sub>,  $-165.5 \pm 5.6$ .

Where feasible, standard enthalpies of sublimation at 298.15 K were determined by measuring vapour pressures as functions of temperature.  $\Delta_{\text{cr}}^\circ H_m^\circ(M(\text{ox})_2)/(\text{kJ mol}^{-1})$  values are: Mg(ox)<sub>2</sub>,  $230.2 \pm 4.0$ ; Cu(ox)<sub>2</sub>,  $168.7 \pm 7.3$ ; Zn(ox)<sub>2</sub>,  $183.2 \pm 6.3$ ; Cd(ox)<sub>2</sub>,  $201.7 \pm 7.5$ ; Pb(ox)<sub>2</sub>,  $187.1 \pm 6.2$ ; Mn(ox)<sub>2</sub>,  $194.6 \pm 10.4$ ; Co(ox)<sub>2</sub>,  $205.3 \pm 4.0$ ; Ni(ox)<sub>2</sub>,  $175.4 \pm 6.7$ . From the standard enthalpies of formation in the gaseous state, the mean metal–ligand dissociation enthalpies were derived and compared with corresponding values for other complexes of these metals.

**Keywords:** Heat of formation; Heat of hydrolysis; Heat of sublimation; Hydroxyquinolate

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## 1. Introduction

8-Hydroxyquinoline, often called oxine and abbreviated in this paper as Hox, was introduced into quantitative inorganic analysis by Berg in 1927 [1] as it forms sparingly soluble complexes with a wide variety of metal ions in neutral or slightly alkaline aqueous solution. In 1985, Jamea and Pilcher [2] reported the enthalpies of formation of several  $M(\text{ox})_2$  complexes determined by reaction-solution calorimetry. Unknown to these authors, simultaneous investigations were being pursued at the Universities of Keele (UK) and Porto (Portugal) and comparison of the results revealed some large differences. This gave rise to an intolerable situation so a collaborative project was mounted to resolve the discrepancies: only the differences from the results of Jamea and Pilcher will be apparent in this paper.

Metal oxine complexes are precipitated from aqueous solution, usually as dihydrates. Jamea and Pilcher [2] dried the precipitates in air at 400 K and analysed them by hydrolysis in acid followed by titration of the liberated Hox with standardized potassium bromate solution. This criterion of purity could mislead if the sample were contaminated with both water and trapped oxine and it has been found since that for some of these complexes, especially those of Fe, Co, and Ni, that effective dehydration requires heating to 400 K in vacuo for extended periods up to 12 h. For this reinvestigation, elemental microanalyses for C, H, and N were used as criteria of sample purity and, where possible, measurements were repeated on samples prepared in different ways. Moreover, results were cross-checked in the three laboratories by measuring the enthalpies of hydrolysis in different acidic solvents; hence the final results reported in this paper for the enthalpies of formation of the crystalline complexes can be fairly regarded as definitive.

To derive the mean metal–ligand dissociation enthalpies, enthalpies of formation of the complexes in the gaseous state are required. Enthalpies of sublimation have been derived from measurements of vapour pressures as functions of temperature using the Knudsen cell method and the observed values were corrected to 298.15 K.

## 2. Experimental

### 2.1. Materials

B.D.H. Analar grade 8-hydroxyquinoline was purified by sublimation in vacuo. The  $M(\text{ox})_2$  complexes were prepared from aqueous solutions of Analar grade salts using the conditions for precipitation as in quantitative inorganic analysis [3]: in some cases preparation was made using oxine dissolved in ethanol, and in others with oxine dissolved in ethanoic acid. The complexes were washed with water and ethanol, and dried in vacuo at 400 K until the purity criteria were satisfied. Elemental microanalysis results for the complexes are given in Table 1; all other samples studied gave analysis results within the experimental uncertainty ( $\pm 0.3$  mass%) of those shown.

Table 1  
Analyses of  $M(\text{ox})_2$  complexes in mass%

	Found			Expected		
	C	H	N	C	H	N
Mg(ox) <sub>2</sub>	68.8	3.8	9.0	69.2	3.9	9.0
Ca(ox) <sub>2</sub>	65.4	3.7	8.7	65.8	3.7	8.5
Sr(ox) <sub>2</sub>	57.9	3.2	7.4	57.5	3.2	7.5
Ba(ox) <sub>2</sub>	50.8	2.8	6.4	50.8	2.8	6.6
Cu(ox) <sub>2</sub>	61.6	3.4	8.0	61.5	3.4	8.0
Zn(ox) <sub>2</sub>	61.3	3.6	7.7	61.1	3.4	7.9
Cd(ox) <sub>2</sub>	53.6	2.8	6.8	53.9	3.0	7.0
Pb(ox) <sub>2</sub>	43.3	2.4	5.6	43.6	2.4	5.6
Mn(ox) <sub>2</sub>	62.7	3.5	8.0	63.0	3.5	8.2
Fe(ox) <sub>2</sub>	62.6	3.4	7.9	62.8	3.5	8.1
Co(ox) <sub>2</sub>	61.7	3.4	7.9	62.3	3.5	8.1
Ni(ox) <sub>2</sub>	62.6	3.5	8.0	62.3	3.5	8.1

The salts used were of B.D.H. AnalaR grade and when necessary, the degree of hydration was checked by chemical analysis. The calorimetric solvents were prepared from B.D.H. AnalaR grade acids and distilled water, and the compositions verified by titration.

## 2.2. Solution-reaction calorimeters

The Manchester solution-reaction calorimeter, ancillary equipment, method of use and tests of its performance have been reported elsewhere [4].

Measurements in Porto were made in two calorimetric systems: (a) the LKB 8700 solution-reaction calorimeter with a reaction vessel of 100 cm<sup>3</sup> capacity and temperature measurements being made using a thermistor; and (b) a Dewar calorimeter [5,6] of design similar to that in Manchester but with temperature measurements made using a quartz thermometer (Hewlett Packard HP 2804-A). Both calorimeters were tested by measuring the enthalpy of solution of tris(hydroxymethyl)aminomethane in 0.1 mol dm<sup>-3</sup> HCl (aq), with the results for (a)  $\Delta_{\text{soln}}H/(\text{kJ mol}^{-1}) = -29.72 \pm 0.03$ , and (b)  $\Delta_{\text{soln}}H/(\text{kJ mol}^{-1}) = -29.75 \pm 0.07$ , in agreement with the value reported by Kilday and Prosen [7],  $-29.77 \pm 0.31 \text{ kJ mol}^{-1}$ .

Measurements in Keele were made in an LKB solution-reaction calorimeter with temperature measurements made using a platinum resistance thermometer forming one arm of a modified wheatstone bridge. The off-balance potential difference was amplified, then fed to an analogue–digital converter and then to a microcomputer for storage of the temperature–time data and subsequent calculation of the adiabatic temperature change. Test measurements on the enthalpy of solution of tris(hydroxymethyl)aminomethane in 0.1 mol dm<sup>-3</sup> HCl(aq) gave results within  $\pm 0.05\%$  of the Kilday and Prosen values [7].

### 2.3. Vapour pressure apparatus

The Knudsen effusion method was used as described by Burkinshaw and Mortimer [8]. The vapour effusing from the Knudsen cell was allowed to condense on a quartz crystal positioned above the effusion hole and changes in frequency of oscillation of the quartz plate were proportional to the mass condensed. From the Knudsen formula

$$p = \frac{\dot{m}}{a} \left( \frac{2\pi RT}{M} \right)^{1/2}$$

where  $\dot{m}$  is the rate of mass loss,  $a$  the effective hole area and  $M$  the molar mass of the effusing vapour; as the rate of change in frequency  $\dot{\nu}$  is proportional to the rate of mass loss, then

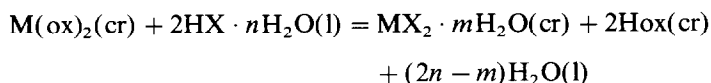
$$\ln p = \ln(\dot{\nu}T^{1/2}) + \ln\left(\frac{2\pi R}{a^2 M}\right)^{1/2}$$

and hence  $\Delta_{\text{cr}}^{\ominus} H_{\text{m}}^{\ominus}$  may be derived from the slope of  $\ln(\dot{\nu}T^{1/2})$  versus  $T^{-1}$  by applying the integrated form of the Clausius–Clapeyron equation.

Measurements were made in Porto using an Edwards 306 vacuum coating unit providing a minimum pressure of  $7 \times 10^{-5}$  Pa, fitted with an FTM3 film thickness monitor incorporating a quartz crystal oscillator (6 MHz), but with some modifications from the apparatus described by Burkinshaw and Mortimer. The cylindrical Knudsen cell was made of steel, external diameter 13 mm, internal diameter 6 mm and depth 8 mm. The lid with an effusion hole diameter of 0.8 mm was screwed on to the cell. The complete cell was screwed into an electrically heated cylindrical steel block, and the temperature was controlled to  $\pm 0.1$  K by a Eurotherm 815 proportional integral derivative controller. Temperatures were measured by a Lab facility P100/0620 platinum sensing detector screwed into the effusion cell. Frequency changes in the quartz crystal oscillator circuit were measured with a Philips Frequency Counter PM 6685 connected to the FTM3 film thickness monitor. The equipment was tested with several compounds of known standard molar enthalpy of sublimation.

### 3. Results

The general thermochemical reaction used for determining the enthalpies of formation of the  $M(\text{ox})_2$  complexes was



The standard enthalpy of this reaction was determined by measuring, or calculating from reference data, the enthalpy of solution of each reactant and product in the acidic calorimetric solvent so that the final solution resulting from the dissolution of

Table 2  
Auxiliary data:  $\Delta_f H_m^\circ / \text{kJ mol}^{-1}$  at 298.15 K

HCl in 7.97H <sub>2</sub> O(l)	-160.00 ± 0.01	HCl in 10H <sub>2</sub> O(l)	-161.32 ± 0.01	HCl in 54.46H <sub>2</sub> O(l)	-165.47 ± 0.01
H <sub>2</sub> SO <sub>4</sub> in 6H <sub>2</sub> O(l)	-874.22 ± 0.30	H <sub>2</sub> SO <sub>4</sub> in 12.61H <sub>2</sub> O(l)	-882.53 ± 0.30	H <sub>2</sub> SO <sub>4</sub> in 53.44H <sub>2</sub> O(l)	-886.83 ± 0.30
H <sub>2</sub> SO <sub>4</sub> in 56.77H <sub>2</sub> O(l)	-886.91 ± 0.30	HNO <sub>3</sub> in 53.00H <sub>2</sub> O(l)	-206.86 ± 0.47	HNO <sub>3</sub> in 53.79H <sub>2</sub> O(l)	-206.86 ± 0.47
Hox(cr)	-83.0 ± 1.5 [10]	Mg(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O(cr)	-2614.66 ± 1.34	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O(cr)	-2133.42 ± 1.12
CaCl <sub>2</sub> · 2H <sub>2</sub> O(cr)	-1396.62 ± 1.26	Sr(NO <sub>3</sub> ) <sub>2</sub> (cr)	-984.07 ± 0.92	SrCl <sub>2</sub> · 6H <sub>2</sub> O(cr)	-2628.81 ± 2.09
Ba(NO <sub>3</sub> ) <sub>2</sub> (cr)	-978.55 ± 2.18	BaCl <sub>2</sub> · 2H <sub>2</sub> O(cr)	-1446.41 ± 2.09	CuSO <sub>4</sub> · 5H <sub>2</sub> O(cr)	-2279.36 ± 1.05
ZnSO <sub>4</sub> · 7H <sub>2</sub> O(cr)	-3078.53 ± 1.46	CdSO <sub>4</sub> · 8/3H <sub>2</sub> O(cr)	-1730.42 ± 0.84	CdCl <sub>2</sub> · 2.5H <sub>2</sub> O(cr)	-1130.68 ± 2.09
Pb(NO <sub>3</sub> ) <sub>2</sub> (cr)	-452.58 ± 1.17	MnSO <sub>4</sub> (cr)	-1066.75 ± 0.92	MnCl <sub>2</sub> · 4H <sub>2</sub> O(cr)	-1687.41 ± 0.63
FeSO <sub>4</sub> · 7H <sub>2</sub> O(cr)	-3015.83 ± 0.84	FeCl <sub>3</sub> (cr)	-341.79 ± 0.50	CoSO <sub>4</sub> (cr)	-888.93 ± 1.97
CoSO <sub>4</sub> · 6H <sub>2</sub> O(cr)	-2685.17 ± 1.97	CoCl <sub>2</sub> · 6H <sub>2</sub> O(cr)	-2113.76 ± 2.09	NiSO <sub>4</sub> · 6H <sub>2</sub> O(cr)	-2683.91 ± 2.55
NiCl <sub>2</sub> · 6H <sub>2</sub> O(cr)	-2107.06 ± 5.02	H <sub>2</sub> O(l)	-285.83 ± 0.04		

the reactants was of the same composition as that resulting from dissolution of the products. The enthalpy of solution of water in the calorimetric solvent was generally calculated but in some instances was also measured. All the experimental uncertainties are quoted as twice the standard deviation of the mean.

To derive the enthalpies of formation of the  $M(\text{ox})_2$  complexes from the enthalpies of the thermochemical reactions, the auxiliary data listed in Table 2 were used, and, unless indicated otherwise, the Russian compilation [9] of thermochemical data was the source.

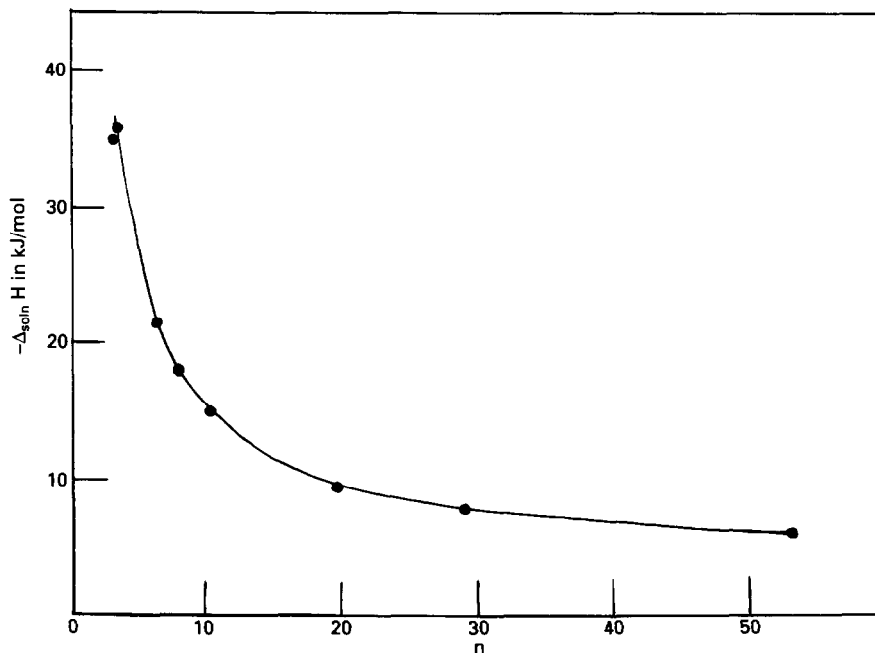
The enthalpy of solution of oxine in a variety of acidic solvents was measured and the results are listed in Table 3. The values in  $\text{HCl} \cdot n\text{H}_2\text{O}$  are plotted against  $n$  in Fig. 1 and give a smooth curve: values in  $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$  and in  $\text{HNO}_3 \cdot n\text{H}_2\text{O}$  lie close to this curve.

Table 3  
Molar enthalpy of solution of Hox in aqueous acids at 298.15 K

Acid	No. of expts.	$\Delta_{\text{soln}} H^\circ / \text{kJ mol}^{-1}$
$\text{HCl} \cdot 3.438\text{H}_2\text{O}$	3	$-35.31 \pm 1.19$
$\text{HCl} \cdot 3.673\text{H}_2\text{O}$	4	$-35.80 \pm 1.40$
$\text{HCl} \cdot 6.53\text{H}_2\text{O}$	4	$-21.62 \pm 0.16$
$\text{HCl} \cdot 7.970\text{H}_2\text{O}$	4	$-18.24 \pm 0.14$
$\text{HCl} \cdot 9.998\text{H}_2\text{O}$	4	$-15.54 \pm 0.56$
$\text{HCl} \cdot 10.01\text{H}_2\text{O}$	4	$-15.43 \pm 0.08$
$\text{HCl} \cdot 19.81\text{H}_2\text{O}$	3	$-9.26 \pm 0.27$
$\text{HCl} \cdot 29.09\text{H}_2\text{O}$	3	$-7.82 \pm 0.52$
$\text{HCl} \cdot 54.46\text{H}_2\text{O}$	3	$-6.13 \pm 0.15$
$\text{H}_2\text{SO}_4 \cdot 6.00\text{H}_2\text{O}$	6	$-26.13 \pm 0.58$
$\text{H}_2\text{SO}_4 \cdot 9.020\text{H}_2\text{O}$	4	$-17.42 \pm 0.49$
$\text{H}_2\text{SO}_4 \cdot 12.61\text{H}_2\text{O}$	5	$-9.31 \pm 0.09$
$\text{H}_2\text{SO}_4 \cdot 54.54\text{H}_2\text{O}$	8	$-4.14 \pm 0.46$
$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	6	$-4.98 \pm 0.39$

Table 4  
Molar enthalpies of reaction and solution for  $\text{Mg}(\text{ox})_2$ ,  $\text{Ca}(\text{ox})_2$ ,  $\text{Sr}(\text{ox})_2$ , and  $\text{Ba}(\text{ox})_2$  in  $\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$  at 298.15 K

$i$	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m^\circ / \text{kJ mol}^{-1}$
1	$\text{H}_2\text{O}(\text{l})$	$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	$\text{A}_1$	–	$0.00 \pm 0.00$
2	Hox(cr)	$\text{A}_1$	$\text{A}_2$	6	$-4.98 \pm 0.39$
3	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$	$\text{A}_2$	$\text{F}_1$	4	$20.68 \pm 0.73$
4	$\text{Mg}(\text{ox})_2(\text{cr})$	$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	$\text{F}_1$	6	$-127.59 \pm 2.69$
5	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{cr})$	$\text{A}_2$	$\text{F}_2$	5	$31.07 \pm 0.69$
6	$\text{Ca}(\text{ox})_2(\text{cr})$	$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	$\text{F}_2$	5	$-112.14 \pm 1.07$
7	$\text{Sr}(\text{NO}_3)_2(\text{cr})$	$\text{A}_2$	$\text{F}_3$	5	$16.04 \pm 0.52$
8	$\text{Sr}(\text{ox})_2(\text{cr})$	$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	$\text{F}_3$	4	$-141.73 \pm 2.04$
9	$\text{Ba}(\text{NO}_3)_2(\text{cr})$	$\text{A}_2$	$\text{F}_4$	5	$32.73 \pm 0.34$
10	$\text{Ba}(\text{ox})_2(\text{cr})$	$\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$	$\text{F}_4$	6	$-136.26 \pm 2.75$

Fig. 1.  $\Delta_{\text{soln}}H$  of 8-hydroxyquinoline in  $\text{HCl} \cdot n\text{H}_2\text{O}(\text{l})$ .

The enthalpies of reaction and solution for  $\text{Mg}(\text{ox})_2$ ,  $\text{Ca}(\text{ox})_2$ ,  $\text{Sr}(\text{ox})_2$  and  $\text{Ba}(\text{ox})_2$  in  $\text{HNO}_3 \cdot 53.00\text{H}_2\text{O}$  are given in Table 4, and in  $\text{HCl} \cdot n\text{H}_2\text{O}$  in Table 5. For the thermochemical reaction

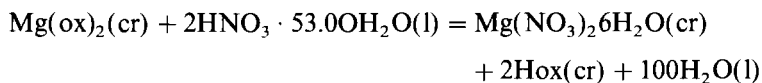


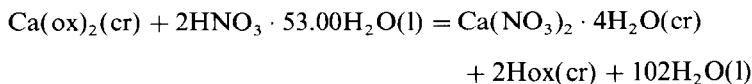
Table 5

Molar enthalpies of reaction and solution for  $\text{Ca}(\text{ox})_2$ ,  $\text{Sr}(\text{ox})_2$ , and  $\text{Ba}(\text{ox})_2$  in  $\text{HCl} \cdot n\text{H}_2\text{O}$  at 298.15 K

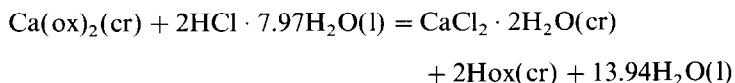
<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m / \text{kJ mol}^{-1}$
11	$\text{H}_2\text{O}(\text{l})$	$\text{HCl} \cdot 7.97\text{H}_2\text{O}$	A <sub>3</sub>	—	$-0.66 \pm 0.02$
12	Hox(cr)	A <sub>3</sub>	A <sub>4</sub>	4	$-18.24 \pm 0.14$
13	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$	A <sub>4</sub>	F <sub>5</sub>	4	$-27.12 \pm 0.15$
14	$\text{Ca}(\text{ox})_2(\text{cr})$	$\text{HCl} \cdot 7.97\text{H}_2\text{O}$	F <sub>5</sub>	3	$-137.47 \pm 3.80$
15	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$	A <sub>4</sub>	F <sub>6</sub>	4	$43.23 \pm 0.04$
16	$\text{Sr}(\text{ox})_2(\text{cr})$	$\text{HCl} \cdot 7.97\text{H}_2\text{O}$	F <sub>6</sub>	5	$-176.50 \pm 1.60$
17	$\text{H}_2\text{O}(\text{l})$	$\text{HCl} \cdot 54.46\text{H}_2\text{O}$	A <sub>5</sub>	—	$-0.02 \pm 0.01$
18	Hox(cr)	A <sub>5</sub>	A <sub>6</sub>	3	$-6.13 \pm 0.15$
19	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})$	A <sub>6</sub>	F <sub>7</sub>	6	$20.87 \pm 0.17$
20	$\text{Ba}(\text{ox})_2(\text{cr})$	$\text{HCl} \cdot 54.46\text{H}_2\text{O}$	F <sub>7</sub>	6	$-128.38 \pm 1.46$

$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_4 H - \Delta_3 H - 2\Delta_2 H - 100\Delta_1 H = -138.3 \pm 3.1$ , leading to  $\Delta_r H_m^\circ (\text{Mg}(\text{ox})_2, \text{cr}) = -513.7 \pm 4.6 \text{ kJ mol}^{-1}$ . Jamea and Pilcher [2] hydrolysed  $\text{Mg}(\text{ox})_2(\text{cr})$  in  $\text{HCl}(\text{aq})$  and derived  $\Delta_r H_m^\circ (\text{Mg}(\text{ox})_2, \text{cr}) = -518.3 \pm 3.3 \text{ kJ mol}^{-1}$ . These values agree to within the limits of experimental uncertainty; hence we accept the mean value,  $\Delta_r H_m^\circ (\text{Mg}(\text{ox})_2, \text{cr}) = 516.0 \pm 4.0 \text{ kJ mol}^{-1}$ .

For the thermochemical reaction

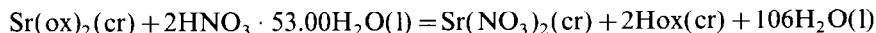


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_6 H - \Delta_5 H - 2\Delta_2 H - 102\Delta_1 H = -133.3 \pm 1.8$ , leading to  $\Delta_r H_m^\circ (\text{Ca}(\text{ox})_2, \text{cr}) = -609.1 \pm 3.8 \text{ kJ mol}^{-1}$ ; and for

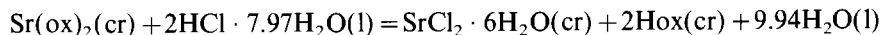


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{14} H - \Delta_{13} H - 2\Delta_{12} H = 13.94\Delta_{11} H = -64.7 \pm 3.8$  leading to  $\Delta_r H_m^\circ (\text{Ca}(\text{ox})_2, \text{cr}) = -606.3 \pm 5.0 \text{ kJ mol}^{-1}$ . The two values agree to within the limits of uncertainty and we accept the mean value,  $\Delta_r H_m^\circ (\text{Ca}(\text{ox})_2, \text{cr}) = -607.7 \pm 4.4 \text{ kJ mol}^{-1}$ . There is a small discrepancy when compared with the value reported by Jamea and Pilcher [2],  $-597.3 \pm 3.9 \text{ kJ mol}^{-1}$ , and the redetermined value is preferred.

For the thermochemical reaction

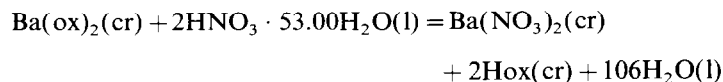


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_8 H - \Delta_7 H - 2\Delta_2 H - 106\Delta_1 H = -147.8 \pm 2.5$ , leading to  $\Delta_r H_m^\circ (\text{Sr}(\text{ox})_2, \text{cr}) = -588.6 \pm 4.1 \text{ kJ mol}^{-1}$ ; and for



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{16} H - 2\Delta_{12} H - \Delta_{15} H - 9.94\Delta_{11} H = -176.7 \pm 1.6$ , leading to  $\Delta_r H_m^\circ (\text{Sr}(\text{ox})_2, \text{cr}) = -583.1 \pm 4.0 \text{ kJ mol}^{-1}$ . These two values agree to within the limits of uncertainty and we accept the mean value,  $\Delta_r H_m^\circ (\text{Sr}(\text{ox})_2, \text{cr}) = -585.9 \pm 4.1 \text{ kJ mol}^{-1}$ . The value calculated from the results of Jamea and Pilcher [2] is  $-643.5 \pm 3.3 \text{ kJ mol}^{-1}$ , and the large discrepancy suggests that their sample was not completely dehydrated.

For the thermochemical reaction



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{10} H - \Delta_9 H - 2\Delta_2 H - 106\Delta_1 H = -159.0 \pm 3.0$ , leading to  $\Delta_r H_m^\circ (\text{Ba}(\text{ox})_2, \text{cr}) = -571.8 \pm 4.9 \text{ kJ mol}^{-1}$ , and for

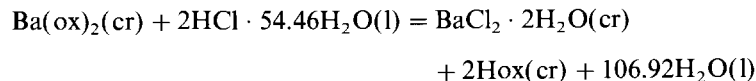




Table 6

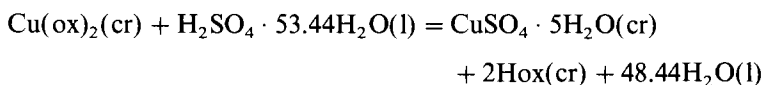
Molar enthalpies of reaction and solution for Cu(ox)<sub>2</sub>, Zn(ox)<sub>2</sub>, and Cd(ox)<sub>2</sub> at 298.15 K

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_f H_m^\circ / \text{kJ mol}^{-1}$
21	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> · 53.44H <sub>2</sub> O	A <sub>7</sub>	–	–0.02 ± 0.01
22	Hox(cr)	A <sub>7</sub>	A <sub>8</sub>	5	–2.90 ± 0.06
23	CuSO <sub>4</sub> · 5H <sub>2</sub> O(cr)	A <sub>8</sub>	F <sub>8</sub>	5	20.80 ± 0.36
24	Cu(ox) <sub>2</sub> (cr)	H <sub>2</sub> SO <sub>4</sub> · 53.44H <sub>2</sub> O	F <sub>8</sub>	5	–11.68 ± 0.43
25	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> · 12.61H <sub>2</sub> O	A <sub>9</sub>	5	–0.60 ± 0.02
26	Hox(cr)	A <sub>9</sub>	A <sub>10</sub>	5	–9.31 ± 0.09
27	CuSO <sub>4</sub> · 5H <sub>2</sub> O(cr)	A <sub>10</sub>	F <sub>9</sub>	5	32.15 ± 0.28
28	Cu(ox) <sub>2</sub> (cr)	H <sub>2</sub> SO <sub>4</sub> · 12.61H <sub>2</sub> O	F <sub>9</sub>	5	–22.61 ± 0.26
29	ZnSO <sub>4</sub> · 7H <sub>2</sub> O(cr)	A <sub>8</sub>	F <sub>10</sub>	5	26.33 ± 0.30
30	Zn(ox) <sub>2</sub> (cr)	H <sub>2</sub> SO <sub>4</sub> · 53.44H <sub>2</sub> O	F <sub>10</sub>	5	–64.75 ± 0.30
31	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> · 6H <sub>2</sub> O	A <sub>11</sub>	–	–2.45 ± 0.02
32	Hox(cr)	A <sub>11</sub>	A <sub>12</sub>	6	–26.13 ± 0.58
33	CdSO <sub>4</sub> · 8/3H <sub>2</sub> O(cr)	A <sub>12</sub>	F <sub>11</sub>	6	15.19 ± 0.30
34	Cd(ox) <sub>2</sub> (cr)	H <sub>2</sub> SO <sub>4</sub> · 6H <sub>2</sub> O	F <sub>11</sub>	5	–126.51 ± 3.16
35	H <sub>2</sub> O(l)	HCl · 10.00H <sub>2</sub> O	A <sub>13</sub>	–	–0.54 ± 0.01
36	Hox(cr)	A <sub>13</sub>	A <sub>14</sub>	4	–15.43 ± 0.08
37	CdCl <sub>2</sub> · 2.5H <sub>2</sub> O(cr)	A <sub>14</sub>	F <sub>12</sub>	4	19.24 ± 0.14
38	Cd(ox) <sub>2</sub> (cr)	HCl · 10.00H <sub>2</sub> O	F <sub>12</sub>	4	–100.09 ± 2.16

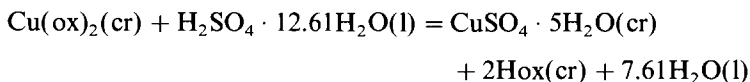
$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{20}H - \Delta_{19}H - 2\Delta_{18}H - 106.92\Delta_{17}H = -134.9 \pm 1.8$ , leading to  $\Delta_r H_m^\circ (\text{Ba(ox)}_2, \text{cr}) = 574.9 \pm 4.1 \text{ kJ mol}^{-1}$ . The two values agree to within the limits of uncertainty giving a mean value,  $\Delta_r H_m^\circ (\text{Ba(ox)}_2, \text{cr}) = -573.4 \pm 4.5 \text{ kJ mol}^{-1}$ . This differs from that calculated from the results of Jamea and Pilcher [2],  $-594.1 \pm 3.5 \text{ kJ mol}^{-1}$ , suggesting that their sample had not been completely dehydrated.

The enthalpies of reaction and solution for Cu(ox)<sub>2</sub>, Zn(ox)<sub>2</sub> and Cd(ox)<sub>2</sub> are listed in Table 6.

For the thermochemical reaction



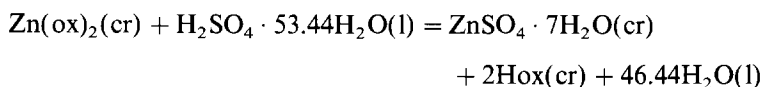
$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{24}H - \Delta_{23}H - 2\Delta_{22}H - 48.44\Delta_{21}H = -25.7 \pm 0.7$ , leading to  $\Delta_r H_m^\circ (\text{Cu(ox)}_2, \text{cr}) = -103.7 \pm 3.3 \text{ kJ mol}^{-1}$ ; and for



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{28}H - \Delta_{27}H - 2\Delta_{26}H - 7.61\Delta_{25}H = -31.6 \pm 0.4$ , leading to  $\Delta_r H_m^\circ (\text{Cu(ox)}_2, \text{cr}) = -102.1 \pm 3.2 \text{ kJ mol}^{-1}$ . The measurements on Cu(ox)<sub>2</sub> in Table 6 were made in Porto, those in H<sub>2</sub>SO<sub>4</sub> · 53.44H<sub>2</sub>O were repeated in Manchester on a different sample yielding similar results are not listed in Table 6 and which gave  $\Delta_r H_m^\circ (\text{Cu(ox)}_2, \text{cr}) = -104.1 \pm 3.5 \text{ kJ mol}^{-1}$ . The three results

agree to within the limits of uncertainty and the mean value is  $\Delta_r H_m^\ominus(\text{Cu}(\text{ox})_2, \text{cr}) = -103.3 \pm 3.3 \text{ kJ mol}^{-1}$ . This value is preferred to that calculated from the results of Jamea and Pilcher [2],  $-98.8 \pm 3.3 \text{ kJ mol}^{-1}$ , although that result is in good agreement.

Measurements were made in Porto for the thermochemical reaction

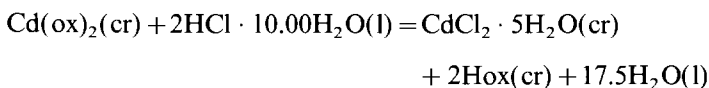


$\Delta_r H_m^\ominus/(\text{kJ mol}^{-1}) = \Delta_{30}H - \Delta_{29}H - 2\Delta_{22}H - 46.44\Delta_{21}H = -84.4 \pm 0.6$ , leading to  $\Delta_r H_m^\ominus(\text{Zn}(\text{ox})_2, \text{cr}) = -272.5 \pm 3.4 \text{ kJ mol}^{-1}$ . These measurements were repeated in Manchester on a different sample yielding similar results not listed in Table 6 and which gave  $\Delta_r H_m^\ominus(\text{Zn}(\text{ox})_2, \text{cr}) = -270.4 \pm 3.7 \text{ kJ mol}^{-1}$ . We accept the mean value,  $\Delta_r H_m^\ominus(\text{Zn}(\text{ox})_2, \text{cr}) = -271.5 \pm 3.6 \text{ kJ mol}^{-1}$  which differs from that reported by Jamea and Pilcher [2],  $-255.9 \pm 3.6 \text{ kJ mol}^{-1}$ , and is the preferred value.

For the thermochemical reaction



$\Delta_r H_m^\ominus/(\text{kJ mol}^{-1}) = \Delta_{34}H - \Delta_{33}H - 2\Delta_{32}H - 3\frac{1}{3}\Delta_{31}H = -81.3 \pm 3.4$ , leading to  $\Delta_r H_m^\ominus(\text{Cd}(\text{ox})_2, \text{cr}) = -178.7 \pm 4.6 \text{ kJ mol}^{-1}$ , and for



$\Delta_r H_m^\ominus/(\text{kJ mol}^{-1}) = \Delta_{38}H - \Delta_{37}H - 2\Delta_{36}H - 17.5\Delta_{31}H = -79.0 \pm 2.2$ , leading to  $\Delta_r H_m^\ominus(\text{Cd}(\text{ox})_2, \text{cr}) = -180.5 \pm 4.3 \text{ kJ mol}^{-1}$ . These results agree to within the limits of uncertainty and we accept the mean value,  $\Delta_r H_m^\ominus(\text{Cd}(\text{ox})_2, \text{cr}) = -179.6 \pm 4.3 \text{ kJ mol}^{-1}$  which differs from that calculated from the results of Jamea and Pilcher [2],  $-196.9 \pm 2.9 \text{ kJ mol}^{-1}$ .

The molar enthalpies of reaction and solution for  $\text{Pb}(\text{ox})_2$  are listed in Table 7.

Table 7

Molar enthalpies of reaction and solution for  $\text{Pb}(\text{ox})_2$  at 298.15 K. Solvent X is  $(2 \text{ mol dm}^{-3} \text{ HNO}_3 + 1,4\text{-dioxan})$  (1:3 by volume)

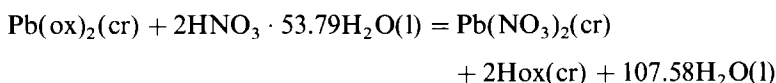
<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m^\ominus/\text{kJ mol}^{-1}$
39	$\text{H}_2\text{O}(\text{l})$	$\text{HNO}_3 \cdot 53.79\text{H}_2\text{O}$	A <sub>15</sub>	–	$0.00 \pm 0.01$
40	Hox(cr)	A <sub>15</sub>	A <sub>16</sub>	5	$-4.69 \pm 0.06$
41	$\text{Pb}(\text{NO}_3)_2(\text{cr})$	A <sub>16</sub>	F <sub>13</sub>	5	$22.35 \pm 0.79$
42	$\text{Pb}(\text{ox})_2(\text{cr})$	$\text{HNO}_3 \cdot 53.79\text{H}_2\text{O}$	F <sub>13</sub>	4	$-47.94 \pm 0.24$
43	$\text{HNO}_3 \cdot 53.79\text{H}_2\text{O}(\text{l})$	X	A <sub>17</sub>	5	$-65.43 \pm 0.39$
44	$\text{Pb}(\text{ox})_2(\text{cr})$	A <sub>17</sub>	F <sub>14</sub>	5	$-47.52 \pm 0.40$
45	$\text{H}_2\text{O}(\text{l})$	X	A <sub>18</sub>	5	$-1.01 \pm 0.01$
46	Hox(cr)	A <sub>18</sub>	A <sub>19</sub>	5	$-5.55 \pm 0.20$
47	$\text{Pb}(\text{NO}_3)_2(\text{cr})$	A <sub>19</sub>	F <sub>14</sub>	5	$-0.44 \pm 0.41$

Table 8

Molar enthalpies of reaction and solution for Mn(ox)<sub>2</sub> at 298.15 K

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_f H_m^\circ / \text{kJ mol}^{-1}$
48	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> · 56.77H <sub>2</sub> O	A <sub>20</sub>	–	–0.02 ± 0.01
49	Hox(cr)	A <sub>20</sub>	A <sub>21</sub>	8	–4.14 ± 0.46
50	MnSO <sub>4</sub> (cr)	A <sub>21</sub>	F <sub>15</sub>	6	–44.75 ± 1.00
51	Mn(ox) <sub>2</sub> (cr)	H <sub>2</sub> SO <sub>4</sub> · 56.77H <sub>2</sub> O	F <sub>15</sub>	5	–93.32 ± 1.45
52	H <sub>2</sub> O(l)	HCl · 9.998H <sub>2</sub> O	A <sub>22</sub>	–	–0.54 ± 0.02
53	Hox(cr)	A <sub>22</sub>	A <sub>23</sub>	4	–15.54 ± 0.56
54	MnCl <sub>2</sub> · 4H <sub>2</sub> O(cr)	A <sub>23</sub>	F <sub>16</sub>	4	13.65 ± 0.15
55	Mn(ox) <sub>2</sub> (cr)	HCl · 9.998H <sub>2</sub> O	F <sub>16</sub>	7	–106.00 ± 1.80

The enthalpy of the thermochemical reaction



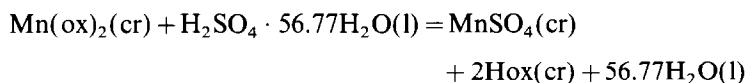
was determined in two ways:

(a) in aqueous solution,  $\Delta_f H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{42}H - \Delta_{41}H - 2\Delta_{40}H - 107.58\Delta_{39}H = -60.9 \pm 1.4$ ;

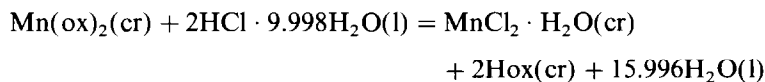
(b) in (2 mol dm<sup>-3</sup> HNO<sub>3</sub>(aq) + 1,4-dioxan) (1:3 by volume),  $\Delta_f H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{43}H + \Delta_{44}H + \Delta_{47}H - 2\Delta_{46}H - 107.58\Delta_{45}H = -58.2 \pm 1.5$ .

The mean value,  $-59.6 \pm 1.5 \text{ kJ mol}^{-1}$  leads to  $\Delta_f H_m^\circ(\text{Pb(ox)}_2, \text{cr}) = -145.3 \pm 3.8 \text{ kJ mol}^{-1}$ . This value is preferred to that of Jamea and Pilcher [2],  $-149.5 \pm 3.6 \text{ kJ mol}^{-1}$ , although the results agree to within the limits of uncertainty because the redetermination was made on a sample of carefully established purity.

The molar enthalpies of reaction and solution for Mn(ox)<sub>2</sub> are listed in Table 8. For the thermochemical reaction



$\Delta_f H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{51}H - \Delta_{50}H - 2\Delta_{49}H - 56.77\Delta_{48}H = -39.2 \pm 2.1$ , leading to  $\Delta_f H_m^\circ(\text{Mn(ox)}_2, \text{cr}) = -306.6 \pm 3.8 \text{ kJ mol}^{-1}$ , and for



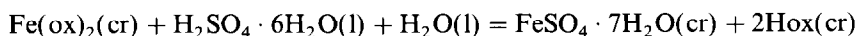
$\Delta_f H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{55}H - \Delta_{54}H - 2\Delta_{53}H - 15.996\Delta_{52}H = -79.9 \pm 2.1$ , leading to  $\Delta_f H_m^\circ(\text{Mn(ox)}_2, \text{cr}) = -307.6 \pm 3.7 \text{ kJ mol}^{-1}$ . These results agree to within the limits of experimental uncertainty with a mean value,  $\Delta_f H_m^\circ(\text{Mn(ox)}_2, \text{cr}) = -307.1 \pm 3.7 \text{ kJ mol}^{-1}$ , in agreement with the value calculated from the results of Jamea and Pilcher [2],  $-307.1 \pm 3.2 \text{ kJ mol}^{-1}$ .

The molar enthalpies of reaction and solution for Fe(ox)<sub>2</sub>, Co(ox)<sub>2</sub> and Ni(ox)<sub>2</sub> are listed in Table 9.

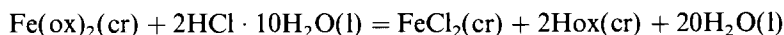
Table 9  
Molar enthalpies of reaction and solution for  $\text{Fe}(\text{ox})_2$ ,  $\text{Co}(\text{ox})_2$  and  $\text{Ni}(\text{ox})_2$  at 298.15 K

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m / \text{kJ mol}^{-1}$
56	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{cr})$	$\text{A}_{11}$	$\text{F}_{17}$	6	$46.82 \pm 1.51$
57	$\text{Fe}(\text{ox})_2(\text{cr})$	$\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\text{F}_{17}$	8	$-88.61 \pm 3.57$
58	$\text{FeCl}_2(\text{cr})$	$\text{A}_{14}$	$\text{F}_{18}$	5	$-55.60 \pm 1.63$
59	$\text{Fe}(\text{ox})_2(\text{cr})$	$\text{HCl} \cdot 10\text{H}_2\text{O}$	$\text{F}_{18}$	7	$-64.22 \pm 1.22$
60	$\text{CoSO}_4(\text{cr})$	$\text{A}_{11}$	$\text{F}_{19}$	5	$-31.25 \pm 0.35$
61	$\text{Co}(\text{ox})_2(\text{cr})$	$\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\text{F}_{19}$	7	$-119.80 \pm 2.80$
62	$\text{H}_2\text{SO}_4 \cdot 53.44\text{H}_2\text{O}(\text{l})$	$\text{HCl} \cdot 12.07\text{H}_2\text{O}$	$\text{A}_{24}$	5	$-8.87 \pm 0.02$
63	$\text{Co}(\text{ox})_2(\text{cr})$	$\text{A}_{24}$	$\text{F}_{20}$	5	$-86.01 \pm 0.68$
64	$\text{H}_2\text{O}(\text{l})$	$\text{HCl} \cdot 12.07\text{H}_2\text{O}$	$\text{A}_{25}$	5	$-0.36 \pm 0.01$
65	$\text{Hox}(\text{cr})$	$\text{A}_{25}$	$\text{A}_{26}$	5	$-12.12 \pm 0.33$
66	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$	$\text{A}_{26}$	$\text{F}_{20}$	5	$33.19 \pm 0.22$
67	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$	$\text{A}_{14}$	$\text{F}_{21}$	4	$27.82 \pm 0.13$
68	$\text{Co}(\text{ox})_2(\text{cr})$	$\text{HCl} \cdot 10\text{H}_2\text{O}$	$\text{F}_{21}$	5	$-93.10 \pm 1.42$
69	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$	$\text{A}_{11}$	$\text{F}_{22}$	6	$39.28 \pm 1.02$
70	$\text{Ni}(\text{ox})_2(\text{cr})$	$\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	$\text{F}_{22}$	4	$-110.53 \pm 2.01$
71	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$	$\text{A}_{14}$	$\text{F}_{23}$	6	$23.40 \pm 0.40$
72	$\text{Ni}(\text{ox})_2(\text{cr})\text{A}$	$\text{HCl} \cdot 10\text{H}_2\text{O}$	$\text{F}_{23}$	5	$-83.63 \pm 1.48$
73	$\text{Ni}(\text{ox})_2(\text{cr})\text{B}$	$\text{HCl} \cdot 10\text{H}_2\text{O}$	$\text{F}_{23}$	6	$-89.91 \pm 1.74$

For the thermochemical reaction

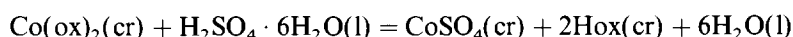


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{57}H + \Delta_{31}H - \Delta_{56}H - 2\Delta_{32}H = -85.6 \pm 4.0$ , leading to  $\Delta_f H_m^\circ(\text{Fe(ox)}_2, \text{cr}) = -221.2 \pm 5.1 \text{ kJ mol}^{-1}$ , and for

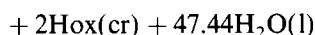
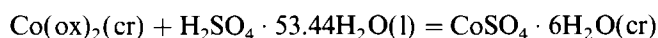


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{59}H - \Delta_{58}H - 2\Delta_{36}H - 20\Delta_{35}H = 33.0 \pm 2.1$ , leading to  $\Delta_f H_m^\circ(\text{Fe(ox)}_2, \text{cr}) = -218.2 \pm 3.7 \text{ kJ mol}^{-1}$ . These results agree to within the limits of experimental uncertainty, giving a mean value  $\Delta_f H_m^\circ(\text{Fe(ox)}_2, \text{cr}) = -219.7 \pm 4.5 \text{ kJ mol}^{-1}$ , showing a considerable difference from the value calculated from the results of Jamea and Pilcher [2],  $-183.9 \pm 3.2 \text{ kJ mol}^{-1}$ , suggesting that their sample had not been completely dehydrated.

For the thermochemical reaction



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{61}H - \Delta_{60}H - 2\Delta_{32}H - 6\Delta_{31}H = -21.6 \pm 3.1$ , leading to  $\Delta_f H_m^\circ(\text{Co(ox)}_2, \text{cr}) = -159.1 \pm 4.8 \text{ kJ mol}^{-1}$ , and for

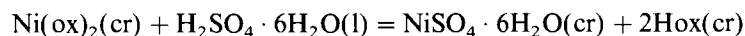


$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{62}H + \Delta_{63}H - \Delta_{66}H - 2\Delta_{65}H - 47.44\Delta_{64}H = -86.6 \pm 1.1$ , leading to  $\Delta_f H_m^\circ(\text{Co(ox)}_2, \text{cr}) = -162.6 \pm 3.8 \text{ kJ mol}^{-1}$ , and for



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{68}H - \Delta_{67}H - 2\Delta_{36}H - 14\Delta_{35}H = -82.5 \pm 1.4$ , leading to  $\Delta_f H_m^\circ(\text{Co(ox)}_2, \text{cr}) = -159.6 \pm 3.9 \text{ kJ mol}^{-1}$ . The results agree to within the limits of uncertainty and give a mean value,  $\Delta_f H_m^\circ(\text{Co(ox)}_2, \text{cr}) = -160.4 \pm 4.2 \text{ kJ mol}^{-1}$ . This value is in marked disagreement with that calculated from the results of Jamea and Pilcher [2],  $-199.4 \pm 3.3 \text{ kJ mol}^{-1}$ , suggesting that their sample was not completely dehydrated.

For the thermochemical reaction



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{70}H - \Delta_{69}H - 2\Delta_{32}H = -97.6 \pm 5.2$ , leading to  $\Delta_f H_m^\circ(\text{Ni(ox)}_2, \text{cr}) = -163.1 \pm 4.7 \text{ kJ mol}^{-1}$ . The following thermochemical reaction was studied using two samples, A and B, both with satisfactory microanalysis results



$\Delta_r H_m^\circ / (\text{kJ mol}^{-1}) = \Delta_{72}H - \Delta_{71}H - 2\Delta_{36}H - 14\Delta_{35}H = -68.6 \pm 1.5$ , leading to  $\Delta_f H_m^\circ(\text{Ni(ox)}_2, \text{cr}) = -166.9 \pm 6.0 / \text{kJ mol}^{-1}$ : for sample B,  $\Delta_f H_m^\circ(\text{Ni(ox)}_2, \text{cr}) = -160.6 \pm 6.1 / \text{kJ mol}^{-1}$ . The three results agree to within the limits of experimental uncertainty and give a mean value,  $\Delta_f H_m^\circ(\text{Ni(ox)}_2, \text{cr}) = -163.5 \pm 5.6 \text{ kJ mol}^{-1}$ , showing a large difference from that of Jamea and Pilcher [2],  $-193.3 \pm 6.0 \text{ kJ mol}^{-1}$ , again suggesting that their sample had not been completely dehydrated.

Table 10  
Enthalpies of sublimation of  $M(\text{ox})_2$  complexes

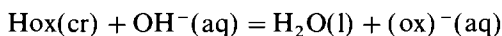
	Temperature range/K	$T/\text{K}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T)/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})/\text{kJ mol}^{-1}$
$\text{Mg}(\text{ox})_2$	605.0–626.2	614.9	$214.39 \pm 3.99$	$230.2 \pm 4.0$
$\text{Cu}(\text{ox})_2$	463.1–489.2	475.8	$159.86 \pm 7.29$	$168.7 \pm 7.3$
$\text{Zn}(\text{ox})_2$	503.2–527.2	513.8	$172.38 \pm 6.30$	$183.2 \pm 6.3$
$\text{Cd}(\text{ox})_2$	533.4–552.5	543.3	$188.94 \pm 7.54$	$201.7 \pm 7.5$
$\text{Pb}(\text{ox})_2$	479.7–505.2	492.4	$177.39 \pm 6.18$	$187.1 \pm 6.2$
$\text{Mn}(\text{ox})_2$	539.3–557.0	547.4	$182.16 \pm 10.42$	$194.6 \pm 10.4$
$\text{Co}(\text{ox})_2$	536.6–562.2	549.6	$192.68 \pm 3.99$	$205.3 \pm 4.0$
$\text{Ni}(\text{ox})_2$	449.3–467.3	458.7	$167.40 \pm 6.70$	$175.4 \pm 6.7$

Table 10 lists the results of the enthalpy of sublimation measurements. To correct  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(T)$  to  $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ , an estimated  $\Delta_{\text{cr}}^{\text{g}}C_{\text{m}}^{\circ} = -50 \text{ J K}^{-1} \text{ mol}^{-1}$  was used.  $\text{Ca}(\text{ox})_2$  did not appear to sublime until the temperature was raised to 720 K, and  $\text{Sr}(\text{ox})_2$  and  $\text{Ba}(\text{ox})_2$  both decomposed at the high temperatures required for sublimation. It would appear that these complexes have very large enthalpies of sublimation.  $\text{Fe}(\text{ox})_2$  at 400 K darkened to give a black powder, a colour typical of  $\text{Fe}(\text{ox})_3$ ; hence the metal was being oxidized by the ligand, making measurement of the enthalpy of the sublimation impossible.

The enthalpies of sublimation reported by Burkinshaw and Mortimer [8] for  $\text{Cu}(\text{ox})_2$  ( $170 \pm 3 \text{ kJ mol}^{-1}$ ),  $\text{Zn}(\text{ox})_2$  ( $178 \pm 6 \text{ kJ mol}^{-1}$ ) and  $\text{Co}(\text{ox})_2$  ( $200 \pm 10 \text{ kJ mol}^{-1}$ ) agree with the values reported here: a small difference is apparent for  $\text{Mn}(\text{ox})_2$  ( $226 \pm 14 \text{ kJ mol}^{-1}$ ) but there are marked disagreements with the values for  $\text{Cd}(\text{ox})_2$  ( $154 \pm 22 \text{ kJ mol}^{-1}$ ) and  $\text{Ni}(\text{ox})_2$  ( $139 \pm 6 \text{ kJ mol}^{-1}$ ), the Burkinshaw and Mortimer values being lower by about  $40 \text{ kJ mol}^{-1}$ . The values in Table 10 are preferred because of the care taken in establishing the purity of the samples studied.

#### 4. Discussion

Charles [10] measured the enthalpies of precipitation of some oxine complexes from alkaline solution, and although the degree of hydration of the complexes was not determined, they are generally precipitated as  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ . Jamea and Pilcher [2] measured the enthalpy of solution of  $\text{Hox}(\text{cr})$  in  $0.03 \text{ mol dm}^{-3}$   $\text{NaOH}(\text{aq})$ , the concentration used by Charles;  $\Delta H_{\text{m}}(\text{solution}) = -3.84 \pm 0.02 \text{ kJ mol}^{-1}$ . This is the enthalpy of the reaction



and as  $\Delta_{\text{r}}H_{\text{m}}^{\circ}(\text{OH}^{-}, \text{aq}) = -230.0 \pm 0.1 \text{ kJ mol}^{-1}$  [11], then  $\Delta_{\text{r}}H_{\text{m}}^{\circ}(\text{ox}^{-}, \text{aq}) = -31.0 \pm 1.5 \text{ kJ mol}^{-1}$ . As the precipitation reaction is

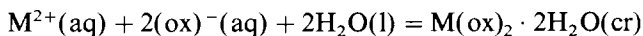
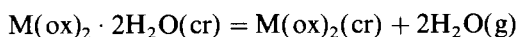


Table 11

Enthalpies of formation of  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  and of the dissociations of  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr}) = M(\text{ox})_2(\text{cr}) + 2\text{H}_2\text{O}(\text{g})$ , and  $M\text{Cl}_2 \cdot 2\text{H}_2\text{O}(\text{cr}) = M\text{Cl}_2(\text{cr}) + 2\text{H}_2\text{O}(\text{g})$

M	$\Delta H_m(\text{precipitation})$ [10]/ $\text{kJ mol}^{-1}$	$\Delta_f H_m^\ominus(\text{M}^{2+}, \text{aq})$ [9]/ $\text{kJ mol}^{-1}$	$M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$		$M\text{Cl}_2 \cdot 2\text{H}_2\text{O}$
			$\Delta_f H_m^\ominus(\text{cr})$ / $\text{kJ mol}^{-1}$	$\Delta H_m(\text{diss})$ / $\text{kJ mol}^{-1}$	$\Delta H_m(\text{diss})$ / $\text{kJ mol}^{-1}$
Mg	$-34.7 \pm 1.0$	$-486.1 \pm 0.6$	$-1136.5 \pm 3.2$	$136.9 \pm 5.1$	$151.1 \pm 1.2$
Ca	$-39.3 \pm 1.0$	$-543.1 \pm 0.8$	$-1216.1 \pm 3.3$	$124.8 \pm 5.5$	$123.5 \pm 1.6$
Sr	$-19.2 \pm 1.0$	$-551.5 \pm 0.6$	$-1204.4 \pm 3.2$	$134.9 \pm 5.2$	$128.1 \pm 1.6$
Ba	$-37.2 \pm 1.0$	$-536.6 \pm 2.1$	$-1207.5 \pm 3.8$	$150.5 \pm 5.9$	$118.8 \pm 3.0$
Mn	$-68.8 \pm 1.4$	$-220.3 \pm 0.6$	$-992.6 \pm 3.4$	$131.9 \pm 5.1$	$126.8 \pm 4.4$
Co	$-81.6 \pm 1.8$	$-56.6 \pm 1.9$	$-771.9 \pm 4.0$	$127.9 \pm 5.8$	$124.0 \pm 2.5$
Ni	$-88.3 \pm 1.9$	$-53.1 \pm 2.5$	$-775.1 \pm 4.3$	$128.0 \pm 7.1$	$127.7 \pm 3.6$
Cu	$-107.5 \pm 2.1$	$66.9 \pm 0.9$	$-674.3 \pm 3.8$	$87.4 \pm 5.0$	$119.4 \pm 2.2$
Zn	$-81.2 \pm 1.7$	$-153.6 \pm 1.4$	$-868.5 \pm 3.7$	$113.4 \pm 5.2$	
Pb	$-78.2 \pm 1.7$	$-0.9 \pm 0.9$	$-712.8 \pm 3.6$	$83.9 \pm 5.2$	

then  $\Delta_f H_m^\ominus(M(\text{ox})_2 \cdot 2\text{H}_2\text{O}, \text{cr})$  can be derived and, subsequently, the enthalpy of the dissociation

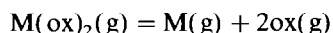


requiring  $\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{g}) = -241.81 \pm 0.04 \text{ kJ mol}^{-1}$  [11]. The results with  $\Delta_f H_m^\ominus(\text{M}^{2+}, \text{aq})$  [9] are listed in Table 11. Inspection of the  $\Delta H_m(\text{diss})$  values shows that the assumption that the precipitates were  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  appears justified. From reference tables [9], the corresponding enthalpy of dissociation of some metal dichloride dihydrates



can be derived and these values are also listed in Table 11, and can all be seen to be of magnitude similar to those for the oxinate dihydrates. Merrit et al. [12] have shown that the  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  complexes of Co, Ni and Cu are isomorphous; the metal and ligand atoms are planar whereas the two water molecules are in the axial positions of a distorted octahedron. The dissociation enthalpies to remove  $\text{H}_2\text{O}$  from  $\text{Ni}(\text{glycinate})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{Cu}(\text{glycinate})_2 \cdot \text{H}_2\text{O}(\text{cr})$  where the water molecules are in axial positions have been reported [13] as  $109.6$  and  $56.0 \text{ kJ mol}^{-1}$  respectively, where the order of magnitude of dissociation enthalpy per water molecule is similar to that in the  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$  complexes.

The mean dissociation enthalpy to be assigned to the metal–ligand binding may be defined as one half of the enthalpy of the disruption reaction



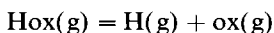
$$\langle D(M-\text{ox}) \rangle = 0.5[\Delta_f H_m^\ominus(M, \text{g}) - \Delta_f H_m^\ominus(M(\text{ox})_2, \text{g})] + \Delta_f H_m^\ominus(\text{ox}, \text{g})$$

Table 12

Standard molar enthalpies of formation of  $M(\text{ox})_2$  in the crystalline and gaseous states at 298.15 K

	$\Delta_f H_m^\ominus(\text{cr})/\text{kJ mol}^{-1}$	$\Delta_{\text{cr}}^\ominus H_m^\ominus/\text{kJ mol}^{-1}$	$\Delta_f H_m^\ominus(\text{g})/\text{kJ mol}^{-1}$
Mg(ox) <sub>2</sub>	-516.0 ± 4.0	230.2 ± 4.0	-285.8 ± 5.7
Ca(ox) <sub>2</sub>	-607.7 ± 4.4	[250 ± 30]	-358 ± 30
Sr(ox) <sub>2</sub>	-585.9 ± 4.1	[250 ± 30]	-336 ± 30
Ba(ox) <sub>2</sub>	-573.4 ± 4.5	[250 ± 30]	-323 ± 30
Cu(ox) <sub>2</sub>	-103.3 ± 3.3	168.7 ± 7.3	65.4 ± 8.0
Zn(ox) <sub>2</sub>	-271.5 ± 3.6	183.2 ± 6.3	-88.3 ± 7.3
Cd(ox) <sub>2</sub>	-179.6 ± 4.3	201.7 ± 7.5	22.1 ± 8.6
Pb(ox) <sub>2</sub>	-145.3 ± 3.8	187.1 ± 6.2	41.8 ± 7.3
Mn(ox) <sub>2</sub>	-307.1 ± 3.7	194.6 ± 10.4	-112.5 ± 11.0
Fe(ox) <sub>2</sub>	-219.7 ± 4.5	[190 ± 20]	-30 ± 21
Co(ox) <sub>2</sub>	-160.4 ± 4.2	205.3 ± 4.0	-44.9 ± 5.8
Ni(ox) <sub>2</sub>	-163.5 ± 5.6	175.4 ± 6.7	11.9 ± 8.7

The dissociation enthalpy of the (O–H) bond in  $\text{Hox}$  is the enthalpy of dissociation



$$D(\text{O–H}) = \Delta_f H_m^\ominus(\text{H}, \text{g}) + \Delta_f H_m^\ominus(\text{ox}, \text{g}) - \Delta_f H_m^\ominus(\text{Hox}, \text{g})$$

Hence

$$\begin{aligned} \langle D(\text{M–ox}) \rangle - D(\text{H–ox}) &= \frac{1}{2} [\Delta_f H_m^\ominus(\text{M}, \text{g}) - \Delta_f H_m^\ominus(\text{M}(\text{ox})_2, \text{g})] \\ &\quad - \Delta_f H_m^\ominus(\text{H}, \text{g}) + \Delta_f H_m^\ominus(\text{Hox}, \text{g}) \end{aligned}$$

To derive  $\langle D(\text{M–ox}) \rangle - D(\text{H–ox})$ , the enthalpies of formation of  $\text{M}(\text{ox})_2(\text{g})$  are required. Table 12 lists the redetermined values of  $\Delta_f H_m^\ominus(\text{M}(\text{ox})_2, \text{cr})$ , the enthalpies of sublimation and the derived enthalpies of formation in the gaseous state. The estimated enthalpies of sublimation are in parentheses: for  $\text{Fe}(\text{ox})_2$  the mean of the values for  $\text{Co}(\text{ox})_2$  and  $\text{Ni}(\text{ox})_2$  was assumed; the enthalpies of sublimation of  $\text{Ca}(\text{ox})_2$ ,  $\text{Sr}(\text{ox})_2$  and  $\text{Ba}(\text{ox})_2$  will be much larger than the rest and a tentative estimate of  $250 \pm 30 \text{ kJ mol}^{-1}$  has been made.

With  $\Delta_f H_m^\ominus(\text{H}, \text{g}) = 218.00 \pm 0.01 \text{ kJ mol}^{-1}$  [11],  $\Delta_f H_m^\ominus(\text{Hox}, \text{g}) = 6.5 \pm 1.7 \text{ kJ mol}^{-1}$  [14], and the corresponding values of  $\Delta_f H_m^\ominus(\text{M}, \text{g})$  [9], the values of  $\langle D(\text{M–ox}) \rangle - D(\text{H–ox})$  were derived and are listed in Table 13.  $\langle D(\text{M–ox}) \rangle - D(\text{H–ox})$  shows a substantial increase in the strength of binding of the ligand to the metal relative to hydrogen for the alkaline earth metals and a marked fall for Cu, Zn, Cd and Pb; for Mn, Fe, Co and Ni, the difference between the binding energy to the metal and that to hydrogen is small. Table 13 also compares the corresponding values for the 2,4-pentanedionate complexes: these values were obtained from Ribeiro da Silva and co-workers [15–17], and as expected,  $\langle D(\text{M–L}) \rangle - D(\text{H–L})$  for the oximates and the 2,4-pentanedionates follow a similar pattern.

Other complexes with binding of the ligand to the metal through oxygen and nitrogen for which experimental results are available are the aminoacid complexes of Cu and Ni, and it has been shown that  $\langle D(\text{M–aminoacid}) \rangle - D(\text{H–aminoacid})$



Table 13  
 $\langle D(M-L) \rangle - D(H-L)$  in  $ML_2$  complexes

	$\Delta_f H_m^\circ (M, g) / \text{kJ mol}^{-1}$	$\langle D(M-L) \rangle - D(H-L) / \text{kJ mol}^{-1}$		$\langle D(M-ox) \rangle / \text{kJ mol}^{-1}$	$\langle D(M-pd) \rangle / \text{kJ mol}^{-1}$
		L = ox	L = pd		
Mg	147.1 ± 0.8	5 ± 3	42 ± 5	368 ± 9	442 ± 20
Ca	177.8 ± 0.8	56 ± 15	92 ± 15	419 ± 17	492 ± 20
Sr	160.7 ± 2.1	37 ± 15	72 ± 4	400 ± 17	472 ± 20
Ba	179.1 ± 2.9	40 ± 15	64 ± 4	403 ± 17	464 ± 20
Cu	337.6 ± 1.3	-75 ± 4	-84 ± 2	288 ± 10	316 ± 20
Zn	130.5 ± 0.2	-102 ± 4	-122 ± 3	261 ± 10	278 ± 20
Cd	111.8 ± 0.4	-167 ± 3	-162 ± 3	196 ± 9	238 ± 20
Pb	195.1 ± 0.8	-135 ± 4		228 ± 10	
Mn	284.5 ± 2.1	-13 ± 6	10 ± 4	350 ± 11	410 ± 20
Fe	417.0 ± 1.3	12 ± 11		375 ± 14	
Co	428.4 ± 4.2	25 ± 4	-11 ± 3	388 ± 10	389 ± 20
Ni	428.8 ± 2.1	-3 ± 5	14 ± 3	360 ± 10	386 ± 20

for Cu is  $-19.7 \pm 7.7$  kJ mol<sup>-1</sup> [18], and for Ni,  $65.8 \pm 8.2$  kJ mol<sup>-1</sup> [19]. The aminoacid ligand is bound more strongly to the metal relative to hydrogen by about  $60 \pm 10$  kJ mol<sup>-1</sup> than is the oxine ligand, but the difference between the values for the Cu and Ni aminoacid complexes is in accord with the corresponding difference for the oxinates.

Although it may be permissible to equate

$$\langle D(\text{M-ox}) \rangle = \langle D(\text{M-O}) \rangle + \langle D(\text{M-N}) \rangle$$

there is no unambiguous way of apportioning  $\langle D(\text{M-ox}) \rangle$  between  $\langle D(\text{M-O}) \rangle$  and  $\langle D(\text{M-N}) \rangle$  and little value in attempting to do so because these bonds occur together and must interact. It seems reasonable however to assume that  $D(\text{H-ox}) = D(\text{O-H})$  in phenol,  $363 \pm 9$  kJ mol<sup>-1</sup> [20], permitting derivation of the  $D(\text{M-ox})$  values listed in Table 13. For comparison the  $\langle D(\text{M-pd}) \rangle$  values are also listed based on  $D(\text{O-H})$ , 2,4-pentanedione, enol =  $400 \pm 20$  kJ mol<sup>-1</sup> [15], and they show similar trends.

### Acknowledgements

Financial support from Instituto Nacional de Investigação Científica through Centro de Investigação Científica de Universidade do Porto (Linha 5) is gratefully acknowledged by the Porto research team; M.A.R. Matos thanks I.N.I.C. for the award of a research grant, and J.M. Goncalves thanks Fundação Gomes Teixeira for a research grant. Thanks are due to Professor C. Mortimer for donation of the apparatus for determining enthalpies of sublimation to the Thermochemistry Group of University of Porto.

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