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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), $\Delta_f H^0_m(M(ox)_2(c))$ (kJ mol^{-1}): Mg(ox)$_2$, -527.7 ± 2.7; Ca(ox)$_2$, -606.2 ± 2.9; Sr(ox)$_2$, -652.4 ± 3.3; Ba(ox)$_2$, -603.0 ± 3.5; Mn(ox)$_2$, -316.0 ± 2.6; Fe(ox)$_2$, -192.9 ± 2.8; Co(ox)$_2$, -208.3 ± 3.3; Ni(ox)$_2$, -205.9 ± 5.7; Cu(ox)$_2$, -107.7 ± 2.9; Zn(ox)$_2$, -265.6 ± 3.0; Cd(ox)$_2$, -205.8 ± 2.9; Pb(ox)$_2$, -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)$_2$ 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

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

EXPERIMENTAL

Materials

BDH Analar grade 8-hydroxyquinoline was used. The $M(ox)_2$ 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^3 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 ΔT_{ad} by the Regnault–Pfaundler method [6]. ΔT_{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 Ω) 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 Ω 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 ± 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^{-1}) at 298.15 K. The result, $\Delta_{sol}H_m$ (kJ mol^{-1}) $= -29.771 \pm 0.029$, is in agreement with the value of Kilday and Prosen [7] (-29.770 ± 0.032).

RESULTS

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

$$M(ox)_2(c) + 2HX \cdot nH_2O(l) = MX_2 \cdot mH_2O(c) + 2Hox(c) + (2n - m)H_2O(l)$$

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 ($HX \cdot nH_2O$) 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 $M(ox)_2$ and on the composition and solubility of the salt $MX_2 \cdot mH_2O$. As an example, the detailed calorimetric results for determining the enthalpy of the thermochemical reaction for $Co(ox)_2$ are given in Table 1, where ϵ 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 $Co(ox)_2$ at 298.15 K

m (g)	ϵ ($J K^{-1}$)	ΔT_{ad} (K)	Δh ($J g^{-1}$)
$Co(ox)_2(c) + 2HCl \cdot 10.01H_2O(l)$ = 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	
$Hox(c) + HCl \cdot 10.01H_2O(l)$ = 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	
$CoCl_2 \cdot 6H_2O(c)$ + solution A_2 = 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, $HCl \cdot 10.01H_2O(l)$: the enthalpy of solution of water in $HCl \cdot 10.01H_2O(l)$ 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:

$$Co(ox)_2(c) + 2HCl \cdot 10.01H_2O(l) = CoCl_2 \cdot 6H_2O(c) + 2Hox(c) + 14.02H_2O(l)$$

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

$$Ni(ox)_2(c) + 2HCl \cdot 10.01H_2O(l) = NiCl_2 \cdot 6H_2O(c) + 2Hox(c) + 14.02H_2O(l)$$

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

$$Mn(ox)_2(c) + 2HCl \cdot 10.01H_2O(l) = MnCl_2 \cdot 4H_2O(c) + 2Hox(c) + 16.02H_2O(l)$$

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

Table 3 lists the molar enthalpies of solution and reaction required for determining the enthalpies of the thermochemical reactions when using the solvent $HCl \cdot 7.97H_2O(l)$: the enthalpy of solution of water in this solvent was calculated. The standard enthalpies of reaction derived from the data in Table 3 were:

$$Mg(ox)_2(c) + 2HCl \cdot 7.97H_2O(l) = MgCl_2 \cdot 6H_2O(c) + 2Hox(c) + 9.94H_2O(l)$$

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

TABLE 2

Molar enthalpies of solution and reaction at 298.15 K in $HCl \cdot 10.01H_2O(l)$

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol^{-1})
1	$H_2O(l)$	$HCl \cdot 10.01H_2O$	A_1		-0.54 ± 0.02
2	Hox(c)	A_1	A_2	4	-15.43 ± 0.08
3	$CoCl_2 \cdot 6H_2O(c)$	A_2	F_1	4	27.82 ± 0.13
4	$Co(ox)_2(c)$	$HCl \cdot 10.01H_2O$	F_1	5	-53.36 ± 0.22
5	$NiCl_2 \cdot 6H_2O(c)$	A_2	F_2	4	23.44 ± 0.49
6	$Ni(ox)_2(c)$	$HCl \cdot 10.01H_2O$	F_2	4	-53.40 ± 0.05
7	$MnCl_2 \cdot 4H_2O(c)$	A_2	F_3	4	13.65 ± 0.25
8	$Mn(ox)_2(c)$	$HCl \cdot 10.01H_2O$	F_3	4	-106.23 ± 0.22

TABLE 3

Molar enthalpies of solution and reaction at 298.15 K in $HCl \cdot 7.97H_2O(l)$

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol^{-1})
9	$H_2O(l)$	$HCl \cdot 7.97H_2O$	A_3		-0.66 ± 0.02
10	Hox(c)	A_3	A_4	4	-18.24 ± 0.14
11	$MgCl_2 \cdot 6H_2O(c)$	A_4	F_4	4	2.66 ± 0.20
12	$Mg(ox)_2(c)$	$HCl \cdot 7.97H_2O$	F_4	4	-151.44 ± 0.09
13	$CaCl_2 \cdot 2H_2O(c)$	A_4	F_5	4	-27.12 ± 0.15
14	$Ca(ox)_2(c)$	$HCl \cdot 7.97H_2O$	F_5	4	-146.48 ± 0.10
15	$SrCl_2 \cdot 6H_2O(c)$	A_4	F_6	4	43.23 ± 0.04
16	$Sr(ox)_2(c)$	$HCl \cdot 7.97H_2O$	F_6	4	-116.13 ± 0.15

$$Ca(ox)_2(c) + 2HCl \cdot 7.97H_2O(l) = CaCl_2 \cdot 2H_2O(c) + 2Hox(c) + 13.94H_2O(l)$$

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

$$Sr(ox)_2(c) + 2HCl \cdot 7.97H_2O(l) = SrCl_2 \cdot 6H_2O(c) + 2Hox(c) + 9.94H_2O(l)$$

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

Table 4 lists the molar enthalpies of solution and reaction required for determining the enthalpies of the thermochemical reactions when using $H_2SO_4 \cdot 53.54H_2O(l)$ 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:

$$\begin{aligned}Fe(ox)_2(c) + H_2SO_4 \cdot 53.54H_2O(l) = FeSO_4 \cdot 7H_2O(c) + 2Hox(c)\\ + 46.54H_2O(l)\end{aligned}$$

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

TABLE 4

Molar enthalpies of solution and reaction at 298.15 K in $H_2SO_4 \cdot 53.54H_2O(l)$

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m$ (kJ mol^{-1})
17	$H_2O(l)$	$H_2SO_4 \cdot 53.54H_2O$	A_5		-0.03 ± 0.01
18	Hox(c)	A_5	A_6	4	-5.91 ± 0.30
19	$FeSO_4 \cdot 7H_2O(c)$	A_6	F_7	3	41.59 ± 0.52
20	$Fe(ox)_2(c)$	$H_2SO_4 \cdot 53.54H_2O$	F_7	2	-81.81 ± 0.08
21	$CuSO_4 \cdot 5H_2O(c)$	A_6	F_8	3	22.59 ± 0.14
22	$Cu(ox)_2(c)$	$H_2SO_4 \cdot 53.54H_2O$	F_8	4	-21.18 ± 0.15
23	$ZnSO_4 \cdot 7H_2O(c)$	A_6	F_9	4	38.86 ± 0.26
24	$Zn(ox)_2(c)$	$H_2SO_4 \cdot 53.54H_2O$	F_9	4	-74.50 ± 0.17

$$\mathrm{Cu(ox)_2(c) + H_2SO_4 \cdot 53.54H_2O(l) = CuSO_4 \cdot 5H_2O(c) + 2Hox(c)} \\ \mathrm{+48.54H_2O(l)}$$

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

$$\mathrm{Zn(ox)_2(c) + H_2SO_4 \cdot 53.54H_2O(l) = ZnSO_4 \cdot 7H_2O(c) + 2Hox(c)} \\ \mathrm{+46.54H_2O(l)}$$

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

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:

$$\mathrm{Cd(ox)_2(c) + H_2SO_4 \cdot 9.02H_2O(l) = CdSO_4 \cdot 8/3H_2O(c) + 2Hox(c)} \\ \mathrm{+6.35H_2O(l)}$$

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

$$\mathrm{Ba(ox)_2(c) + 2HCl \cdot 54.46H_2O(l) = BaCl_2 \cdot 2H_2O(c) + 2Hox(c)} \\ \mathrm{+106.92H_2O(l)}$$

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

TABLE 5

Molar enthalpies of solution and reaction at 298.15 K

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_r H_m$ (kJ mol^{-1})
25	$H_2O(l)$	$H_2SO_4 \cdot 9.02H_2O$	A_7		-1.14 ± 0.01
26	Hox(c)	A_7	A_8	4	-17.42 ± 0.49
27	$CdSO_4 \cdot 8/3H_2O(c)$	A_8	F_{10}	4	13.82 ± 0.19
28	$Cd(ox)_2(c)$	$H_2SO_4 \cdot 9.02H_2O$	F_{10}	4	-86.16 ± 0.15
29	$H_2O(l)$	$HCl \cdot 54.46H_2O$	A_9		-0.02 ± 0.01
30	Hox(c)	A_9	A_{10}	4	-4.95 ± 0.19
31	$BaCl_2 \cdot 2H_2O(c)$	A_{10}	F_{11}	6	20.87 ± 0.17
32	$Ba(ox)_2(c)$	$HCl \cdot 54.46H_2O$	F_{11}	4	-106.89 ± 0.51
33	$H_2O(l)$	$HNO_3 \cdot 53.79H_2O$	A_{11}		-0.00 ± 0.01
34	Hox(c)	A_{11}	A_{12}	4	-6.47 ± 0.11
35	$Pb(NO_3)_2(c)$	A_{12}	F_{12}	4	22.55 ± 0.41
36	$Pb(ox)_2(c)$	$HNO_3 \cdot 53.79H_2O$	F_{12}	4	-41.19 ± 0.17

$$\mathrm{Pb(ox)_2(c) + 2HNO_3 \cdot 53.79H_2O(l) = Pb(NO_3)_2(c) + 2Hox(c)} \\ \mathrm{+ 107.58H_2O(l)}$$

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

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 $\Delta_f H^0_m/(\mathrm{kJ\ mol^{-1}})$: HCl in $7.97H_2O(l)$, -160.00 ± 0.01; HCl in $10.01H_2O(l)$, -161.32 ± 0.01; HCl in $54.46H_2O(l)$, -165.47 ± 0.01; H_2SO_4 in $9.02H_2O(l)$, -879.44 ± 0.30; H_2SO_4 in $53.54H_2O(l)$, -886.89 ± 0.30; HNO_3 in $53.79H_2O(l)$, -206.86 ± 0.47; $MgCl_2 \cdot 6H_2O(c)$, -2498.85 ± 0.84, $CaCl_2 \cdot 2H_2O(c)$, -1396.62 ± 1.26; $SrCl_2 \cdot 6H_2O(c)$, -2628.81 ± 2.09; $BaCl_2 \cdot 2H_2O(c)$, -1446.41 ± 2.09; $MnCl_2 \cdot 4H_2O(c)$, -1687.41 ± 0.63; $CoCl_2 \cdot 6H_2O(c)$, -2113.76 ± 2.09; $NiCl_2 \cdot 6H_2O(c)$, -2107.06 ± 5.02; $CuSO_4 \cdot 5H_2O(c)$, -2279.36 ± 1.05; $ZnSO_4 \cdot 7H_2O(c)$, -3078.53 ± 1.46; $CdSO_4 \cdot 8/3H_2O(c)$, -1730.42 ± 0.84; $FeSO_4 \cdot 7H_2O(c)$, -3015.83 ± 0.84; $Pb(NO_3)_2(c)$, -452.58 ± 1.17; Hox(c) [11], -87.45 ± 1.26; $H_2O(l)$ [12], -285.83 ± 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

	$\Delta_f H^0_m(c)$ (kJ mol^{-1})	$\Delta_{sub} H^0_m$ (kJ mol^{-1})	$\Delta_f H^0_m(g)$ (kJ mol^{-1})
$Mg(ox)_2$	-527.7 ± 2.7	(180 ± 15)	-348 ± 16
$Ca(ox)_2$	-606.2 ± 2.9	(180 ± 15)	-426 ± 16
$Sr(ox)_2$	-652.4 ± 3.3	(180 ± 15)	-472 ± 16
$Ba(ox)_2$	-603.0 ± 3.5	(180 ± 15)	-423 ± 16
$Mn(ox)_2$	-316.0 ± 2.6	226 ± 14	-90 ± 15
$Fe(ox)_2$	-192.9 ± 2.8	(180 ± 15)	-13 ± 16
$Co(ox)_2$	-208.3 ± 3.3	200 ± 10	-8 ± 11
$Ni(Ox)_2$	-205.9 ± 5.7	139 ± 6	-67 ± 8
$Cu(ox)_2$	-107.7 ± 2.9	170 ± 3	62 ± 4
$Zn(ox)_2$	-265.6 ± 3.0	178 ± 6	-88 ± 7
$Cd(ox)_2$	-205.8 ± 2.9	154 ± 22	-52 ± 23
$Pb(ox)_2$	-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 $M(ox)_2 \cdot 2H_2O(c)$. We have measured the enthalpy of solution of Hox(c) in NaOH (0.03 mol l^{-1}), the concentration used by Charles, and obtained ΔH_m(solution) (kJ mol^{-1}) = -3.84 ± 0.02. This is the enthalpy of the reaction

$$Hox(c) + OH^-(aq) = H_2O(l) + (ox)^-(aq)$$

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

$$M^{2+}(aq) + 2(ox^-, aq) + 2H_2O(l) = M(ox)_2 \cdot 2H_2O(c)$$

then $\Delta_f H_m^0(M(ox)_2 \cdot 2H_2O, c)$ may be derived, together with the enthalpy of dissociation

$$M(ox)_2 \cdot 2H_2O(c) = M(ox)_2(c) + 2H_2O(g)$$

requiring $\Delta_f H_m^0(H_2O, g) = -241.81 \pm 0.04$ [12]. Table 7 lists the values reported by Charles for ΔH_m (precipitation), $\Delta_f H_m^0(M^{2+}, aq)$ [10], $\Delta_f H_m^0(M(ox)_2 \cdot 2H_2O, c)$ and ΔH_m(dissociation).

Inspection of the ΔH_m (dissociation) values shows the assumption that the precipitates were $M(ox)_2 \cdot 2H_2O(c)$ 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 kJ mol^{-1}, for Co, Ni and Cu it is about 45 kJ mol^{-1} and for Pb it is about 35 kJ mol^{-1}. Merrit et al. [13] have shown that the $M(ox)_2 \cdot 2H_2O(c)$ complexes of Co, Ni, Cu and Zn are isomorphous; the metal and bonded ligand atoms are planar whilst the two H_2O molecules are in the axial positions of a distorted octahedron. The dissociation enthalpies

TABLE 7

Enthalpies of formation of $M(ox)_2 \cdot 2H_2O(c)$ and of the dissociation $M(ox)_2 \cdot 2H_2O(c) = M(ox)_2(c) + 2H_2O(g)$

M	ΔH_m(precipitation) (kJ mol^{-1})	$\Delta_f H_m^0(M^{2+}, aq)$ (kJ mol^{-1})	$\Delta_f H_m^0(M(ox)_2 2H_2O(c))$ (kJ mol^{-1})	ΔH_m(diss.) (kJ mol^{-1})
Mg	-34.7 ± 1.0	-468.1 ± 0.6	-1145.5 ± 1.3	134.2 ± 3.0
Ca	-39.3 ± 1.0	-543.1 ± 0.8	-1225.7 ± 1.3	135.9 ± 3.2
Sr	-19.2 ± 1.0	-551.5 ± 0.6	-1213.4 ± 1.3	77.4 ± 3.5
Ba	-37.2 ± 1.0	-536.6 ± 2.1	-1216.5 ± 1.3	129.9 ± 4.2
Mn	-68.6 ± 1.4	-220.3 ± 0.6	-931.6 ± 1.5	132.0 ± 3.0
Co	-81.6 ± 1.8	-56.6 ± 1.9	-780.9 ± 2.6	89.0 ± 4.2
Ni	-88.3 ± 1.9	-53.1 ± 2.5	-784.1 ± 3.1	94.6 ± 6.5
Cu	-107.5 ± 2.1	66.9 ± 0.9	-683.3 ± 2.3	92.0 ± 3.7
Zn	-81.2 ± 1.7	-153.6 ± 1.4	-877.5 ± 2.2	128.3 ± 3.7
Pb	-78.2 ± 1.7	-0.9 ± 0.9	-721.8 ± 1.9	75.2 ± 3.7

to remove H_2O from Ni(glycinate)$_2 \cdot 2H_2O$(c) and Cu(glycinate)$_2 \cdot H_2O$(c), where the H_2O molecules are also in axial positions, have been reported [14] as 54.8 and 56.0 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

$$\mathrm{M(ox)_2(g) = M(g) + 2ox(g)}$$

$$\bar{D}(\mathrm{M{-}ox}) = \tfrac{1}{2}\left[\Delta_f H^0_m(\mathrm{M, g}) - \Delta_f H^0_m(\mathrm{M(ox)_2, g})\right] + \Delta_f H^0_m(\mathrm{ox, g})$$

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

$$\mathrm{Hox(g) = H(g) + ox(g)}$$

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

Hence

$$\bar{D}(\mathrm{M{-}ox}) - D(\mathrm{H{-}ox}) = \tfrac{1}{2}\left[\Delta_f H^0_m(\mathrm{M, g}) - \Delta_f H^0_m(\mathrm{M(ox)_2, g})\right] - \Delta_f H^0_m(\mathrm{H, g}) + \Delta_f H^0_m(\mathrm{Hox, g})$$

To calculate $\bar{D}$(M–ox) – D(H–ox), $\Delta_f H^0_m$(H, g) (kJ mol^{-1}) = 218.00 ± 0.01 [12], $\Delta_f H^0_m$(Hox, g) (kJ mol^{-1}) = 21.3 ± 2.1 [11] and the $\Delta_f H^0_m$(M, g) values given by Pilcher and Skinner [15] were used. The values are listed in Table 8. $\bar{D}$(M–ox) – D(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 M(pyridine)$_2$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 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 glycinates of Cu and Ni [14]. With estimated enthalpies of sublimation, $\bar{D}$(M–gly) – D(H–gly) for Ni = 26, and for Cu = –49, kJ mol^{-1} in accord with the values for oxine.

Although it may be permissible to write

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

there is no unambiguous way of apportioning $\bar{D}$(M–ox) between $\bar{D}$(M–O) and $\bar{D}$(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(H–ox) = D(O–H) in phenol (363 ± 9 kJ mol^{-1} [18]) allowing the calculation of the $\bar{D}$(M–ox) values listed in Table 8.

TABLE 8

$\bar{D}$(M–L)$-$ D(H–L) in ML_2 complexes

	$\Delta_f H_m^0$(M, g) (kJ mol^{-1})	$\bar{D}$(M–L)$-$ D(H–L) (kJ mol^{-1})		$\bar{D}$(M–ox) (kJ mol^{-1})
		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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