

## STANDARD ENTHALPIES OF FORMATION OF SOME CRYSTALLINE BIS(8-HYDROXYQUINOLATE)METAL COMPLEXES BY SOLUTION-REACTION CALORIMETRY

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### ABSTRACT

The standard enthalpies of formation at 298.15 K of some crystalline bis(8-hydroxyquinolate)metal complexes were determined by solution-reaction calorimetry (8-hydroxyquinoline is written as Hox),  $\Delta_f H_m^0(M(ox)_2(c))$  (kJ mol<sup>-1</sup>): Mg(ox)<sub>2</sub>, -527.7 ± 2.7; Ca(ox)<sub>2</sub>, -606.2 ± 2.9; Sr(ox)<sub>2</sub>, -652.4 ± 3.3; Ba(ox)<sub>2</sub>, -603.0 ± 3.5; Mn(ox)<sub>2</sub>, -316.0 ± 2.6; Fe(ox)<sub>2</sub>, -192.9 ± 2.8; Co(ox)<sub>2</sub>, -208.3 ± 3.3; Ni(ox)<sub>2</sub>, -205.9 ± 5.7; Cu(ox)<sub>2</sub>, -107.7 ± 2.9; Zn(ox)<sub>2</sub>, -265.6 ± 3.0; Cd(ox)<sub>2</sub>, -205.8 ± 2.9; Pb(ox)<sub>2</sub>, -163.0 ± 3.2.

The standard enthalpies of formation in the gaseous state were derived using literature values and some estimates of enthalpies of sublimation. The differences between the mean metal–ligand dissociation enthalpies,  $\bar{D}(M-ox)$ , and the (O–H) bond dissociation enthalpy in 8-hydroxyquinoline,  $D(H-ox)$ , were calculated and compared with corresponding differences for some other complexes of these metals.

### 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. Very few thermochemical data are available for these readily accessible complexes which contain interesting chelate rings involving both oxygen and nitrogen atoms bound to the metal. Charles, in 1957 [2], measured the enthalpies of precipitation of some of these complexes from alkaline solution but did not investigate the degree of hydration of the precipitates formed. In this paper we report the standard enthalpies of formation of the anhydrous crystalline M(ox)<sub>2</sub> complexes with M = Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, determined using solution-reaction calorimetry. The enthalpies of sublimation of some of these complexes were reported recently by Birkinshaw and Mortimer [3] and these were used together with some estimates to derive the enthalpies of formation in the gaseous state. The binding enthalpy of the ligand to the metal was

assessed and compared with corresponding values in other complexes of these metals.

## EXPERIMENTAL

### *Materials*

BDH Analar grade 8-hydroxyquinoline was used. The  $M(\text{ox})_2$  complexes were prepared from aqueous solutions of Analar grade salts using the same conditions for precipitation as those in quantitative inorganic analysis [4]. The complexes were dried in air at 400 K and analysed by hydrolysis in acid followed by titration of the liberated 8-hydroxyquinoline with standard potassium bromate solution. Only samples for which analysis indicated a purity greater than 99.9% were studied. The salts used were BDH Analar grade and, when necessary, the degree of hydration of the salts was checked using the same analytical method. The calorimetric solvents were prepared from BDH Analar grade acids and distilled water.

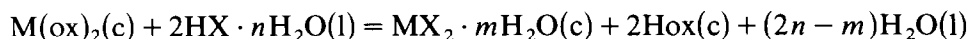
### *Solution-reaction calorimeter*

The calorimeter has been previously reported [5] and only a brief description is given here. A glass unsilvered Dewar vessel containing 130 cm<sup>3</sup> of solvent was used. Reactants were sealed in thin glass ampoules which were broken under the solvent at the appropriate times by compression between two glass rings. The calorimeter was equipped with a twin-bladed glass stirrer rotated at 7.5 Hz. Calorimeter temperatures were measured by a thermistor; the thermistor resistance was recorded at 30-s intervals by a Solartron 7065 digital voltmeter and the values transferred to a Commodore PET computer to compute  $\Delta T_{\text{ad}}$  by the Regnault–Pfaundler method [6].  $\Delta T_{\text{ad}}$  is the temperature rise that would have occurred if the calorimeter were adiabatic and there were no work of stirring. An electric heater (100  $\Omega$ ) placed in a mercury-filled glass tube was used for electrical calibration of the calorimeter. The potential difference across the heater was measured with a Solartron A210 digital voltmeter and the current determined from the potential drop across a standard 1  $\Omega$  resistance. The time for electrical heating was controlled by generating 0.1-s square-wave pulses from the 200 kHz Droitwich signal, then switching the current to the calorimeter for a pre-set pulse count. The calorimeter top plate was sealed to the Dewar using an O-ring, and the calorimeter was submerged in a water thermostat maintained at  $298.150 \pm 0.001$  K.

The accuracy of the calorimeter was tested by measuring the enthalpy of solution of THAM (NBS Standard Reference Material 724) in HCl (0.1 mol l<sup>-1</sup>) at 298.15 K. The result,  $\Delta_{\text{sol}}H_{\text{m}}$  (kJ mol<sup>-1</sup>) =  $-29.771 \pm 0.029$ , is in agreement with the value of Kilday and Prosen [7] ( $-29.770 \pm 0.032$ ).

## 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 [8] the enthalpy of solution of each reactant and product successively in the acidic calorimetric solvent ( $\text{HX} \cdot n\text{H}_2\text{O}$ ) so that the final solution resulting from the dissolution of the reactants was of the same composition as that from dissolution of the products. The calorimetric solvent chosen for a particular complex depended on the rate of hydrolysis of the complex  $M(\text{ox})_2$  and on the composition and solubility of the salt  $\text{MX}_2 \cdot m\text{H}_2\text{O}$ . As an example, the detailed calorimetric results for determining the enthalpy of the thermochemical reaction for  $\text{Co}(\text{ox})_2$  are given in Table 1, where  $\epsilon$  is the effective energy equivalent of the (calorimeter + contents) measured for each experiment electrically. In accord with normal thermochemical practice, all errors given are uncertainty intervals, i.e., twice the standard deviation of the mean.

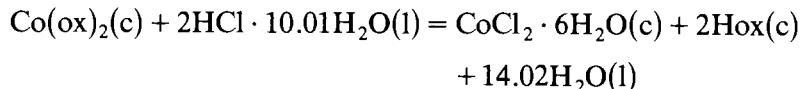
Table 2 lists the mean values of the molar enthalpies of solution and reaction required for determining the enthalpies of the thermochemical

TABLE 1

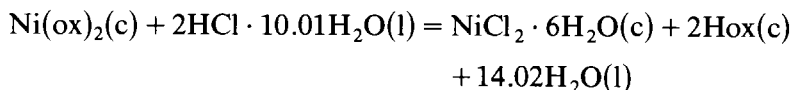
Calorimetric results for determining the enthalpy of hydrolysis of  $\text{Co}(\text{ox})_2$  at 298.15 K

$m$ (g)	$\epsilon$ (J K <sup>-1</sup> )	$\Delta T_{\text{ad}}$ (K)	$\Delta h$ (J g <sup>-1</sup> )
$\text{Co}(\text{ox})_2(\text{c}) + 2\text{HCl} \cdot 10.01\text{H}_2\text{O}(\text{l}) = \text{solution F}_1$			
0.8010	502.69	0.2439	-153.07
0.8003	514.70	0.2379	-153.00
0.7811	501.50	0.2394	-153.70
0.8457	508.19	0.2567	-154.25
0.7598	513.43	0.2277	-153.86
		Mean: -153.58 ± 0.48	
$\text{Hox}(\text{c}) + \text{HCl} \cdot 10.01\text{H}_2\text{O}(\text{l}) = \text{solution A}_2$			
0.4984	507.02	0.1052	-107.02
0.4991	514.79	0.1049	-106.13
0.4954	499.12	0.1049	-105.69
0.4976	512.23	0.1032	-106.23
		Mean: -106.26 ± 0.55	
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{c}) + \text{solution A}_2 = \text{solution F}_1$			
0.5069	511.13	-0.1165	117.47
0.6289	498.09	-0.1467	116.19
0.5032	500.41	-0.1176	116.94
0.5534	513.33	-0.1262	117.06
		Mean: 116.92 ± 0.53	

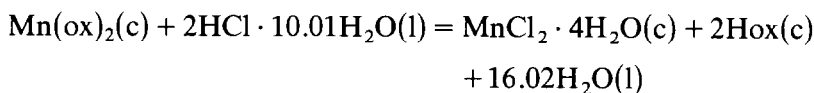
reactions when using the solvent,  $\text{HCl} \cdot 10.01\text{H}_2\text{O}(\text{l})$ : the enthalpy of solution of water in  $\text{HCl} \cdot 10.01\text{H}_2\text{O}(\text{l})$  was calculated. The relative atomic masses used were those recommended by IUPAC [9]. The thermochemical reactions, and the standard enthalpies of reaction derived from the data in Table 2 were:



$$\Delta_r H_m^0(\text{Co}(\text{ox})_2)(\text{kJ mol}^{-1}) = \Delta_4 H_m - \Delta_3 H_m - 2\Delta_2 H_m - 14.02\Delta_1 H_m \\ = -42.75 \pm 0.41$$



$$\Delta_r H_m^0(\text{Ni}(\text{ox})_2)(\text{kJ mol}^{-1}) = \Delta_6 H_m - \Delta_5 H_m - 2\Delta_2 H_m - 14.02\Delta_1 H_m \\ = -38.41 \pm 0.59$$



$$\Delta_r H_m^0(\text{Mn}(\text{ox})_2)(\text{kJ mol}^{-1}) = \Delta_8 H_m - \Delta_7 H_m - 2\Delta_2 H_m - 16.02\Delta_1 H_m \\ = -80.37 \pm 0.49$$

Table 3 lists the molar enthalpies of solution and reaction required for determining the enthalpies of the thermochemical reactions when using the solvent  $\text{HCl} \cdot 7.97\text{H}_2\text{O}(\text{l})$ : the enthalpy of solution of water in this solvent was calculated. The standard enthalpies of reaction derived from the data in Table 3 were:



$$\Delta_r H_m^0(\text{Mg}(\text{ox})_2)(\text{kJ mol}^{-1}) = \Delta_{12} H_m - \Delta_{11} H_m - 2\Delta_{10} H_m - 9.94\Delta_9 H_m \\ = -111.06 \pm 0.41$$

TABLE 2

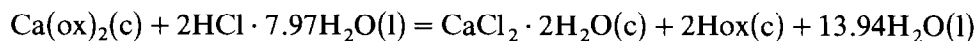
Molar enthalpies of solution and reaction at 298.15 K in  $\text{HCl} \cdot 10.01\text{H}_2\text{O}(\text{l})$ 

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m$ (kJ mol <sup>-1</sup> )
1	H <sub>2</sub> O(l)	HCl·10.01H <sub>2</sub> O	A <sub>1</sub>		-0.54 ± 0.02
2	Hox(c)	A <sub>1</sub>	A <sub>2</sub>	4	-15.43 ± 0.08
3	CoCl <sub>2</sub> ·6H <sub>2</sub> O(c)	A <sub>2</sub>	F <sub>1</sub>	4	27.82 ± 0.13
4	Co(ox) <sub>2</sub> (c)	HCl·10.01H <sub>2</sub> O	F <sub>1</sub>	5	-53.36 ± 0.22
5	NiCl <sub>2</sub> ·6H <sub>2</sub> O(c)	A <sub>2</sub>	F <sub>2</sub>	4	23.44 ± 0.49
6	Ni(ox) <sub>2</sub> (c)	HCl·10.01H <sub>2</sub> O	F <sub>2</sub>	4	-53.40 ± 0.05
7	MnCl <sub>2</sub> ·4H <sub>2</sub> O(c)	A <sub>2</sub>	F <sub>3</sub>	4	13.65 ± 0.25
8	Mn(ox) <sub>2</sub> (c)	HCl·10.01H <sub>2</sub> O	F <sub>3</sub>	4	-106.23 ± 0.22

TABLE 3

Molar enthalpies of solution and reaction at 298.15 K in HCl·7.97H<sub>2</sub>O(l)

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol <sup>-1</sup> )
9	H <sub>2</sub> O(l)	HCl·7.97H <sub>2</sub> O	A <sub>3</sub>		-0.66 ± 0.02
10	Hox(c)	A <sub>3</sub>	A <sub>4</sub>	4	-18.24 ± 0.14
11	MgCl <sub>2</sub> ·6H <sub>2</sub> O(c)	A <sub>4</sub>	F <sub>4</sub>	4	2.66 ± 0.20
12	Mg(ox) <sub>2</sub> (c)	HCl·7.97H <sub>2</sub> O	F <sub>4</sub>	4	-151.44 ± 0.09
13	CaCl <sub>2</sub> ·2H <sub>2</sub> O(c)	A <sub>4</sub>	F <sub>5</sub>	4	-27.12 ± 0.15
14	Ca(ox) <sub>2</sub> (c)	HCl·7.97H <sub>2</sub> O	F <sub>5</sub>	4	-146.48 ± 0.10
15	SrCl <sub>2</sub> ·6H <sub>2</sub> O(c)	A <sub>4</sub>	F <sub>6</sub>	4	43.23 ± 0.04
16	Sr(ox) <sub>2</sub> (c)	HCl·7.97H <sub>2</sub> O	F <sub>6</sub>	4	-116.13 ± 0.15

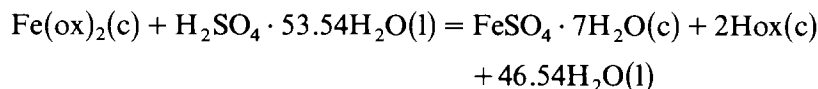


$$\begin{aligned} \Delta_r H_m^0(\text{Ca(ox)}_2)(\text{kJ mol}^{-1}) &= \Delta_{14} H_m - \Delta_{13} H_m - 2\Delta_{10} H_m - 13.94\Delta_9 H_m \\ &= -73.68 \pm 0.43 \end{aligned}$$



$$\begin{aligned} \Delta_r H_m^0(\text{Sr(ox)}_2)(\text{kJ mol}^{-1}) &= \Delta_{16} H_m - \Delta_{15} H_m - 2\Delta_{10} H_m - 9.94\Delta_9 H_m \\ &= -116.32 \pm 0.38 \end{aligned}$$

Table 4 lists the molar enthalpies of solution and reaction required for determining the enthalpies of the thermochemical reactions when using H<sub>2</sub>SO<sub>4</sub>·53.54H<sub>2</sub>O(l) as solvent: the enthalpy of solution of water in this solvent was calculated. The standard enthalpies of reaction derived from the data in Table 4 were:

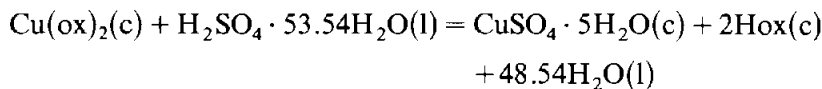


$$\begin{aligned} \Delta_r H_m^0(\text{Fe(ox)}_2)(\text{kJ mol}^{-1}) &= \Delta_{20} H_m - \Delta_{19} H_m - 2\Delta_{18} H_m - 46.54\Delta_{17} H_m \\ &= -110.18 \pm 0.92 \end{aligned}$$

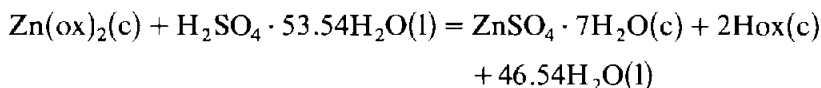
TABLE 4

Molar enthalpies of solution and reaction at 298.15 K in H<sub>2</sub>SO<sub>4</sub>·53.54H<sub>2</sub>O(l)

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol <sup>-1</sup> )
17	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> ·53.54H <sub>2</sub> O	A <sub>5</sub>		-0.03 ± 0.01
18	Hox(c)	A <sub>5</sub>	A <sub>6</sub>	4	-5.91 ± 0.30
19	FeSO <sub>4</sub> ·7H <sub>2</sub> O(c)	A <sub>6</sub>	F <sub>7</sub>	3	41.59 ± 0.52
20	Fe(ox) <sub>2</sub> (c)	H <sub>2</sub> SO <sub>4</sub> ·53.54H <sub>2</sub> O	F <sub>7</sub>	2	-81.81 ± 0.08
21	CuSO <sub>4</sub> ·5H <sub>2</sub> O(c)	A <sub>6</sub>	F <sub>8</sub>	3	22.59 ± 0.14
22	Cu(ox) <sub>2</sub> (c)	H <sub>2</sub> SO <sub>4</sub> ·53.54H <sub>2</sub> O	F <sub>8</sub>	4	-21.18 ± 0.15
23	ZnSO <sub>4</sub> ·7H <sub>2</sub> O(c)	A <sub>6</sub>	F <sub>9</sub>	4	38.86 ± 0.26
24	Zn(ox) <sub>2</sub> (c)	H <sub>2</sub> SO <sub>4</sub> ·53.54H <sub>2</sub> O	F <sub>9</sub>	4	-74.50 ± 0.17

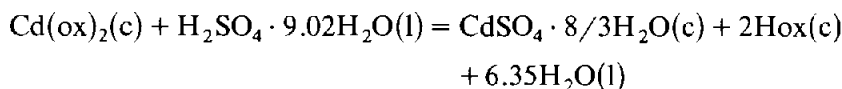


$$\Delta_r H_m^0(\text{Cu(ox)}_2)(\text{kJ mol}^{-1}) = \Delta_{22}H_m - \Delta_{21}H_m - 2\Delta_{18}H_m - 48.54\Delta_{17}H_m \\ = -30.49 \pm 0.80$$

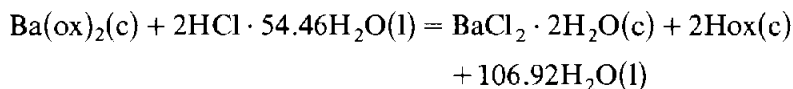


$$\Delta_r H_m^0(\text{Zn(ox)}_2)(\text{kJ mol}^{-1}) = \Delta_{24}H_m - \Delta_{23}H_m - 2\Delta_{18}H_m - 46.54\Delta_{17}H_m \\ = -100.14 \pm 0.82$$

Table 5 lists the enthalpies of solution and reaction required for determining the enthalpies of the thermochemical reactions when using the other acids as solvent: the enthalpies of solution of water in these acids were calculated. The standard enthalpies of reaction derived from the data in Table 5 were:



$$\Delta_r H_m^0(\text{Cd(ox)}_2)(\text{kJ mol}^{-1}) = \Delta_{28}H_m - \Delta_{27}H_m - 2\Delta_{26}H_m - 6.35\Delta_{25}H_m \\ = -57.90 \pm 1.01$$

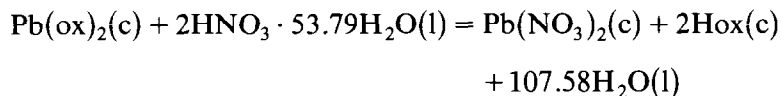


$$\Delta_r H_m^0(\text{Ba(ox)}_2)(\text{kJ mol}^{-1}) = \Delta_{32}H_m - \Delta_{31}H_m - 2\Delta_{30}H_m - 106.92\Delta_{29}H_m \\ = -115.72 \pm 1.26$$

TABLE 5

Molar enthalpies of solution and reaction at 298.15 K

<i>i</i>	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m$ (kJ mol <sup>-1</sup> )
25	H <sub>2</sub> O(l)	H <sub>2</sub> SO <sub>4</sub> · 9.02H <sub>2</sub> O	A <sub>7</sub>		-1.14 ± 0.01
26	Hox(c)	A <sub>7</sub>	A <sub>8</sub>	4	-17.42 ± 0.49
27	CdSO <sub>4</sub> · 8/3H <sub>2</sub> O(c)	A <sub>8</sub>	F <sub>10</sub>	4	13.82 ± 0.19
28	Cd(ox) <sub>2</sub> (c)	H <sub>2</sub> SO <sub>4</sub> · 9.02H <sub>2</sub> O	F <sub>10</sub>	4	-86.16 ± 0.15
29	H <sub>2</sub> O(l)	HCl · 54.46H <sub>2</sub> O	A <sub>9</sub>		-0.02 ± 0.01
30	Hox(c)	A <sub>9</sub>	A <sub>10</sub>	4	-4.95 ± 0.19
31	BaCl <sub>2</sub> · 2H <sub>2</sub> O(c)	A <sub>10</sub>	F <sub>11</sub>	6	20.87 ± 0.17
32	Ba(ox) <sub>2</sub> (c)	HCl · 54.46H <sub>2</sub> O	F <sub>11</sub>	4	-106.89 ± 0.51
33	H <sub>2</sub> O(l)	HNO <sub>3</sub> · 53.79H <sub>2</sub> O	A <sub>11</sub>		-0.00 ± 0.01
34	Hox(c)	A <sub>11</sub>	A <sub>12</sub>	4	-6.47 ± 0.11
35	Pb(NO <sub>3</sub> ) <sub>2</sub> (c)	A <sub>12</sub>	F <sub>12</sub>	4	22.55 ± 0.41
36	Pb(ox) <sub>2</sub> (c)	HNO <sub>3</sub> · 53.79H <sub>2</sub> O	F <sub>12</sub>	4	-41.19 ± 0.17



$$\Delta_f H_m^0(\text{Pb(ox)}_2)(\text{kJ mol}^{-1}) = \Delta_{36} H_m - \Delta_{35} H_m - 2\Delta_{34} H_m - 107.58\Delta_{33} H_m \\ = -50.80 \pm 1.18$$

The Russian compilation of the thermochemical data [10] was preferred to the NBS compilation [8] as the source of the auxiliary data needed to derive the enthalpies of formation because most of the Russian compilation is more recent than the NBS, and it gives the experimental uncertainties and the original references from which the values were derived. With the following auxiliary data at 298.15 K for  $\Delta_f H_m^0/(\text{kJ mol}^{-1})$ : HCl in  $7.97\text{H}_2\text{O}(\text{l})$ ,  $-160.00 \pm 0.01$ ; HCl in  $10.01\text{H}_2\text{O}(\text{l})$ ,  $-161.32 \pm 0.01$ ; HCl in  $54.46\text{H}_2\text{O}(\text{l})$ ,  $-165.47 \pm 0.01$ ;  $\text{H}_2\text{SO}_4$  in  $9.02\text{H}_2\text{O}(\text{l})$ ,  $-879.44 \pm 0.30$ ;  $\text{H}_2\text{SO}_4$  in  $53.54\text{H}_2\text{O}(\text{l})$ ,  $-886.89 \pm 0.30$ ;  $\text{HNO}_3$  in  $53.79\text{H}_2\text{O}(\text{l})$ ,  $-206.86 \pm 0.47$ ;  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{c})$ ,  $-2498.85 \pm 0.84$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}(\text{c})$ ,  $-1396.62 \pm 1.26$ ;  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{c})$ ,  $-2628.81 \pm 2.09$ ;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{c})$ ,  $-1446.41 \pm 2.09$ ;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}(\text{c})$ ,  $-1687.41 \pm 0.63$ ;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{c})$ ,  $-2113.76 \pm 2.09$ ;  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}(\text{c})$ ,  $-2107.06 \pm 5.02$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{c})$ ,  $-2279.36 \pm 1.05$ ;  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{c})$ ,  $-3078.53 \pm 1.46$ ;  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}(\text{c})$ ,  $-1730.42 \pm 0.84$ ;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{c})$ ,  $-3015.83 \pm 0.84$ ;  $\text{Pb(NO}_3)_2(\text{c})$ ,  $-452.58 \pm 1.17$ ;  $\text{Hox}(\text{c})$  [11],  $-87.45 \pm 1.26$ ;  $\text{H}_2\text{O}(\text{l})$  [12],  $-285.83 \pm 0.04$ ; and the enthalpies of the thermochemical reactions; the standard enthalpies of formation of the crystalline solids were derived and are listed in Table 6. Table 6 also lists the enthalpies of sublimation: those in parentheses were estimated as the mean of the measured values [3]. The enthalpies of formation of these complexes in the gaseous state are also listed.

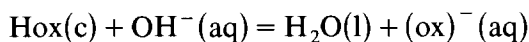
TABLE 6

Standard molar enthalpies of formation in the crystalline and gaseous states at 298.15 K

	$\Delta_f H_m^0(\text{c})$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{sub}} H_m^0$ (kJ mol <sup>-1</sup> )	$\Delta_f H_m^0(\text{g})$ (kJ mol <sup>-1</sup> )
Mg(ox) <sub>2</sub>	-527.7 ± 2.7	(180 ± 15)	-348 ± 16
Ca(ox) <sub>2</sub>	-606.2 ± 2.9	(180 ± 15)	-426 ± 16
Sr(ox) <sub>2</sub>	-652.4 ± 3.3	(180 ± 15)	-472 ± 16
Ba(ox) <sub>2</sub>	-603.0 ± 3.5	(180 ± 15)	-423 ± 16
Mn(ox) <sub>2</sub>	-316.0 ± 2.6	226 ± 14	-90 ± 15
Fe(ox) <sub>2</sub>	-192.9 ± 2.8	(180 ± 15)	-13 ± 16
Co(ox) <sub>2</sub>	-208.3 ± 3.3	200 ± 10	-8 ± 11
Ni(Ox) <sub>2</sub>	-205.9 ± 5.7	139 ± 6	-67 ± 8
Cu(ox) <sub>2</sub>	-107.7 ± 2.9	170 ± 3	62 ± 4
Zn(ox) <sub>2</sub>	-265.6 ± 3.0	178 ± 6	-88 ± 7
Cd(ox) <sub>2</sub>	-205.8 ± 2.9	154 ± 22	-52 ± 23
Pb(ox) <sub>2</sub>	-163.0 ± 3.2	(180 ± 15)	17 ± 16

## DISCUSSION

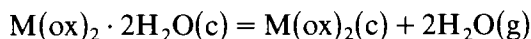
Although Charles [2] did not investigate the degree of hydration of the oxine precipitates formed in his calorimeter, these complexes are generally precipitated from aqueous solutions as  $M(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c})$ . We have measured the enthalpy of solution of  $\text{Hox}(\text{c})$  in  $\text{NaOH}$  ( $0.03 \text{ mol l}^{-1}$ ), the concentration used by Charles, and obtained  $\Delta H_{\text{m}}(\text{solution}) (\text{kJ mol}^{-1}) = -3.84 \pm 0.02$ . This is the enthalpy of the reaction



and as  $\Delta_f H_{\text{m}}^0(\text{OH}^-, \text{aq}) (\text{kJ mol}^{-1}) = -230.0 \pm 0.1$  [12], then  $\Delta_f H_{\text{m}}^0(\text{ox}^-, \text{aq}) (\text{kJ mol}^{-1}) = -35.5 \pm 0.2$ . Assuming the reactions studied by Charles to be



then  $\Delta_f H_{\text{m}}^0(\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}, \text{c})$  may be derived, together with the enthalpy of dissociation



requiring  $\Delta_f H_{\text{m}}^0(\text{H}_2\text{O}, \text{g}) = -241.81 \pm 0.04$  [12]. Table 7 lists the values reported by Charles for  $\Delta H_{\text{m}}$  (precipitation),  $\Delta_f H_{\text{m}}^0(\text{M}^{2+}, \text{aq})$  [10],  $\Delta_f H_{\text{m}}^0(\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}, \text{c})$  and  $\Delta H_{\text{m}}$ (dissociation).

Inspection of the  $\Delta H_{\text{m}}$  (dissociation) values shows the assumption that the precipitates were  $\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c})$  is justified, except possibly for the Sr complex. For the complexes of Mg, Ca, Ba and Zn the dissociation enthalpy per water molecule is about  $65 \text{ kJ mol}^{-1}$ , for Co, Ni and Cu it is about  $45 \text{ kJ mol}^{-1}$  and for Pb it is about  $35 \text{ kJ mol}^{-1}$ . Merrit et al. [13] have shown that the  $\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c})$  complexes of Co, Ni, Cu and Zn are isomorphous; the metal and bonded ligand atoms are planar whilst the two  $\text{H}_2\text{O}$  molecules are in the axial positions of a distorted octahedron. The dissociation enthalpies

TABLE 7

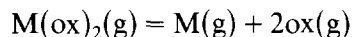
Enthalpies of formation of  $\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c})$  and of the dissociation  $\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c}) = \text{M}(\text{ox})_2(\text{c}) + 2\text{H}_2\text{O}(\text{g})$

M	$\Delta H_{\text{m}}(\text{precipitation})$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H_{\text{m}}^0(\text{M}^{2+}, \text{aq})$ ( $\text{kJ mol}^{-1}$ )	$\Delta_f H_{\text{m}}^0(\text{M}(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{c}))$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_{\text{m}}(\text{diss.})$ ( $\text{kJ mol}^{-1}$ )
Mg	$-34.7 \pm 1.0$	$-468.1 \pm 0.6$	$-1145.5 \pm 1.3$	$134.2 \pm 3.0$
Ca	$-39.3 \pm 1.0$	$-543.1 \pm 0.8$	$-1225.7 \pm 1.3$	$135.9 \pm 3.2$
Sr	$-19.2 \pm 1.0$	$-551.5 \pm 0.6$	$-1213.4 \pm 1.3$	$77.4 \pm 3.5$
Ba	$-37.2 \pm 1.0$	$-536.6 \pm 2.1$	$-1216.5 \pm 1.3$	$129.9 \pm 4.2$
Mn	$-68.6 \pm 1.4$	$-220.3 \pm 0.6$	$-931.6 \pm 1.5$	$132.0 \pm 3.0$
Co	$-81.6 \pm 1.8$	$-56.6 \pm 1.9$	$-780.9 \pm 2.6$	$89.0 \pm 4.2$
Ni	$-88.3 \pm 1.9$	$-53.1 \pm 2.5$	$-784.1 \pm 3.1$	$94.6 \pm 6.5$
Cu	$-107.5 \pm 2.1$	$66.9 \pm 0.9$	$-683.3 \pm 2.3$	$92.0 \pm 3.7$
Zn	$-81.2 \pm 1.7$	$-153.6 \pm 1.4$	$-877.5 \pm 2.2$	$128.3 \pm 3.7$
Pb	$-78.2 \pm 1.7$	$-0.9 \pm 0.9$	$-721.8 \pm 1.9$	$75.2 \pm 3.7$



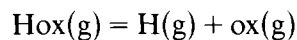
to remove  $\text{H}_2\text{O}$  from  $\text{Ni}(\text{glycinate})_2 \cdot 2\text{H}_2\text{O}(\text{c})$  and  $\text{Cu}(\text{glycinate})_2 \cdot \text{H}_2\text{O}(\text{c})$ , where the  $\text{H}_2\text{O}$  molecules are also in axial positions, have been reported [14] as 54.8 and 56.0  $\text{kJ mol}^{-1}$ , respectively, slightly greater than the values for the corresponding oxine derivatives.

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



$$\bar{D}(\text{M-ox}) = \frac{1}{2} [\Delta_f H_m^0(\text{M}, \text{g}) - \Delta_f H_m^0(\text{M}(\text{ox})_2, \text{g})] + \Delta_f H_m^0(\text{ox}, \text{g})$$

The dissociation enthalpy of the (O–H) bond in Hox is the enthalpy of the dissociation



$$D(\text{H-ox}) = \Delta_f H_m^0(\text{H}, \text{g}) - \Delta_f H_m^0(\text{Hox}, \text{g}) + \Delta_f H_m^0(\text{ox}, \text{g})$$

Hence

$$\begin{aligned} \bar{D}(\text{M-ox}) - D(\text{H-ox}) &= \frac{1}{2} [\Delta_f H_m^0(\text{M}, \text{g}) - \Delta_f H_m^0(\text{M}(\text{ox})_2, \text{g})] - \Delta_f H_m^0(\text{H}, \text{g}) \\ &\quad + \Delta_f H_m^0(\text{Hox}, \text{g}) \end{aligned}$$

To calculate  $\bar{D}(\text{M-ox}) - D(\text{H-ox})$ ,  $\Delta_f H_m^0(\text{H}, \text{g})$  ( $\text{kJ mol}^{-1}$ ) = 218.00  $\pm$  0.01 [12],  $\Delta_f H_m^0(\text{Hox}, \text{g})$  ( $\text{kJ mol}^{-1}$ ) = 21.3  $\pm$  2.1 [11] and the  $\Delta_f H_m^0(\text{M}, \text{g})$  values given by Pilcher and Skinner [15] were used. The values are listed in Table 8.  $\bar{D}(\text{M-ox}) - D(\text{H-ox})$  shows a large increase in the strength of the binding of the ligand to the metal relative to hydrogen for the alkaline earth metals, smaller values for the series Mn to Zn with a peak at Ni and a marked fall for Cu and Zn. A peak in metal–ligand binding energy at Ni has been observed for complexes of the type  $\text{M}(\text{pyridine})_2\text{Cl}_2$  for those elements where the ligand binding is through an N atom [16]. Table 8 also compares the corresponding values, where available, for the 2,4-pentanedionate complexes: the values were derived from the data reviewed by Ribeiro da Silva [17]. Relative to binding with H, the 2,4-pentanedionate ligand is more weakly bound to metals than is the oxine ligand by approximately 30  $\text{kJ mol}^{-1}$ , and the values do not show a peak at Ni.

The only other complexes with binding to the metal through oxygen and nitrogen for which experimental data are available are the glycinate complexes of Cu and Ni [14]. With estimated enthalpies of sublimation,  $\bar{D}(\text{M-gly}) - D(\text{H-gly})$  for Ni = 26, and for Cu = –49,  $\text{kJ mol}^{-1}$  in accord with the values for oxine.

Although it may be permissible to write

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

there is no unambiguous way of apportioning  $\bar{D}(\text{M-ox})$  between  $\bar{D}(\text{M-O})$  and  $\bar{D}(\text{M-N})$  and there would be little value in attempting to do so because these bonds occur together and must interact. It would, however, be reasonable to assume  $D(\text{H-ox}) = D(\text{O-H})$  in phenol (363  $\pm$  9  $\text{kJ mol}^{-1}$  [18]) allowing the calculation of the  $\bar{D}(\text{M-ox})$  values listed in Table 8.

TABLE 8

 $\bar{D}(\text{M-L}) - D(\text{H-L})$  in  $\text{ML}_2$  complexes

	$\Delta_f H_m^0(\text{M, g})$ (kJ mol <sup>-1</sup> )	$\bar{D}(\text{M-L}) - D(\text{H-L})$ (kJ mol <sup>-1</sup> )		$\bar{D}(\text{M-ox})$ (kJ mol <sup>-1</sup> )
		L = ox	L = pd	
Mg	147.1 ± 0.8	51 ± 8		414 ± 12
Ca	177.8 ± 0.8	105 ± 8	96 ± 6	468 ± 12
Sr	163.6 ± 4.2	121 ± 9		484 ± 13
Ba	177.8 ± 4.2	104 ± 8		467 ± 12
Mn	279.1 ± 5.5	-12 ± 8	10 ± 4	351 ± 12
Fe	416.3 ± 4.2	18 ± 8		381 ± 12
Co	425.1 ± 6.2	20 ± 7	-14 ± 3	383 ± 11
Ni	430.1 ± 6.0	52 ± 5	-14 ± 3	415 ± 10
Cu	337.6 ± 1.2	-59 ± 3	-84 ± 2	304 ± 10
Zn	130.4 ± 0.2	-88 ± 3	-111 ± 5	275 ± 10
Cd	110.0 ± 0.4	-116 ± 12		247 ± 15
Pb	195.2 ± 0.8	-108 ± 8		255 ± 12

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