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STANDARD ENTHALPIES OF FORMATION OF BIS(FLUORO-SUBSTITUTED PENTANE-2,4-DIONATO) HYDRATES OF Mn(II), Co(II) and Ni(II): THE MEAN (M–O) BOND DISSOCIATION ENTHALPIES *

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ABSTRACT

The following standard molar enthalpies of formation of the crystalline solids were determined, at 298.15 K, by solution-reaction calorimetry.

$\Delta_f H_m^\ominus(\mathrm{Mn(TFAC)_2 \cdot H_2O, cr}) = -2609 \pm 10\ \mathrm{kJ\ mol^{-1}}$

$\Delta_f H_m^\ominus(\mathrm{Mn(HFAC)_2 \cdot 2H_2O, cr}) = -4163 \pm 10\ \mathrm{kJ\ mol^{-1}}$

$\Delta_f H_m^\ominus(\mathrm{Co(HFAC)_2 \cdot 2H_2O, cr}) = -4009 \pm 10\ \mathrm{kJ\ mol^{-1}}$

$\Delta_f H_m^\ominus(\mathrm{Ni(HFAC)_2 \cdot 2H_2O, cr}) = -4003 \pm 10\ \mathrm{kJ\ mol^{-1}}$

The standard enthalpies of the decomposition processes

$\mathrm{M(HFAC)_2 \cdot 2H_2O(cr) = M(HFAC)_2(g) + 2H_2O(g)}$

were measured by high-temperature microcalorimetry. From the enthalpies of formation of the gaseous complexes, the average molar bond-dissociation enthalpies, $\langle D \rangle$(M–O), were derived. (TFAC, 1,1,1-trifluoropentane-2,4-dionato; HFAC, 1,1,1,5,5,5-hexafluoropentane-2,4-dionato)

INTRODUCTION

Several thermochemical studies of metal β-diketonate complexes [1] have investigated the effect of structural changes in the ligand upon the mean molar metal–oxygen bond-dissociation enthalpy. In this work, the standard molar enthalpies of formation of four bis(fluoro-substituted pentane-2,4-dionato)metal(II) complexes were determined using the solution-reaction calorimetric method, to investigate the effect of the $-\mathrm{CF_3}$ groups in the ligand upon the (M–O) dissociation enthalpy.

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

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EXPERIMENTAL

Materials

1,1,1-Trifluoro-2,4-pentanedione (HTFAC) (Koch-Light Laboratories Ltd.), was purified by repeated fractional distillation. Purity was assessed as better than 99.9 mol.% by g.l.c. using two different columns. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (HHFAC) (Koch-Light Laboratories Ltd.) was dehydrated using the method of Belford et al. [2], purified by repeated fractional distillation, and kept over P_4O_{10}. Purity was assessed as better than 99.9 mol.% by g.l.c. using two different columns. The purified liquid β-diketones were stored under nitrogen and were freshly distilled prior to use.

All the complexes were obtained commercially (Research Organic/Inorganic Co.) as hydrates and were purified by crystallization from (ethanol + water), with the exception of the Ni(II) complex which was purified by vacuum sublimation at 130 °C. Attempts to dehydrate these complexes by heating in vacuo for several days, at temperatures close to the sublimation temperature, were unsuccessful. It has been noted [3] that the hexafluoroacetylacetonates of these metals form very stable hydrates, and various authors [3,4] report that the water could not be removed by heating in vacuo. Inspection of the IR spectra of the complexes in the 3300–3500 cm^{-1} region confirmed the presence of coordinated water. The mass percentage analyses of the complexes are given in Table 1.

Manganese(II) chloride tetrahydrate (BDH AnalaR), cobalt(II) sulphate heptahydrate (BDH AnalaR) and nickel(II) chloride hexahydrate (BDH AnalaR) were dried over silica gel. Their compositions were confirmed by means of metal analyses, and found to be $MnCl_2 \cdot 4.00H_2O$, $CoSO_4 \cdot 6.00H_2O$ and $NiCl_2 \cdot 6.00H_2O$. Hydrochloric acid (BDH AnalaR) was used and a 1.000 mol dm^{-3} H_2SO_4 was made from BDH concentrated solution. 1,4-Dioxan (Carl Erba) was purified as described in ref. 5.

TABLE 1

Mass percentage analyses

	C	H	M	C	H	M
	Found			Expected		
Mn(TFAC)$\cdot H_2O$	31.91	2.44	14.39	31.68	2.66	14.49
$Mn(HFAC)_2 \cdot 2H_2O$	23.72	1.12	10.85	23.78	1.20	10.88
$Co(HFAC)_2 \cdot 2H_2O$	23.46	1.14	11.39	23.59	1.19	11.58
$Ni(HFAC)_2 \cdot 2H_2O$	24.02	1.22	11.47	23.60	1.19	11.54

Solution-reaction calorimeter

The isoperibol LKB 8700 reaction-and-solution precision calorimeter was used. Tests of the accuracy of its performance have been reported recently [6].

High-temperature microcalorimeter

The enthalpies of decomposition of the complexes were measured by the 'vacuum sublimation' drop-microcalorimetric method [7]. Samples (about 2–3 mg) of each complex, contained in a small thin glass capillary tube sealed at one end, were dropped at room temperature into the hot reaction vessel in a Calvet high-temperature microcalorimeter held at a constant temperature, between 396 and 472 K, and then removed from the hot-zone of the calorimeter by application of a vacuum. The calorimeter was calibrated in situ for these experiments by making use of the reported enthalpy of sublimation of naphthalene [8]. The observed enthalpies $[H_m^\ominus(\mathrm{g}, T) - H_m^\ominus(\mathrm{cr}, 298.15\ \mathrm{K})]$ were corrected to 298.15 K using values of $[H_m^\ominus(\mathrm{g}, T) - H_m^\ominus(\mathrm{g}, 298.15\ \mathrm{K})]$ estimated by group-additivity methods using data given by Stull et al. [8]. The gas was assumed to have the composition $\mathrm{M(HFAC)_2 + 2H_2O}$.

The relative atomic masses used are as recommended by the IUPAC Commission [9]. All uncertainty intervals given are twice the standard deviation of the mean.

Carbon and hydrogen analyses were carried out by the Microanalytical Service, University of Surrey, U.K.

RESULTS

Preliminary tests of solubility showed that rapid hydrolysis occurred with a mixture of composition [0.75(1,4-dioxan) + 0.25HCl(aq, 4.2 mol $\mathrm{dm^{-3}}$)] by volume as initial calorimetric solvent. Various batches of solvent were used.

The thermochemical reactions for determining the enthalpies of formation of the metal β-diketonate complexes were as follows

for M = Mn(II), with L = TFAC, HFAC

$$\mathrm{MnL_2 \cdot \mathit{n}H_2O(cr) + 2HCl \cdot 10.98H_2O(l)}$$
$$\mathrm{= (17.96 + \mathit{n})H_2O(l) + MnCl_2 \cdot 4.00H_2O(cr) + 2HL(l)} \qquad (1)$$

for M = Co(II)

$$\mathrm{Co(HFAC)_2 \cdot 2H_2O(cr) + H_2SO_4 \cdot 53.54H_2O(l)}$$
$$\mathrm{= 49.54H_2O(l) + CoSO_4 \cdot 6.00H_2O(cr) + 2HHFAC(l)} \qquad (2)$$

for M = Ni(II)

$$\mathrm{Ni(HFAC)_2 \cdot 2H_2O(cr) + 2HCl \cdot 10.98H_2O(l)}$$
$$\mathrm{= 17.96H_2O(l) + NiCl_2 \cdot 6.00H_2O(cr) + 2HHFAC(l)} \qquad (3)$$

TABLE 2

$Mn(TFAC)_2 \cdot H_2O$ and $Mn(HFAC)_2 \cdot 2H_2O$: molar enthalpies of reaction and solution at 298.15 K

i	Reactant	Solvent	Solution	Number of expts.	$\Delta_i H_m^\ominus$ (kJ mol^{-1})
1	$HCl \cdot 10.98H_2O(l)$	Initial	A_1	5	-21.18 ± 0.20
2	$Mn(TFAC)_2 \cdot H_2O(cr)$	A_1	B_1	5	-27.12 ± 0.10
3	$Mn(HFAC)_2 \cdot 2H_2O(cr)$	A_1	B_2	5	-107.9 ± 0.9
4	$MnCl_2 \cdot 4.00H_2O(cr)$	Initial	A_2	6	-6.27 ± 0.12
5	$H_2O(l)$	A_2	A_3	5	-0.935 ± 0.009
6	HTFAC(l)	A_3	B_1	5	-23.14 ± 0.20
7	HHFAC(l)	A_3	B_2	5	-74.15 ± 0.60

The standard enthalpies of these reactions were determined by measuring the enthalpies of solution and reaction of each reactant and product successively in the calorimetric solvent, so that the final solution resulting from dissolution of the reactants was of the same composition as that from dissolution of the products. Special attention was paid to control of the stoichiometric ratios of the reagents.

Table 2 lists the molar enthalpies of solution and reaction for the study of the manganese(II) β-diketonates. From the data in Table 2 the following standard molar enthalpies of the thermochemical reactions were derived

$$\Delta_r H_m^\ominus[Mn(TFAC)_2 \cdot H_2O]$$
$$= 2\ \Delta_1 H_m + \Delta_2 H_m - \Delta_4 H_m - 18.96\ \Delta_5 H_m - 2\ \Delta_6 H_m$$
$$= +0.8 \pm 0.6 \text{ kJ mol}^{-1}$$

$$\Delta_r H_m^\ominus[Mn(HFAC)_2 \cdot 2H_2O]$$
$$= 2\ \Delta_1 H_m + \Delta_3 H_m - \Delta_4 H_m - 19.96\ \Delta_5 H_m - 2\ \Delta_7 H_m$$
$$= +23.0 \pm 1.6 \text{ kJ mol}^{-1}$$

The molar enthalpies of solution and reaction from the study of the cobalt(II) and nickel(II) β-diketonates are listed in Table 3. The standard molar enthalpies of the corresponding thermochemical reactions are

$$\Delta_r H_m^\ominus[Co(HFAC)_2 \cdot 2H_2O]$$
$$= \Delta_8 H_m + \Delta_9 H_m - 49.54\ \Delta_{10} H_m - \Delta_{11} H_m - 2\ \Delta_{12} H_m$$
$$= +8.4 \pm 1.0 \text{ kJ mol}^{-1}$$

$$\Delta_r H_m^\ominus[Ni(HFAC)_2 \cdot 2H_2O]$$
$$= 2\ \Delta_{13} H_m + \Delta_{14} H_m - 17.96\ \Delta_{15} H_m - \Delta_{16} H_m - 2\ \Delta_{17} H_m$$
$$= +18.7 \pm 0.9 \text{ kJ mol}^{-1}$$

With the following auxiliary data, $\Delta_f H_m^\ominus$ (kJ mol^{-1}): $H_2O(l)$, -285.83 ± 0.04 [10]; HCl in $10.98H_2O(l)$, -161.77 ± 0.01 [11]; H_2SO_4 in

TABLE 3

$Co(HFAC)_2 \cdot 2H_2O$ and $Ni(HFAC)_2 \cdot 2H_2O$: molar enthalpies of reaction and solution at 298.15 K

i	Reactant	Solvent [a]	Solution	Number of expts.	$\Delta_i H_m^{\ominus}$ (kJ mol^{-1})
8	$H_2SO_4 \cdot 53.54H_2O(l)$	$(Initial)_1$	C_1	6	-57.93 ± 0.27
9	$Co(HFAC)_2 \cdot 2H_2O(cr)$	C_1	D_1	5	-86.14 ± 0.54
10	$H_2O(l)$	$(Initial)_2$	C_2	5	-0.999 ± 0.004
11	$CoSO_4 \cdot 6.00H_2O(cr)$	C_2	C_3	6	$+41.92 \pm 0.55$
12	HHFAC(l)	C_3	D_1	5	-72.43 ± 0.30
13	$HCl \cdot 10.98H_2O(l)$	$(Initial)_2$	C_4	5	-20.68 ± 0.06
14	$Ni(HFAC)_2 \cdot 2H_2O(cr)$	C_4	D_2	5	-102.5 ± 0.5
15	$H_2O(l)$	$(Initial)_2$	C_5	5	-0.970 ± 0.007
16	$NiCl_2 \cdot 6.00H_2O(cr)$	C_5	C_6	5	$+1.39 \pm 0.14$
17	HHFAC(l)	C_6	D_2	5	-73.25 ± 0.34

[a] $(Initial)_1$ and $(Initial)_2$ are different batches of solvent.

$53.54H_2O(l)$, -886.87 ± 0.01 [11]; $MnCl_2 \cdot 4.00H_2O(cr)$, -1687.4 ± 2.1 [11]; $CoSO_4 \cdot 6.00H_2O(cr)$, -2683.6 ± 2.1 [11]; $NiCl_2 \cdot 6.00H_2O(cr)$, -2103.17 ± 0.21 [11]; HTFAC(l), -1051.0 ± 5.0 [12]; HHFAC(l), -1673.9 ± 5.0 [12], the following standard molar enthalpies of formation of the hydrated crystalline metal(II) β-diketonates were derived:

$$\Delta_f H_m^{\ominus}[Mn(TFAC)_2 \cdot H_2O, cr] = -2609 \pm 10 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^{\ominus}[Mn(HFAC)_2 \cdot 2H_2O, cr] = -4163 \pm 10 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^{\ominus}[Co(HFAC)_2 \cdot 2H_2O, cr] = -4009 \pm 10 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^{\ominus}[Ni(HFAC)_2 \cdot 2H_2O, cr] = -4003 \pm 10 \text{ kJ mol}^{-1}$$

To derive the standard enthalpies of formation in the gaseous state, the enthalpies of sublimation of these complexes are required. Initial measurements of enthalpies of sublimation of the HFAC complexes gave values of about 250 kJ mol^{-1} for the Co(II) and Ni(II) complexes, and about 200 kJ mol^{-1} for the Mn(II) complex. Such large values cannot be attributed to straightforward sublimation of the hydrated complexes; as for those metal β-diketonates for which enthalpies of sublimation have been measured [13], all the values are less than 200 kJ mol^{-1}, the hexafluorinated complexes being the most volatile. Microanalysis of the condensate in the cold zone of the microcalorimeter showed that these complexes transferred through the vapour phase with composition unchanged. The measured enthalpies were assigned to the decomposition

$$M(HFAC)_2 \cdot 2H_2O(cr) = M(HFAC)_2(g) + 2H_2O(g) \qquad (4)$$

Arguments in favour of these decomposition processes are given in the Appendix. To study these processes, the enthalpies of decomposition for

TABLE 4

Enthalpy of decomposition of $Mn(HFAC)_2 \cdot 2H_2O$

T (K)	Mass (mg)	$\Delta_{dec}H_m(\text{obs}, T)$ (kJ mol^{-1})	$H_m^\ominus(\text{g}, T) - H_m^\ominus(\text{g}, 298.15\ \text{K})$ (kJ mol^{-1})	$\Delta_{dec}H_m^\ominus(298.15\ \text{K})$ (kJ mol^{-1})
413	2.541	255.8	54.4	201.4
408	2.397	254.4	51.6	202.8
408	3.044	258.9	51.6	207.3
408	2.307	255.0	51.6	203.4
				Mean 204 ± 3 kJ mol^{-1}

TABLE 5

Enthalpy of decomposition of $Co(HFAC)_2 \cdot 2H_2O$

T (K)	Mass (mg)	$\Delta_{dec}H_m(\text{obs}, T)$ (kJ mol^{-1})	$H_m^\ominus(\text{g}, T) - H_m^\ominus(\text{g}, 298.15\ \text{K})$ (kJ mol^{-1})	$\Delta_{dec}H_m^\ominus(298.15\ \text{K})$ (kJ mol^{-1})
396	3.056	300.8	45.5	255.3
396	2.688	298.9	45.5	253.4
396	2.640	296.1	45.5	250.6
396	2.443	292.6	45.5	247.4
405	2.793	301.4	49.7	251.7
405	2.618	301.2	49.7	251.5
405	2.491	300.7	49.7	251.0
451	1.600	324.2	73.7	250.5
				Mean 251 ± 2 kJ mol^{-1}

TABLE 6

Enthalpy of decomposition of $Ni(HFAC)_2 \cdot 2H_2O$

T (K)	Mass (mg)	$\Delta_{dec}H_m(\text{obs}, T)$ (kJ mol^{-1})	$H_m^\ominus(\text{g}, T) - H_m^\ominus(\text{g}, 298.15\ \text{K})$ (kJ mol^{-1})	$\Delta_{dec}H_m^\ominus(298.15\ \text{K})$ (kJ mol^{-1})
449	1.739	319.8	73.0	246.8
451	1.810	325.8	74.3	251.5
451	1.900	324.9	74.3	245.6
458	1.625	332.6	77.7	254.9
458	1.644	334.5	77.7	256.8
472	1.931	332.6	85.1	247.8
472	1.858	337.2	85.1	252.1
				Mean 251 ± 3 kJ mol^{-1}

each complex were measured over a range of temperatures, and the results corrected to 298.15 K. Detailed results of these measurements are given in Tables 4–6. Attempts to measure the enthalpy of the decomposition

$$Mn(TFAC)_2 \cdot H_2O(cr) = Mn(TFAC)_2(g) + H_2O(g) \qquad (5)$$

by the same method failed because of extensive thermal decomposition of the dehydrated complex.

From the enthalpies of decomposition at 298.15 K listed in Table 7, and $\Delta_f H_m^\ominus(H_2O, g) = -241.81 \pm 0.04$ kJ mol^{-1} [10], the standard enthalpies of formation of the metal(II) β-diketonates in the gaseous state were derived. There are listed in Table 8.

TABLE 7

Standard molar enthalpies of formation and decomposition at 298.15 K

Complex	$\Delta_f H_m^\ominus$(cr) (kJ mol^{-1})	$\Delta_{dec} H_m^\ominus$ (kJ mol^{-1})
$Mn(TFAC)_2 \cdot H_2O$	-2609 ± 10	$[170 \pm 10]$ [a]
$Mn(HFAC)_2 \cdot 2H_2O$	-4163 ± 10	204 ± 3
$Co(HFAC)_2 \cdot 2H_2O$	-4009 ± 10	251 ± 2
$Ni(HFAC)_2 \cdot 2H_2O$	-4003 ± 10	251 ± 3

[a] Estimated value [27].

TABLE 8

Derived molar values at 298.15 K

Complex	$\Delta_f H_m^\ominus$(g) (kJ mol^{-1})	$\Delta_{disr} H_m^\ominus$ (kJ mol^{-1})	$\langle D \rangle$(M–O) (kJ mol^{-1})
$Mn(TFAC)_2$	-2197 ± 14	850 ± 44	213 ± 11
$Mn(HFAC)_2$	-3475 ± 10	869 ± 43	217 ± 11
$Co(HFAC)_2$	-3274 ± 10	812 ± 43	203 ± 11
$Ni(HFAC)_2$	-3268 ± 10	811 ± 43	203 ± 11

DISCUSSION

The mean metal–oxygen bond-dissociation enthalpy, $\langle D \rangle$(M–O), in ML_2, may be defined as 1/4 of the enthalpy of the disruption reaction

$$ML_2(g) = M(g) + 2L(g) \tag{6}$$

$$4\langle D \rangle(\text{M–O}) = \Delta_{disr} H_m^\ominus = \Delta_f H_m^\ominus(\text{M, g}) + 2\,\Delta_f H_m^\ominus(\text{HL, g}) - 2\,\Delta_f H_m^\ominus(\text{H, g}) - \Delta_f H_m^\ominus(ML_2\text{, g}) + 2D(\text{O–H, HL, enol})$$

where D(O–H, HL, enol) is the molar enthalpy of dissociation of the enolic hydrogen in the parent ligand

$$HL(g) = H(g) + L(g) \tag{7}$$

With D(O–H, HL, enol) $= 418 \pm 20$ kJ mol^{-1} [13] and the following auxiliary data, $\Delta_f H_m^\ominus$(kJ mol^{-1}): HTFAC(enol, g), -1013.8 ± 5.0 [12];

TABLE 9

Mean metal–oxygen bond-dissociation enthalpies in some metal(II) β-diketonates

β-Diketone	$\langle D\rangle$(M–O) (kJ mol^{-1})		
	Mn(II)	Co(II)	Ni(II)
HACAC	216 ± 10 [a,b]	202 ± 11 [d]	202 ± 10 [f]
HBZAC		201 ± 10 [e]	203 ± 11 [g]
HTFAC	213 ± 11	206 ± 11 [e]	
HHFAC	217 ± 11	203 ± 11	203 ± 11
HDPM	201 ± 10 [c]	209 ± 11 [c]	202 ± 11 [f]

[a] Ref. 14. [b] Ref. 15. [c] Ref. 16. [d] Ref. 17. [e] Ref. 18. [f] Ref. 19. [g] Ref. 20.

HHFAC(enol, g), −1643.3 ± 5.0 [12]; H(g), 218.00 ± 0.01 [11]; Mn(g), 280.7 ± 4.2 [11]; Co(g), 424.7 ± 4.2 [11]; Ni(g), 429.7 ± 4.2 [11], we can calculate $\Delta_{\mathrm{disr}}H_{\mathrm{m}}^{\ominus}$ and $\langle D\rangle$(M–O) for the complexes studied in this paper. These values are given in Table 8.

Previously reported values for $\langle D\rangle$(M–O) in other metal(II) β-diketonates of Mn(II) [14–16], Co(II) [16–18] and Ni(II) [19,20] are summarized in Table 9, together with the values calculated in the present paper. The large uncertainties associated with these derived values mainly arise from the large uncertainties assigned to the estimated values of the standard enthalpies of formation of the fluorinated β-diketone ligands (± 5.0 kJ mol^{-1}) and D(O–H, HL, enol) (± 20 kJ mol^{-1}). Clearly, within the associated uncertainties the mean metal–oxygen bond-dissociation enthalpy values, $\langle D\rangle$(M–O), are almost constant, so only a very small effect, if any, can be ascribed to the inductive effect of fluorine substitution in the ligand upon the energetics of the metal–oxygen bonds in the β-diketonate complexes studied. This conclusion is supported by the results of previous studies on other metal β-diketonates: Be(II) [21], Al(III) [21], Cu(II) [22,23], Cr(III) [12], Fe(III) [24] and Co(III) [6,25].

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APPENDIX

Decomposition reaction $M(HFAC)_2 \cdot 2H_2O(cr) = M(HFAC)_2(g) + 2H_2O(g)$

From experimental vapour pressures and enthalpies of sublimation, $\Delta S^\ominus$ for sublimation can be derived from

$$-RT \ln P/\text{atm} = \Delta H^\ominus - T\Delta S^\ominus$$

For a series of Be(II) bis diketonate complexes at 400 K, $\Delta S^\ominus$ was found to be 195 J K^{-1} mol^{-1} [26]. This is considerably smaller than the value found for the Al(III) and Cr(III) tris diketonate complexes (250 J K^{-1} mol^{-1}) [27].

If, for the hypothetical sublimation of $M(HFAC)_2 \cdot 2H_2O$, we assume $\Delta S^\ominus$ to have the value given above for the bis diketonate complexes and $\Delta H^\ominus$ to be that measured in the microcalorimeter, then the vapour pressures at the temperature of sublimation can be derived. For the three hydrated hexafluoroacetylacetonates studied, the calculated vapour pressures range from 9×10^{-26} to 2×10^{-20} mmHg; these are too small for sublimation to be possible under the experimental conditions.

If we assume that the process occurring in the microcalorimeter sublimation experiment is as indicated in eqn. (4), then the entropy change can be estimated as follows

$$\begin{tikzcd}
M(HFAC)_2 \cdot 2H_2O(cr) \arrow[r, "\Delta S_1^\ominus"] \arrow[dr, "\Delta S^\ominus"'] & M(HFAC)_2(cr) + 2H_2O(g) \arrow[d, "\Delta S_2^\ominus"] \\
 & M(HFAC)_2(g) + 2H_2O(g)
\end{tikzcd}$$

with $\Delta S^\ominus = \Delta S_1^\ominus + \Delta S_2^\ominus$

$$\Delta S_1^\ominus = S^\ominus[M(HFAC)_2, cr] - S^\ominus[M(HFAC)_2 \cdot 2H_2O, cr] + 2S^\ominus[H_2O, g] \qquad (8)$$

The entropy difference between the anhydrous and the hydrated complexes can be estimated to be −42 J K^{-1} mol^{-1} of water. This estimate is based on the literature values for the standard entropies of the Mn(II), Co(II) and Ni(II) hydrated chlorides, and the Co(II), Ni(II) and Cu(II) hydrated sulphates [11]. With $S^\ominus(H_2O, g) = 188.7$ J K^{-1} mol^{-1} [11], then $\Delta S_1^\ominus \approx 293$ J K^{-1} mol^{-1}. Assuming $\Delta S_2^\ominus = 195$ J K^{-1} mol^{-1}, $\Delta S^\ominus$ can be estimated to be about 488 J K^{-1} mol^{-1}, and given the measured values of $\Delta H^\ominus$, $\Delta G^\ominus$ for the process of eqn. (4) can be derived. This leads to a total pressure for the products of between 2 and 3×10^{-2} mmHg. Given pressures of this magnitude, the process (eqn. (4)) of transporting the hydrated complex through the vapour phase unchanged becomes understandable.

If $Mn(HFAC)_2 \cdot 2H_2O$ did sublime it would be reasonable to expect $\Delta_{sub}H_m^{\ominus}$ to be slightly larger than the average value of 120 kJ mol^{-1} for other $M(diketone)_2$ complexes because of its larger molecular weight. A reasonable estimate would be 140 kJ mol^{-1}, implying an average bonding energy of H_2O to Mn(II) of about 30 kJ mol^{-1}. This assumed value formed the basis of the estimate of $\Delta_{dec}H_m^{\ominus}$ of $Mn(TFAC)_2 \cdot H_2O$ [27].

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