Thermochemistry of Cobalt(III) β-Diketonates

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The standard molar enthalpies of formation of the crystalline complexes of cobalt(III) with 1-phenyl-1,3-butanedione (Hbzac), 2,2,6,6-tetramethyl-3,5-heptanedione(Hdpm), and 1,1,1-trifluoro-2,4-pentanedione (Htfac) were determined, at 298.15 K, by solution-reaction calorimetry:

$$\Delta_f H^\circ_m[\mathrm{Co(bzac)_3, cr}] = -877.1 \pm 8.7\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H^\circ_m[\mathrm{Co(dpm)_3, cr}] = -1708 \pm 12\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H^\circ_m[\mathrm{Co(tfac)_3, cr}] = -3191 \pm 15\ \mathrm{kJ \cdot mol^{-1}}.$$

The enthalpies of sublimation of Co(dpm)$_3$ and Co(tfac)$_3$, at 298.15 K, determined by high-temperature microcalorimetry were 126±3 and 114±2 kJ·mol^{-1}, respectively. From the enthalpies of formation of the gaseous complexes, the average molar bond-dissociation enthalpies, $\langle D \rangle$(Co–O), were derived.

Previous thermochemical studies of cobalt(III) β-diketonates are limited to tris(2,4-pentanedionato)-cobalt(III), made by Wood and Jones,[1] using static-bomb calorimetry. These early combustion results have been shown to be unreliable,[2] probably because insufficient attention was paid to controlling the combustion with auxiliary combustion aids and in defining the completeness of combustion and the nature of the combustion products.

The solution-reaction calorimetric method has proved bo be reliable for determining enthalpies of formation of metal β-diketonates.[3] In this paper, using the solution-reaction calorimetric method, the standard molar enthalpies of formation of three cobalt(III) β-diketonates were determined, to permit consideration of the effect of structural changes in the ligand upon the mean molar (Co–O) bond-dissociation enthalpies.

Experimental

The Solution Calorimeter. The isoperibol LKB 8700 reaction-and-solution precision calorimeter was used. The operation and calculations methods have been reported.[4] The molar enthalpy of reaction was calculated from the relation $\Delta H = \varepsilon \Delta R / n R_m$, where $\Delta R = R_i - R_f$, $R_m = (R_i + R_f)/2$, n=number of moles of reactant, and R_i and R_f are the initial and final thermistor resistances (Ω) as determined by the Dickinson method.[5] The energy constant, ε, of the calorimetric system is given by $\varepsilon = Q_c R_{mc} / \Delta R_c$, where Q_c is an accurately defined quantity of heat supplied electrically via the built-in heater, $Q_c = R_h I^2 t$(R_h is the resistance of the calibrating heater (Ω), I the calibratrion current (A), and t the heating time (s)), and R_{mc} and ΔR_c have the same significance in a calibration experiment as R_m and ΔR have in a reaction. The ratio $\Delta R / R_m$ is directly proportional to the temperature change. The accuracy of the calorimeter was checked by measuring the molar enthalpy of solution of tris(hydroxymethyl)aminomethane (THAM) in aqueous 0.1000 mol·dm^{-3} HCl at 298.15 K: $\Delta_{sol} H_m = -29.769 \pm 0.024$ kJ·mol^{-1}, in agreement with the value of Kilday and Prosen,[6] $\Delta_{sol} H_m = -29.770 \pm 0.032$ kJ·mol^{-1}.

High-Temperature Microcalorimeter. The enthalpies of sublimation of the complexes were measured by the "vacuum sublimation" drop-microcalorimetric method.[7] Samples (about 4 mg) of each complex contained in a small thin-glass capilary tube sealed at one end, were dropped, at room temperature, into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter held at constant temperature, between 407 and 490 K, and then removed from the hot zone by vacuum sublimation. At these temperatures, the complexes showed no signs of decomposition, and sublimed completely in less than 30 min. The observed standard molar enthalpies of sublimation [H°_m(g, T)−H°_m(cr,298.15K)] were corrected to 298.15 K using values of [H°_m(g, T)−H°_m(g, 298.15K)] estimated by group-additivity methods based on data given by Stull et al.[8] The microcalorimeter was calibrated in situ for the measurements by making use of the known molar enthalpies of sublimation of iodine,[9] naphthalene,[8] and benzoic acid.[10,11]

All uncertainty intervals given are twice the standard deviation of the mean.

Materials. 1-Phenyl-1,3-butanedione: Hbzac (Koch-Light Laboratories Ltd.) was purified by repeated recrystallization from ethanol–water; mp 56 °C (lit, 56 °C[12]). Found: C, 73.89; H, 6.25%. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22%.

2,2,6,6-Tetramethyl-3,5-heptanedione: Hdpm was prepared by Claisen condensation according to the methods of Adams and Hauser[13] and of Kopecky et al.,[14] was purified by fractional distillation in vacuum and the purity was assessed as better than 99.9 mole per cent by GLC using two different columns.

1,1,1-Trifluoro-2,4-pentanedione: Htfac (Kock-Light Laboratories Ltd.) was purified by fractional distillation and the purity was assessed as greater than 99.9 mole per cent by GLC using two different columns. The purified liquid β-diketones were stored under nitrogen in the dark and were freshly distilled prior to use.

Tris(1-phenyl-1,3-butanedionato)cobalt(III): Co(bzac)$_3$ was prepared as described by Bauer and Drinkard[15] and was purfied by crystallization from acetone–hexane; mp 184—185 °C(lit, 213 °C[15]). Found: C, 66.45; H, 4.89; Co, 10.78%. Calcd for $C_{30}H_{27}O_6Co$: C, 66.42; H, 5.03; Co, 10.87%.

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III): Co(dpm)$_3$ was prepared as described by Bauer and Drinkard[15] and was purified by vacuum sublimation; mp 244—245 °C (lit, 244—245 °C[16]). Found: C, 65.11; H, 9.38; Co, 9.54%. Calcd for $C_{33}H_{57}O_6Co$: C, 65.11; H, 9.44; Co, 9.68%.

Tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III): Co(tfac)$_3$ (Koch-Light Laboratories Ltd.) was crystallized from carbon tetrachloride; mp 152 °C (lit, 156 °C[17]). Found: C, 34.72; H, 2.19; Co, 11.30%. Calcd for $C_{15}H_{12}O_6Co$: C, 34.77; H, 2.33; Co, 11.37%.

Cobalt(II) Sulfate Hexahydrate: Cobalt(II) sulfate heptahydrate (AnalaR BDH) was dried over silica gel; its composition was determined by means of cobalt analyses and found to be $CoSO_4\cdot6.00H_2O$.

Iron(II) and Iron(III) Chloride: CERAC samples of $FeCl_2$ and $FeCl_3$(stated minimum purity 99.99%) were used.

Sulfuric Acid: A 1 $mol\cdot dm^{-3}$ H_2SO_4 was made from Merck concentrated volumetric solution; the concentration was checked by titration against $Na_2B_4O_7\cdot10H_2O$ and found to be (series of six titrations) 1.000 ± 0.003 $mol\cdot dm^{-3}$, which corresponds[12] to the composition $H_2SO_4\cdot53.54H_2O$.

Hydrochloric Acid: Concentrated HCl (AnalaR BDH) was diluted with distilled water. The concentration was determined by titration against $Na_2B_4O_7\cdot10H_2O$ and found to be (series of six titrations) 4.590 ± 0.003 $mol\cdot dm^{-3}$, which corresponds[12] to the composition $HCl\cdot10.98H_2O$.

1,4-Dioxane: 1,4-Dioxane (Carl Erba) was purified according to Ref. 18.

Analyses: Carbon and hydrogen analyses were carried out in the Microanalytical Service of the University of Surrey; cobalt was analyzed by the ethylenediaminetetracetic acid method.[19]

For the hydrolysis and oxidation reaction the solvents were degassed and saturated with purified nitrogen prior to each determination.

The relative atomic masses used were the recommended by the IUPAC Commission.[20]

Results and Discussion

Preliminary tests of solubility showed that rapid hydrolyses and oxidation occurred using [0.90(1,4-dioxane)+0.10HCl(aq, 3.0 $mol\cdot dm^{-3}$)] by volume, as the initial calorimetric solvent.

The thermochemical reaction for determining the standard molar enthalpy of formation of Co(bzac)$_3$, Co(dpm)$_3$, and Co(tfac)$_3$ was:

$$\begin{aligned}&CoL_3(cr) + HCl\cdot10.98H_2O(l) + H_2SO_4\cdot53.54H_2O(l)\\&\quad + FeCl_2(cr) = 58.52H_2O(l) + FeCl_3(cr)\\&\quad + 3HL(cr\ or\ l) + CoSO_4\cdot6.00H_2O(cr)\end{aligned} \tag{1}$$

The reaction was studied in the presence of an excess of $FeCl_3$: to the calorimetric solvent (100.0 cm^3), 1.00 cm^3 of $FeCl_3$ 0.1 $mol\cdot dm^{-3}$ was added. The same batch of solvent was used for the three cobalt(III) complexes.

The enthalpies of the thermochemical reactions were determined by measuring the enthalpies of reaction and solution of the reactants and products, $\Delta_i H_m$, in succession in the initial calorimetric solvent. The thermochemical cycle and the general procedure for the calorimetric study of the cobalt(III) complexes

$$HCl\cdot10.98H_2O(l)+H_2SO_4\cdot53.54H_2O(l)+FeCl_2(cr)+CoL_3(cr)=58.52H_2O(l)+FeCl_3(cr)+3HL(cr\ or\ l)+CoSO_4\cdot6.00H_2O(cr)$$

$$\downarrow\Delta_1H_m \quad \downarrow\Delta_2H_m \quad \downarrow\Delta_3H_m \quad \downarrow\Delta_4H_m \quad \downarrow\Delta_5H_m \quad \downarrow\Delta_6H_m \quad \downarrow\Delta_7H_m \quad \downarrow\Delta_8H_m$$

$$Solvent\{0.90(dioxane)+0.10HCl(aq,\ 3.0\ mol\cdot dm^{-3})\}+FeCl_3 \qquad Solvent\{0.90(dioxane)+0.10HCl(aq,\ 3.0\ mol\cdot dm^{-3})\}+FeCl_3$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$Solution\ A_4 \xrightarrow{\Delta_9H_m=0} Solution\ B_4$$

$$\begin{aligned}
&Solvent+HCl\cdot10.98H_2O(l) \xrightarrow{\Delta_1H_m} Solution\ A_1\\
&Solution\ A_1+H_2SO_4\cdot53.54H_2O(l) \xrightarrow{\Delta_2H_m} Solution\ A_2\\
&Solution\ A_2+FeCl_2(cr) \xrightarrow{\Delta_3H_m} Solution\ A_3\\
&Solution\ A_3+CoL_3(cr) \xrightarrow{\Delta_4H_m} Solution\ A_4\\
&Solvent+H_2O(l) \xrightarrow{\Delta_5H_m} Solution\ B_1\\
&Solution\ B_1+FeCl_3(cr) \xrightarrow{\Delta_6H_m} Solution\ B_2\\
&Solution\ B_2+HL(cr\ or\ l) \xrightarrow{\Delta_7H_m} Solution\ B_3\\
&Solution\ B_3+CoSO_4\cdot6.00H_2O(cr) \xrightarrow{\Delta_8H_m} Solution\ B_4
\end{aligned}$$

$$\Delta_rH_m=\Delta_1H_m+\Delta_2H_m+\Delta_3H_m+\Delta_4H_m-58.52\Delta_5H_m-\Delta_6H_m-3\Delta_7H_m-\Delta_8H_m$$

Scheme 1.

is given in the Scheme 1. The difference between the molar enthalpies of solution of the products and reactants in the correct stoichiometric ratio gives the enthalpy of the thermochemical reaction, $\Delta_r H^\circ_m$, provided equilibrium is reached from either side within the period of the experiment. The amounts of reactants in a particular series of experiments were determined by the amount of CoL_3(cr), approximately 2.5×10^{-4} mol for $Co(bzac)_3$ and $Co(tfac)_3$ and 1.2×10^{-4} mol for $Co(dpm)_3$. Since the amounts used for the reactants in the study of the $Co(dpm)_3$ complex were different from the other complexes, this made necessary remeasurement of the enthalpies of solution of $HCl\cdot10.98H_2O$(l), $H_2SO_4\cdot53.54H_2O$(l), $FeCl_3$(cr), $FeCl_2$(cr), H_2O(l), and $CoSO_4\cdot6.00H_2O$(cr). These results were found to be the same, within the experimental errors, as determined previously in the study of $Co(bzac)_3$ and $Co(tfac)_3$, hence the previously determined values were used.

The detailed calorimetric results required for determination of the enthalpies of the thermochemical reactions are given in Tables 1—3.

The enthalpies of the thermochemical reactions were derived from the values presented in Tables 1—3

Table 1. Calorimetric Study, at 298.15K, of $Co(bzac)_3$

(a) $HCl\cdot10.98H_2O(l)+solvent=solution\ A_1$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_1H_m/kJ·mol^{-1}
2.4638	10.101	5380.1	−22.058
2.4933	10.124	5395.3	−21.907
2.5449	10.327	5426.5	−22.020
2.4775	9.9694	5386.5	−21.675
2.4749	9.9983	5405.2	−21.836

Mean: $\Delta_1H_m=-21.90\pm0.14$ kJ·mol^{-1}

(b) $H_2SO_4\cdot53.54H_2O(l)+solution\ A_1=solution\ A_2$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_2H_m/kJ·mol^{-1}
2.4648	1.4183	5414.2	−31.155
2.4976	1.4299	5414.1	−30.995
2.5380	1.4631	5439.3	−31.356
2.4493	1.4071	5415.8	−31.112
2.4795	1.4193	5422.7	−31.040

Mean: $\Delta_2H_m=-31.13\pm0.12$ kJ·mol^{-1}

(c) $FeCl_2(cr)+solution\ A_2=solution\ A_3$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_3H_m/kJ·mol^{-1}
2.4670	3.3817	5415.4	−72.135
2.5348	3.4255	5429.4	−73.372
2.4709	3.2824	5443.4	−72.310
2.5341	3.3521	5455.8	−72.170
2.4204	3.2131	5459.8	−72.477

Mean: $\Delta_3H_m=-72.69\pm0.47$ kJ·mol^{-1}

(d) $Co(bzac)_3(cr)+solution\ A_3+solution\ A_4$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_4H_m/kJ·mol^{-1}
2.4146	3.9881	5430.5	+8.969
2.3051	3.5768	5445.0	+8.449
2.5880	4.3724	5426.7	+9.168
2.4807	4.0486	5419.9	+8.845
2.3510	3.8266	5430.5	+8.839

Mean: $\Delta_4H_m=+8.85\pm0.24$ kJ·mol^{-1}

(e) $H_2O(l)+solvent=solution\ B_1$

10^2n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_5H_m/kJ·mol^{-1}
1.4479	1.3966	5424.5	−0.5232
1.5377	1.4837	5427.3	−0.5236
1.5482	1.4956	5414.5	−0.5230
1.3532	1.3096	5428.7	−0.5254
1.6031	1.5567	5433.5	−0.5276

Mean: $\Delta_5H_m=-0.524\pm0.002$ kJ·mol^{-1}

(f) $FeCl_3(cr)+solution\ B_1=solution\ B_2$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_6H_m/kJ·mol^{-1}
2.4802	3.9086	5438.4	−85.705
2.6281	4.0756	5431.3	−84.227
2.3113	3.6221	5439.8	−85.249
2.5005	3.8360	5449.2	−83.594
2.6510	4.1685	5436.0	−85.479
2.7453	4.2115	5446.6	−83.557

Mean: $\Delta_6H_m=-84.64\pm0.79$ kJ·mol^{-1}

(g) $Hbzac(cr)+solution\ B_2=solution\ B_3$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_7H_m/kJ·mol^{-1}
7.5233	3.3298	5450.4	+24.123
7.6306	3.3527	5459.3	+23.987
7.1897	3.1858	5449.8	+24.148
6.8802	3.3739	5459.8	+24.288
7.5073	3.3249	5450.9	+24.141

Mean: $\Delta_7H_m=+24.14\pm0.10$ kJ·mol^{-1}

(h) $CoSO_4\cdot6.00H_2O(cr)+solution\ B_3=solution\ B_4$

10^4n/mol	$10^3(\Delta R/R_m)$	ε/J	Δ_8H_m/kJ·mol^{-1}
2.5015	1.4526	5449.3	+31.644
2.6824	1.5772	5424.0	+31.892
2.6390	1.5247	5446.0	+31.466
2.7808	1.6341	5453.5	+32.047
2.6349	1.5457	5456.0	+32.006

Mean: $\Delta_8H_m=+31.81\pm0.22$ kJ·mol^{-1}

Table 2. Calorimetric Study, at 298.15 K, of $Co(dpm)_3$

(a) $Co(dpm)_3(cr)+solution\ A_3=solution\ A_4$

10^4n/mol	$10^4(\Delta R/R_m)$	ε/J	Δ_4H_m/kJ·mol^{-1}
1.2442	6.7948	5404.2	+29.513
1.2549	6.9226	5425.6	+29.931
1.2422	6.6561	5467.7	+29.297
1.1284	6.0971	5432.5	+29.354
1.1974	6.5578	5432.5	+29.753

Mean: $\Delta_4H_m=+29.57\pm0.24$ kJ·mol^{-1}

(b) $Hdpm(l)+solution\ B_2=solution\ B_3$

10^4n/mol	$10^4(\Delta R/R_m)$	ε/J	Δ_7H_m/kJ·mol^{-1}
4.0444	4.9170	5377.4	+6.538
4.0265	4.9881	5351.5	+6.630
3.5240	4.3888	5295.6	+6.595
3.3997	4.1227	5365.9	+6.507
4.1860	5.0328	5367.0	+6.453

Mean: $\Delta_7H_m=+6.54\pm0.06$ kJ·mol^{-1}

Table 3. Calorimetric Study, at 298.15 K, of $Co(tfac)_3$

(a) $Co(tfac)_3(cr)+solution\ A_3=solution\ A_4$				(b) $Htfac(l)+solution\ B_2=solution\ B_3$			
$10^4n/mol$	$10^3(\Delta R/R_m)$	ε/J	$\Delta_4H_m/kJ\cdot mol^{-1}$	$10^4n/mol$	$10^3(\Delta R/R_m)$	ε/J	$\Delta_7H_m/kJ\cdot mol^{-1}$
2.4646	1.1083	5430.4	+24.420	7.5047	3.6182	5444.8	−26.251
2.5277	1.1025	5439.2	+23.724	7.9006	3.7799	5419.2	−25.927
2.4428	1.1046	5420.0	+24.508	7.9824	3.7770	5448.0	−25.778
2.4648	1.1119	5433.5	+24.511	8.2545	3.9619	5441.8	−26.119
2.4793	1.1078	5447.8	+24.344	8.0083	3.8513	5437.1	−26.146
Mean: $\Delta_4H_m=+24.30\pm0.30$ kJ·mol^{-1}				Mean: $\Delta_7H_m=-26.04\pm0.17$ kJ·mol^{-1}			

Table 4. Molar Enthalpies of Sublimation of Cobalt(III) Complexes

Complex	No. of exp.	T	$\Delta_{sub}H_m(obs,\ T)$	$H^\circ_m(g,\ T)-H^\circ_m(g,\ 298.15\ K)$	$\Delta_{sub}H^\circ_m(298.15\ K)$
		K	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
$Co(dpm)_3$	5	490	318±3	192	126±3
$Co(tfac)_3$	3	407	168±2	54	114±2

Table 5. Standard Molar Enthalpies of Formation and Vaporization/Sublimation of β-Diketones

β-Diketone	$\Delta_fH^\circ_m$(cr or l)	$\Delta_{vap/sub}H^\circ_m$	$\Delta_fH^\circ_m$(g)
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
Hbzac(cr)	−335.1±2.8a)	+83.8±0.4b)	−251.3±2.9
Hdpm(l)	−587.7±3.8a)	+59.5±0.1c)	−528.2±3.8
Htfac(l)	−1051.0±5.0	+37.2±0.2c)	−1013.8±5.0d)

a) Ref. 24. b) Ref. 25. c) Ref. 26. d) Estimated by using a group scheme.

Table 6. Standard Molar Enthalpies of Formation and Sublimation at 298.15 K

Complex	$\Delta_fH^\circ_m$(cr)	$\Delta_{sub}H^\circ_m$	$\Delta_fH^\circ_m$(g)
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
$Co(bzac)_3$	−877.1±8.7	[165±10]a)	−712±13
$Co(dpm)_3$	−1708±12	126±3	−1582±12
$Co(tfac)_3$	−3191±15	114±2	−3077±15

a) Estimated.

and the equation in the Scheme 1, leading to

$$\Delta_rH^\circ_m[Co(bzac)_3]=-105.8\pm1.0\ kJ\cdot mol^{-1}$$

$$\Delta_rH^\circ_m[Co(dpm)_3]=+32.3\pm1.0\ kJ\cdot mol^{-1}$$

$$\Delta_rH^\circ_m[Co(tfac)_3]=+60.2\pm1.3\ kJ\cdot mol^{-1}$$

The experimental results for determination of the standard molar enthalpies of sublimation of $Co(dpm)_3$ and $Co(tfac)_3$ are listed in Table 4. Attempts to measure the enthalpy of sublimation of $Co(bzac)_3$ were unsuccessful because, for temperatures at which vapour pressure was sufficiently high to permit vacuum sublimation, partial thermal decomposition occurred.

To derive the standard molar enthalpies of formation of the crystalline cobalt(III) complexes, the following auxiliary data, at 298.15 K, was used: $\Delta_fH^\circ_m(H_2O,\ l)=-285.83\pm0.04$ kJ·mol^{-1};21) $\Delta_fH^\circ_m(HCl$ in $10.98H_2O,\ l)=-161.77\pm0.01$ kJ·mol^{-1};22) $\Delta_fH^\circ_m(H_2SO_4$ in $53.54H_2O,\ l)=-886.87\pm0.01$ kJ·mol^{-1};22) $\Delta_fH^\circ_m(FeCl_3,\ cr)=-399.49\pm0.29$ kJ·mol^{-1};22,23) $\Delta_fH^\circ_m(FeCl_2,\ cr)=-341.79\pm0.21$ kJ·mol^{-1};22,23) $\Delta_fH^\circ_m(CoSO_4\cdot6.00H_2O,\ cr)=-2683.6\pm2.1$ kJ·mol^{-1};22) as well as the standard enthalpies of formation of the ligands (Table 5), and the above derived molar enthalpies of the thermochemical reactions. Table 6 lists the derived standard molar enthalpies of formation of the crystalline cobalt(III) complexes, their standard molar enthalpies of sublimation and of formation in the gaseous state. The molar enthalpy of sublimation of $Co(bzac)_3$ was estimated on the basis of its structure, molecular weight and other known values for similar complexes, using an estimation scheme.3)

From the molar enthalpies of the homolytic dissociation of the gaseous molecules into metal atoms and ligand radicals

$$CoL_3(g)=Co(g)+3L^\cdot(g) \qquad (2)$$

the mean cobalt–oxygen bond-dissociation enthalpies, $\langle D\rangle$(Co–O), were derived. Since the oxygens atoms in metal β-diketonates are equivalent,27) $\langle D\rangle$(Co–O) may be defined as 1/6 of the molar enthalpy of the disruption Reaction 2.

$$\begin{aligned}\Delta_{disr}H^\circ_m(2)=&\ \Delta_fH^\circ_m(Co,\ g)+3\Delta_fH^\circ_m(HL,\ g)\\&-3\Delta_fH^\circ_m(H,\ g)-\Delta_fH^\circ_m(CoL_3,\ g)\\&+3D(O\text{–}H,\ HL,\ enol)\end{aligned}$$

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

Table 7. $<D>$(Co–O) at 298.15 K

Complex	$\Delta_{\mathrm{disr}}H^{\circ}_{\mathrm{m}}$	$<D>$(Co–O)
	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$
Co(bzac)$_3$	984±62	164±10
Co(dpm)$_3$	1023±62	171±10
Co(tfac)$_3$	1060±65	177±10

$$\mathrm{H\text{-}L(g) = L^{\cdot}(g) + H(g)} \qquad (3)$$

There are no measured values for the molar enthalpy of dissociation of the enolic hydrogen from β-diketones. Different values have been estimated for this parameter, and the situation has been recently reviewed.[3] In this work, for comparison reasons, the value of D(O–H, HL, enol)=418±20 kJ·mol^{-1} [3] is used.

With $\Delta_f H^{\circ}_{\mathrm{m}}$(H, g)=218.00±0.01 kJ·mol^{-1} [22] and $\Delta_f H^{\circ}_{\mathrm{m}}$(Co, g)=424.7±4.2 kJ·mol^{-1} [22] the derived values of $\Delta_{\mathrm{disr}}H^{\circ}_{\mathrm{m}}$ and $\langle D \rangle$(Co–O), for the complexes studied are given in Table 7.

As noted previously[28,29] in attempting a rigorous determination of bond-dissociation enthalpies, estimates of some enthalpies of formation were necessary, as well as the enthalpy of dissociation of the enolic hydrogen from the parent β-diketone. The resulting bond-dissociation enthalpies, therefore, have a large uncertainty attached to them, and this makes almost impossible a definite conclusion concerning the magnitude of the bond dissociation enthalpies. Within the uncertainties attached to the mean cobalt(III)–oxygen bond-dissociation enthalpies, there are no significant differences in $\langle D \rangle$(Co–O) for the three cobalt(III) β-diketonates studied in this paper. This shows that there is no effect, or only a very small one, of $-\mathrm{C(CH_3)_3}$, $-\mathrm{C_6H_5}$, or $-\mathrm{CF_3}$ substitution in the ligand, upon $\langle D \rangle$(Co–O). This effect has already been observed for complexes of β-diketones with Be(II),[30] Al(III),[30] Cr(III),[31] Fe(III),[32] and Cu(II).[33]

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