Thermochemistry of Tris(1,1,1-trifluoropentane-2,4-dionato)- and Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)-aluminium(III)

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Enthalpies of formation of the crystalline title complexes have been determined at 298.15 K by solution calorimetry: ΔH_f°[Al(tfpd)$_3$(c)] = −892.7 ± 3.1 and ΔH_f°[Al(tmhd)$_3$(c)] = −571.5 ± 3.1 kcal mol^{-1}. Gas-phase enthalpies have been calculated, and from these the Al–O bond energies have been derived.

THE variation of the strength of a chemical bond between a metal and ligand atom in a series of related ligands has been interpreted in terms of various ligand parameters, particularly the acid or base dissociation constant. The quantitative measurements on which these generalizations depend are derived almost entirely from 'stability-constant' measurements in aqueous solution, so the chemical species to which the measurements refer are not the isolated molecule but some hydrated form. The hydration energy is comparable in magnitude to the lattice energy, a property not normally taken into account in discussions on stability yet which could vary over quite a large range for a series of compounds. 'Stability constants' are an index of reactivity rather than of thermodynamic stability, and although of great importance for reactions in aqueous solution they can only yield indirect information on the stability of the metal–ligand bond.

In this paper we present experimental data on some aluminium β-diketonates which give information on the metal–ligand bond strength of the isolated molecule in the vapour state.

EXPERIMENTAL

The calorimeter and its mode of operation have been described previously.[1] Aluminium chloride hexahydrate, 'constant-boiling' hydrochloric acid, and the ligands were prepared, purified, and analyzed as described before.[1,2]

Tris(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)*aluminium*(III), [Al(tmhd)$_3$].—This complex was prepared by a modification of the method of Hammond *et al.*[3] A solution of AnalaR aluminium potassium sulphate dodecahydrate (10 g) in water (200 cm^3) was buffered with sodium acetate (15 g). A solution of 2,2,6,6-tetramethylheptane-3,5-dione (10.8 g) in ethanol (15 cm^3) was added slowly with stirring to the aluminium solution until no further precipitation occurred. The solution was boiled for 1 h, cooled, and the aluminium complex filtered and dried. The complex was recrystallized twice from ethanol and sublimed, m.p. 263—264 °C (lit.,[3] 264—265 °C) (Found: C, 68.75; H, 10.05; Al, 4.70. Calc. for $C_{33}H_{57}AlO_6$: C, 68.75; H, 9.95; Al, 4.70%).

Tris(1,1,1-*trifluoropentane*-2,4-*dionato*)*aluminium*(III), [Al(tfpd)$_3$].—This complex was prepared by the method of Berg and Truemper,[4] extracted with benzene, dried, and twice sublimed, m.p. 122.0—122.5 °C (lit.,[4–6,7–8] 117 and 121—122 °C) (Found: C, 37.2; H, 2.55; Al, 5.55. Calc. for $C_{15}H_{12}AlF_9O_6$: C, 37.05; H, 2.50; Al, 5.55%).

Analyses.—All the carbon and hydrogen analyses were by the Microanalytical Service, University of Surrey; aluminium was analyzed both by ignition to the oxide Al_2O_3 and by a compleximetric method with ethylenediaminetetra-acetic acid (H_4edta).[9]

Method of Solution Calorimetry.—Decomposition of the complexes into metal ions and free ligands was extremely slow in dilute acid solutions, but satisfactory results could be obtained using the following solvents: dioxan–10 mol dm^{-3} sulphuric acid (4 : 1) for [Al(tmhd)$_3$]; dioxan–4.4 mol dm^{-3} hydrochloric acid (3 : 1) for [Al(tfpd)$_3$].

RESULTS AND DISCUSSION

The standard enthalpy of formation of the different aluminium complexes can be determined from reaction (1) between the ligand and aluminium chloride hexahydrate, to give a solution of the appropriate aluminium complex and hydrochloric acid. The difference between

$$3HL(l) + AlCl_3{\cdot}6H_2O(c) \xrightarrow{\Delta H_R} 3HCl{\cdot}2H_2O(aq) + [AlL_3]\ (c) \quad (1)$$

the enthalpies of solution of the products and reactants in the same stoicheiometric ratio gives the required enthalpy of formation, provided equilibrium is reached from either side within the period of the experiment.

To the calorimetric solvent (100 cm^3), ampoules of water, ligand, and $AlCl_3{\cdot}6H_2O$ were added consecutively and ΔH_1, ΔH_2, and ΔH_3 were measured. To a second portion of the same solvent (100.0 cm^3) were added consecutively ampoules of $HCl{\cdot}11.60H_2O$ and the aluminium complex, and ΔH_4 and ΔH_5 were measured. The general procedure, together with the general thermochemical cycle, is given in the Scheme. Thermochemical functions are expressed in terms of the thermochemical calorie (1 thermochemical calorie = 4.184 J) and refer to the isothermal process at 298.15 K. The uncertainty interval is twice the standard deviation of the mean.

The quantities of reactants in a series of experiments were determined by the amount of $AlCl_3{\cdot}6H_2O$ in the

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$$\begin{tikzcd}
\mathrm{AlCl_3{\cdot}6H_2O(c)} \arrow[dr, "\Delta H_3"] & + \mathrm{3HL(l)} \arrow[d, "\Delta H_2"] & + \mathrm{28.80H_2O(l)} \arrow[dl, "\Delta H_1"] \arrow[r, "\Delta H_\mathrm{R}"] & \mathrm{3(HCl{\cdot}11.60H_2O)} \arrow[d, "\Delta H_4"] & + \mathrm{[AlL_3](c)} \arrow[dl, "\Delta H_5"] \\
 & \text{Calorimetric solvent} & & \text{Calorimetric solvent} & \\
 & \text{Solution (A}_3\text{)} \arrow[rr, "\Delta H_6 = 0"] & & \text{Solution (B}_2\text{)} &
\end{tikzcd}$$

$$\text{Solvent} + \mathrm{H_2O} \xrightarrow{\Delta H_1} \text{Solution (A}_1\text{)}$$

$$\text{Solution (A}_1\text{)} + \mathrm{HL} \xrightarrow{\Delta H_2} \text{Solution (A}_2\text{)}$$

$$\text{Solution (A}_2\text{)} + \mathrm{AlCl_3{\cdot}6H_2O} \xrightarrow{\Delta H_3} \text{Solution (A}_3\text{)}$$

$$\text{Solvent} + \mathrm{HCl{\cdot}11.60H_2O} \xrightarrow{\Delta H_4} \text{Solution (B}_1\text{)}$$

$$\text{Solution (B}_1\text{)} + \mathrm{[AlL_3]} \xrightarrow{\Delta H_5} \text{Solution (B}_2\text{)}$$

$$\Delta H_\mathrm{R} = 28.80\,\Delta H_1 + 3\Delta H_2 + \Delta H_3 - 3\Delta H_4 - \Delta H_5 + \Delta H_6$$

SCHEME

particular ampoule; strict control of stoicheiometry was maintained throughout each series. When this procedure is used the value calculated for ΔH_R refers to the reaction indicated in the first line of the Scheme, provided that solutions (A_3) and (B_2) are identical and that

TABLE 1

Calorimetric study of $[\mathrm{Al(tmhd)_3}]$

(*a*) Addition of water to the solvent (dioxan–H_2SO_4)

H_2O (10^3 amount/mol)	$10^3(\Delta R/R_\mathrm{m})$	ε	ΔH_1/kcal mol^{-1}
2.894 7	5.546 4	1 366.2	−2.617
2.874 7	5.547 4	1 349.8	−2.605
2.889 6	5.552 2	1 349.8	−2.594
2.888 0	5.439 3	1 357.1	−2.556
2.653 8	5.014 5	1 360.1	−2.570
		Mean:	−2.59 ± 0.02

(*b*) Addition of Htmhd to solution (A_1)

Htmhd (10^4 amount/mol)	$10^4(\Delta R/R_\mathrm{m})$	ε	ΔH_2/kcal mol^{-1}
2.992 2	4.437 0	1 356.6	2.012
2.998 1	4.453 4	1 351.4	2.007
3.000 9	4.245 9	1 359.9	1.924
3.007 9	4.339 9	1 339.7	1.933
2.854 3	4.181 3	1 356.6	1.987
		Mean:	1.97 ± 0.04

(*c*) Addition of $AlCl_3{\cdot}6H_2O$ to solution (A_2)

$AlCl_3{\cdot}6H_2O$ (10^4 amount/mol)	$10^4(\Delta R/R_\mathrm{m})$	ε	ΔH_3/kcal mol^{-1}
0.992 8	2.555 8	1 377.6	3.291
0.999 8	2.434 7	1 340.4	3.264
1.006 5	2.589 6	1 301.7	3.349
1.011 0	2.589 5	1 301.8	3.334
0.879 7	2.211 5	1 279.0	3.215
		Mean:	3.29 ± 0.05

(*d*) Addition of $HCl{\cdot}11.60H_2O$ to solvent (dioxan–H_2SO_4)

$HCl{\cdot}11.60H_2O$ (10^4 amount/mol)	$10^4(\Delta R/R_\mathrm{m})$	ε	ΔH_4/kcal mol^{-1}
2.931 8	4.828 9	1 313.3	−21.631
2.993 4	4.828 8	1 357.6	−21.901
3.041 5	4.802 4	1 357.3	−21.431
3.144 2	4.877 4	1 402.8	−21.760
2.903 7	4.762 8	1 313.6	−21.546
		Mean:	−21.65 ± 0.16

(*e*) Addition of $[\mathrm{Al(tmhd)_3}]$ to solution (B_1)

$10^4[\mathrm{Al(tmhd)_3}] = 0.9685 - 1.0485$ mol

Mean: $\Delta H_5 = 0.00 \pm 0.02$ kcal mol^{-1}

In this reaction there was no temperature change. For the definitions of the resistances ΔR and R_m, and that of the energy constant, ε, of the calorimetric system, see ref. 1.

TABLE 2

Calorimetric study of $[\mathrm{Al(tfpd)_3}]$

(*a*) Addition of water to solvent (dioxan–HCl)

H_2O (10^3 amount/mol)	$10^4(\Delta R/R_\mathrm{m})$	ε	ΔH_1/kcal mol^{-1}
14.396 0	22.807 1	1 592.4	−0.252
7.197 4	10.276 4	1 618.8	−0.231
7.185 8	9.699 0	1 621.1	−0.219
7.191 9	8.102 4	1 627.8	−0.222
7.199 7	8.646 5	1.637 5	−0.197
6.537 9	8.064 4	1.621 8	−0.200
		Mean:	−0.22 ± 0.02

(*b*) Addition of Htpfd to solution (A_1)

Htfpd (10^4 amount/mol)	$10^3(\Delta R/R_\mathrm{m})$	ε	ΔH_2/kcal mol^{-1}
14.991 9	5.261 1	1 591.6	−5.585
7.514 5	2.565 0	1 615.5	−5.514
7.503 4	2.550 6	1 623.8	−5.520
7.509 3	2.528 8	1 624.8	−5.472
7.532 0	2.565 6	1 614.7	−5.500
6.938 8	2.329 4	1 600.8	−5.374
		Mean:	−5.49 ± 0.06

(*c*) Addition of $AlCl_3{\cdot}6H_2O$ to solution (A_2)

$AlCl_3{\cdot}6H_2O$ (10^4 amount/mol)	$10^3(\Delta R/R_\mathrm{m})$	ε	ΔH_3/kcal mol^{-1}
4.766 4	3.828 8	1 584.8	−12.730
2.511 6	1.999 3	1 619.3	−12.890
2.503 3	2.012 6	1 612.5	−12.964
2.507 0	2.011 3	1 620.7	−13.002
2 652 4	1.998 4	1 708.1	−12.869
2.493 8	1.979 2	1 612.5	−12.799
		Mean:	−12.88 ± 0.09

(*d*) Addition of $HCl{\cdot}11.60H_2O$ to solvent (dioxan–HCl)

$HCl{\cdot}11.60H_2O$ (10^4 amount/mol)	$10^3(\Delta R/R_\mathrm{m})$	ε	ΔH_4/kcal mol^{-1}
11.896 5	4.227 4	$\begin{cases} 1\,358.8 \\ 1\,358.6 \end{cases}$	−4.828
7.503 2	2.306 9	1 657.1	−5.095
7.027 1	2.127 8	1 616.5	−4.895
7.497 1	2.281 2	1 623.8	−4.941
7.506 5	2.298 9	1 613.4	−4.941
6.830 6	2.082 4	1 622.2	−4.946
		Mean:	−4.94 ± 0.07

(*e*) Addition of $[\mathrm{Al(tfpd)_3}]$ to solution (B_1)

$[\mathrm{Al(tfpd)_3}]$ (10^4 amount/mol)	$10^3(\Delta R/R_\mathrm{m})$	ε	ΔH_5/kcal mol^{-1}
5.001 6	2.569 2	1 619.1	−8.317
2.500 9	1.264 8	1 617.9	−8.182
2.340 3	1.213 6	1 614.1	−8.370
2.500 5	1.336 3	1 624.4	−8.681
2.558 3	1.388 8	1 617.5	−8.780
2.276 7	1.170 0	1 626.1	−8.356
		Mean:	−8.45 ± 0.19

the value of ΔH_6 is zero. As a check of the validity of this, ampoules of solutions (B_2) were broken into solution (A_3) in the calorimeter; no detectable heat change occurred. The experimental data for the different compounds studied is presented in Tables 1 and 2 leading to the ΔH_R values of -0.44 ± 0.76 kcal mol^{-1} for [Al(tmhd)$_3$] and -12.42 ± 0.67 kcal mol^{-1} for [Al(tfpd)$_3$].

The following data were used to calculate the enthalpies of formation of the crystalline and gaseous complexes: $\Delta H_f^\ominus[AlCl_3{\cdot}6H_2O(c)] = -643.3$;[10] $\Delta H_f^\ominus[HCl{\cdot}2H_2O(aq)] = -170.32$;[10] $\Delta H_f^\ominus$[Htmhd(l)] $= -146.2 \pm 1.0$;[11] $\Delta H_f^\ominus$[Htmhd(g)] $= -132.0 \pm 1.0$;[11] $\Delta H_f^\ominus$[Htfpd(l)] $= -249.3 \pm 1.0$;[11] $\Delta H_f^\ominus$[Htfpd(g)] $= -240.4 \pm 1.0$;[11] $\Delta H^\ominus$(subl) [Al(tmhd)$_3$] $= 28.53 \pm 0.28$;[12] and $\Delta H^\ominus$(subl)[Al(tfpd)$_3$] $= 25.51 \pm 0.41$ kcal mol^{-1}.[12] The results are given in Table 3 together with the corresponding values for the pentane-2,4-dionato-, tropolonato-, and 4-methyltropolonato-complexes.

TABLE 3

Standard enthalpies of formation (kcal mol^{-1})

Complex	$\Delta H_f^\ominus$(c)	$\Delta H^\ominus$(subl)	$\Delta H_f^\ominus$(g)
[Al(pd)$_3$] [a]	-428.46 ± 0.67 [b]	29.1 ± 1.0 [c]	-399.4 ± 1.2
[Al(tmhd)$_3$]	-571.5 ± 3.1	28.53 ± 0.28 [c]	-543.0 ± 3.1
[Al(tfpd)$_3$]	-892.7 ± 3.1	25.51 ± 0.41 [c]	-867.2 ± 3.1
[Al(trop)$_3$]	-361.96 ± 0.66 [d]	30.0 ± 5.0 [e]	-287.0 ± 5.0 [d]
[Al(4-Metrop)$_3$]	-329.8 ± 2.2 [d]	30.0 ± 5.0 [e]	-299.8 ± 5.5 [d]

[a] The values presented for this complex were recalculated from experimental data [J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 971] using more recent literature data. [b] R. J. Irving and M. A. V. Ribeiro da Silva, *Proc. 3rd Internat. Conf. Chem. Thermodynamics*, Baden bei Wien, 1973, **1**, 157. [c] Ref. 12. [d] Ref. 1. [e] Estimated.

The metal–oxygen bond strength can be related to the energy needed to break the molecule into metal and ligands. In order to remove condensed-state effects, this process must refer to the gaseous state as represented by equation (2). As the oxygens in β-diketonates are

$$Al(g) + 3L{\cdot}(g) \xrightarrow{\Delta H_f(r)} [AlL_3](g) \qquad (2)$$

known to be equivalent,[13] the aluminium–oxygen bond energy can be equated to one-sixth of this enthalpy of reaction, $E(Al{-}O) = -\frac{1}{6}\Delta H_f(r)$. As described in a previous paper,[1] we have taken 100 ± 5 kcal mol^{-1} for the dissociation energy of the enolic hydrogen. On this assumption and using the value of $\Delta H_f^\ominus$ [H·(g)] $= 52.095$ kcal mol^{-1},[10] the enthalpies of formation of the gaseous free radicals of the different ligands were calculated to be $\Delta H_f^\ominus$[(pd·(g)] $= -43.6 \pm 5.0$, $\Delta H_f^\ominus$[tmhd·(g)] $= -84.1 \pm 5.1$, and $\Delta H_f^\ominus$[tfpd(g)] $= -192.5 \pm 5.1$ kcal mol^{-1}. As $\Delta H_f^\ominus$[Al(g)] $= 78.0$ kcal mol^{-1},[10] values of ΔH_f(r) for the formation reaction of the different complexes can be calculated and hence the homolytic aluminium–oxygen bond-energy values, E(Al–O), as defined by the radical gas reaction. These values are presented in Table 4.

TABLE 4

Enthalpies of formation and bond energies (kcal mol^{-1}) for the gas and ionic complex-formation reactions

Complex	ΔH_f(r)	E (Al–O)	ΔH_f(i)	E' (Al–O)
[Al(pd)$_3$] [a]	-347 ± 15	58 ± 3	$-1\,478 \pm 15$	246 ± 3
[Al(tmhd)$_3$]	-369 ± 15	61 ± 3	$-1\,503 \pm 15$	250 ± 3
[Al(tfpd)$_3$]	-368 ± 15	61 ± 3	$-1\,502 \pm 15$	250 ± 3
[Al(trop)$_3$] [b]	-368 ± 15	61 ± 3	$-1\,468 \pm 15$	250 ± 3
[Al(4-Metrop)$_3$] [b]	-357 ± 15	60 ± 3	$-1\,487 \pm 15$	248 ± 3

[a] Recalculated from experimental data [J. O. Hill and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 971] using more accurate literature data.[1] [b] Ref. 1.

The bond energy in terms of the ions is defined by

$$Al^{3+}(g) + 3L^{-}(g) \xrightarrow{\Delta H_f(i)} [AlL_3](g) \qquad (3)$$

equation (3). Estimating the electron affinity, E_L, of the different ligands to be approximately equal to that of the oxygen atom for one electron ($E_L = 1.465$ eV $= 33.8$ kcal mol^{-1}),[14] the enthalpies of formation of the gaseous anions of the different ligands were calculated to be $\Delta H_f^\ominus[tmhd^{-}(g)] = -116.9 \pm 5$ and $\Delta H_f^\ominus[tfpd^{-}(g)] = -225.3 \pm 5$ kcal mol^{-1}. Values of ΔH_f(i) for the ionic gas formation reaction of the different complexes were calculated and hence the so-called heterolytic aluminium–oxygen bond-energy values, E' (Al-O), as defined by the ionic gas reaction (Table 4).

In attempting a rigorous determination of the bond energies, estimates of some enthalpies of formation and sublimation had to be made and, in addition, it was also necessary to estimate the dissociation energy of the enolic hydrogen from the parent ketoenolates. The resulting bond energies, therefore, have a large uncertainty attached to them. In spite of this uncertainty it is apparent that the Al–O bond energy is virtually identical in all the complexes. Inductive effects due to fluoride or the tropolone ring appear to have no influence on the donor properties of the oxygen, and the differences in the stability constants in solution could well be due to entropy effects associated with solute–solvent interactions.

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