Standard Enthalpies of Formation of Bis(pentane-2,4-dionato)copper(II) and Tetrakis[bis(pentane-2,4-dionato)cobalt(II)] and an Estimation of the Metal–Oxygen Bond Energies

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Standard enthalpies of formation of the title compounds have been determined by solution calorimetry at 298.15 K as −181.8 ± 0.5 and −826.6 ± 2.2 kcal mol^{-1} respectively. Estimates of the gas-phase enthalpies of the monomeric forms of the complexes lead to average bond energies of 38 kcal for Cu–O and 48 kcal for Co–O. In the solid tetramer the terminal Co–O bonds are almost twice as strong as the bridging Co–O bonds.

COBALT and copper both form complexes with acetylacetone (pentane-2,4-dione) of the form $M(acac)_2$. In neither case however is the structure that of a simple monomer. Copper acetylacetonate molecules are stacked in the crystal lattice in such a way that there is a weak interaction between the copper atom of one molecule with the C(3) atom of the neighbouring molecule.[1,2] Cobalt acetylacetonate is tetrameric with the metal atoms in a pseudo-octahedral environment and as in anhydrous nickel acetylacetonate there are both bridging and terminal oxygens.[3,4] As molecular-weight determinations give results which are a function of solvent and concentration, it appears that the octahedral environment persists to some extent in solution.[5,6]

In a previous paper [7] we reported thermochemical data for trimeric nickel acetylacetonate and showed that it was possible to subdivide the sum of bond energies so that values could be obtained for M–O bond energies where the oxygen was in either a terminal or a bridging situation with respect to the nickel atoms. We now extend this approach to cobalt and copper acetylacetonates.

EXPERIMENTAL

The Solution Calorimeter.—The isoperibol LKB 8 700 reaction-and-solution precision calorimeter was used for all the solution reactions. The operation and calculation methods have been described previously [7,8] and the symbols used here have the same meaning as before.

Thermochemical functions are expressed in terms of the ' thermochemical calorie ' (=4.814 J) and refer to the isothermal process at 298.15 K and the true mass. The uncertainty interval is twice the standard deviation of the mean. The accuracy of the calorimeter was checked by determining the heat of dissolution of tris[(hydroxymethyl)-amino]methane (tham) in dilute hydrochloric acid. The result, −7.118 ± 0.006 kcal mol^{-1}, is in good agreement with the literature [9] (−7.120 ± 0.007 kcal mol^{-1}).

Decomposition of the complexes into metal ion and free ligand is very rapid in 1 mol dm^{-3} sulphuric acid.

Materials.—Cobalt(II) sulphate hexahydrate was obtained from the corresponding heptahydrate (AnalaR) by dehydration in a vacuum desiccator until the composition was $Co[SO_4]\cdot 6.00\ H_2O$. Copper(II) sulphate pentahydrate was prepared as described before.[8] These compounds were stored in air-tight bottles for 2 weeks: analysis then showed no change in composition.

AnalaR grade B.D.H. acetylacetone (Hacac) was purified by successive fractional distillations (b.p. 140 °C at 760 mmHg †) and then stored under nitrogen in the dark. No impurities were detected by g.l.c. (Found: C, 60.1; H, 8.00. Calc. for $C_5H_8O_2$: C, 60.0; H, 8.05%).

Bis(pentane-2,4-dionato)copper(II) {copper acetylacetonate, $[Cu(acac)_2]$} was prepared by slowly adding a solution of copper(II) sulphate pentahydrate (4.0 g) and sodium acetate (7.5 g) in water (60 cm^3) to a solution of acetylacetone (4.0 g) in ethanol (100 cm^3). The complex was filtered off, washed with cold ethanol, dried, recrystallised from light petroleum (b.p. 60—80 °C), and sublimed at 200 °C (1 mmHg), m.p. =237 °C (lit.,[10] 235 °C) (Found: C, 45.8; H, 5.45; Cu, 24.4. Calc. for $C_{10}H_{14}CuO_4$: C, 45.9; H, 5.40; Cu, 24.3%).

Tetrakis[bis(pentane-2,4-dionato)cobalt(II)] (cobalt acetylacetonate, $[\{Co(acac)_2\}_4]$) was prepared by precipitating $[Co(acac)_2]\cdot 2H_2O$ as orange needles by the addition of an alkaline solution of acetylacetone to a cobalt(II) chloride solution. The dihydrate was dehydrated under vacuum [11] at 58 °C and the purple anhydrous compound was obtained. This was recrystallised from dried methanol and sublimed under vacuum (water pump), m.p. =100 °C (sublimes) (Found: C, 46.6; H, 5.40; Co, 22.8. Calc. for $C_{10}H_{14}CoO_4$: C, 46.7; H, 5.50; Co, 22.9%).

A 1 mol dm^{-3} solution of sulphuric acid was made from an AnalaR grade concentrated volumetric solution and checked by titration. It corresponded to the composition $H_2SO_4\cdot 53.544(l)H_2O$. All the carbon and hydrogen analyses were carried out by the Microanalytical Service of the University of Surrey; copper and cobalt were analysed by the ethylenediaminetetra-acetic acid methods.[12]

RESULTS AND DISCUSSION

The standard enthalpies of formation of the cobalt(II) and copper(II) acetylacetonates can be obtained from the heat change which occurs as a result of reactions (1) and (2). As equilibrium is rapidly reached from either side,

$$2\ Hacac(l) + Cu[SO_4]\cdot 5H_2O(c) \longrightarrow [Cu(acac)_2](c) + H_2SO_4\cdot 5H_2O(l) \quad (1)$$

$$8\ Hacac(l) + 4\ Co[SO_4]\cdot 6H_2O(c) \longrightarrow [\{Co(acac)_2\}_4](c) + 4\ H_2SO_4\cdot 6H_2O(l) \quad (2)$$

the difference between the enthalpies of solution of the products and reactants in the required stoicheiometric ratio gives the enthalpy of formation.

To the calorimetric solvent (100.0 cm^3), ampoules of

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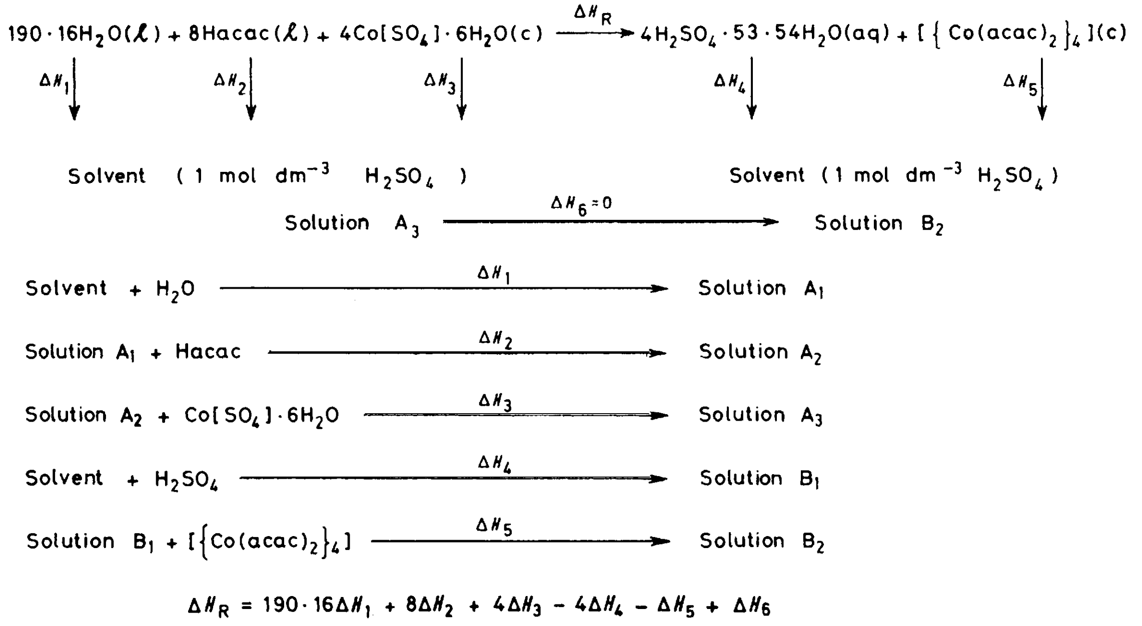
† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

water, acetylacetone, and the appropriate metal sulphate were added consecutively and ΔH_1, ΔH_2, and ΔH_3 were measured. In a second series of measurements ampoules of sulphuric acid and metal acetylacetonate were added to the calorimetric solvent, and ΔH_4 and ΔH_5 were obtained. The thermochemical cycle is shown in the Scheme. The quantities of reactants in any series of experiments were determined by the amount of metal sulphate in a particular ampoule.

The value obtained for ΔH_R refers to the reaction represented in the Scheme, provided that solutions A_3 and B_2 are identical and that the value of ΔH_6 is zero. This can only occur if precise stoicheiometry is realised. As a check, several ampoules of solution B_2 were broken into solution A_3 in the calorimeter and in no case could a heat change be detected (<5 × 10^{-5} °C).



SCHEME For copper the equation is: $48.54H_2O(l) + 2Hacac(l) + Cu[SO_4]\cdot5H_2O \xrightarrow{\Delta H_R} H_2SO_4\cdot53.54H_2O(aq) + [Cu(acac)_2]$ (c) and $\Delta H_R = 48.54\Delta H_1 + 2\Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 + \Delta H_6$

For $[\{Co(acac)_2\}_4]$.*—(*a*) *Addition of water to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). The heat change was calculated from published data[13] as $\Delta H_1 = -0.029$ kcal mol^{-1}.

(*b*) *Addition of* Hacac(l) *to solution* A_1. This enthalpy of solution has been determined before, during the study of tris[bis(pentane-2,4-dionato)nickel(II)],[7] and so $\Delta H_2 = 1.48 \pm 0.05$ kcal mol^{-1} (mean from five experiments).

(*b*) *Addition of* $Co[SO_4]\cdot6H_2O$(c) *to solution* A_2. $\Delta H_3 = 4.34 \pm 0.03$ kcal mol^{-1} (mean from five experiments). In a typical experiment, a solution of $Co[SO_4]\cdot6H_2O$ (49.312 mmol) in solution A_2 (100 cm^3) gave $\Delta R/R_m = 8.310\,6 \times 10^{-4}$; taking $\varepsilon = 2\,570.6$ cal, this leads to $\Delta H = 4.332$ kcal mol^{-1}.

(*d*) *Addition of* $H_2SO_4\cdot53.54H_2O$(aq) *to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). This heat change was calculated from published data[13] as $\Delta H_4 = 0.000$ kcal mol^{-1}.

(*e*) *Addition of* $[\{Co(acac)_2\}_4]$ *to solution* B_1. $\Delta H_5 = -38.22 \pm 0.24$ kcal mol^{-1} (mean from five experiments). In a typical experiment a solution of $[\{Co(acac)_2\}_4]$ (12.277 mmol) in solution B_1 (100 cm^3) gave $\Delta R/R_m = 1.847\,9 \times 10^{-3}$; taking $\varepsilon = 2\,570.4$ cal this leads to $\Delta H = -38.689$ kcal mol^{-1}.

The above results lead to $\Delta H_R = 61.92 \pm 0.48$ kcal mol^{-1} for the formation reaction of $[\{Co(acac)_2\}_4]$(c).

For $[Cu(acac)_2]$—(*a*) *Addition of water to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). The heat change was calculated from published data[13] as $\Delta H_1 = -0.029$ kcal mol^{-1}.

(*b*) *Addition of* Hacac(l) *to solution* A_1. This enthalpy of solution has been measured before:[7] $\Delta H_2 = 1.48 \pm 0.05$ kcal mol^{-1} (mean from five experiments).

(*c*) *Addition of* $Cu[SO_4]\cdot5H_2O$(c) *to solution* A_2. $\Delta H_3 = 5.36 \pm 0.03$ kcal mol^{-1} (mean from six experiments). In a typical experiment, a solution of $Cu[SO_4]\cdot5H_2O$ (48.923 mmol) in solution A_2 (100 cm^3) gave $\Delta R/R_m = 1.028\,4 \times 10^{-3}$; taking $\varepsilon = 2\,571.3$ cal, this leads to $\Delta H_3 = 5.405$ kcal mol^{-1}.

(*d*) *Addition of* $H_2SO_4\cdot53.54H_2O$(aq) *to* 100.0 cm^3 *of solvent* (1 mol dm^{-3} H_2SO_4). This heat change was calculated from published data[13] as $\Delta H_4 = 0.000$ kcal mol^{-1}.

(*e*) *Addition of* $[Cu(acac)_2]$ *to solution* B_1. $\Delta H_5 = -5.18 \pm 0.01$ kcal mol^{-1} (mean from five experiments). In a typical experiment a solution of $[Cu(acac)_2]$ (49.099 mmol) in solution B_1 (100 cm^3) gave $\Delta R/R_m = 9.920\,5 \times 10^{-4}$; taking $\varepsilon = 2\,573.0$ cal this leads to $\Delta H = -5.199$ kcal mol^{-1}.

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* Further details of the calorimetric data for both complexes are available as Supplementary Publication No. SUP 22878 (3 pp.). See Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

The above results lead to $\Delta H_{\mathrm{R}} = 12.09 \pm 0.10$ kcal mol^{-1} for the formation reaction of $[\mathrm{Cu(acac)_2}](\mathrm{c})$.

The following data (kcal mol^{-1}) were used to calculate the standard enthalpies of formation of the crystalline complexes: $\Delta H_f^{\ominus}(\mathrm{Hacac,l}) = -101.29 \pm 0.37$;[14,15] $\Delta H_f^{\ominus}(\mathrm{Cu[SO_4]\cdot 5H_2O}) = -544.85$;[16] $\Delta H_f^{\ominus}(\mathrm{Co[SO_4]\cdot 6H_2O}) = -641.4$;[16] $\Delta H_f^{\ominus}(\mathrm{H_2O,l}) = -68.315$;[13] and $\Delta H_f^{\ominus}(\mathrm{H_2SO_4\cdot 53.54H_2O,aq}) = -3\,869.551$.[13] The results are $\Delta H_f^{\ominus}[\{\mathrm{Co(acac)_2}\}_4,\mathrm{c}] = -826.6 \pm 2.2$ and $\Delta H_f^{\ominus}[\mathrm{Cu(acac)_2,c}] = -181.8 \pm 0.5$ kcal mol^{-1}.

A previously reported value for the enthalpy of formation of crystalline cobalt(II) acetylacetonate is -208.8 ± 0.9 kcal mol^{-1},[17] in reasonable agreement with the value obtained in this work. Published values for copper(II) acetylacetonate, -185.0 [18] and -187.0 ± 0.7 kcal mol^{-1},[17,19] are both somewhat higher than our value, and at present there is no explanation for this difference.

There is no direct information available on the heat of sublimation of either copper or cobalt acetylacetonate so it is necessary to make an estimate of this to permit the calculation of bond energies. Beryllium acetylacetonate with a tetrahedral structure has an enthalpy of sublimation [20] of 22.5 kcal mol^{-1}, whilst nickel acetylacetonate which is monomeric and planar in the vapour state has an enthalpy of sublimation [20] of 22.9 kcal mol^{-1}. It appears that it is the number of ligand molecules rather than the stereochemistry or the particular metal which determines the enthalpy of sublimation,[21] so the value for copper acetylacetonate is taken to be 25 ± 4 kcal mol^{-1} after an allowance of 2 kcal has been made for the weak intermolecular interaction in the solid state.[22] In the case of cobalt acetylacetonate a value of 23 kcal mol^{-1} would be reasonable for sublimation of solid monomer. The heat of tetramerisation will be at the most 5 kcal per cobalt atom, by analogy with the value obtained for nickel acetylacetonate,[7] so the enthalpy of sublimation of tetrameric cobalt acetylacetonate to the monomeric gas is estimated to be 28 ± 4 kcal mol^{-1} and refers to the process (3).

$$\tfrac{1}{4}[\{\mathrm{Co(acac)_2}\}_4](\mathrm{c}) \longrightarrow [\mathrm{Co(acac)_2}](\mathrm{g}) \qquad (3)$$

The enthalpies of formation of the gaseous molecules are $\Delta H_f^{\ominus}[\mathrm{Cu(acac)_2,g}] = -156.8 \pm 4.0$ and $\Delta H_f^{\ominus}[\mathrm{Co(acac)_2,g}] = -178.6 \pm 4.0$ kcal mol^{-1}. Using the values $\Delta H_f^{\ominus}(\mathrm{H\cdot,g}) = 52.1$,[13] $\Delta H_f^{\ominus}(\mathrm{acac\cdot,g}) = -43.6 \pm 5.1$,[23] $\Delta H_f^{\ominus}(\mathrm{Cu,g}) = 80.86$,[16] and $\Delta H_f^{\ominus}(\mathrm{Co,g}) = 101.5$ kcal mol^{-1},[16] the enthalpy change can be calculated for the radical reaction (4). The value obtained, -150 ± 7 kcal mol^{-1}, is the sum of the Cu–O bond energies and the average Cu–O homolytic bond energy is 38 ± 2 kcal.

$$\mathrm{Cu(g)} + 2\mathrm{acac\cdot(g)} \longrightarrow [\mathrm{Cu(acac)_2}](\mathrm{g}) \qquad (4)$$

This is very close to the value which has been determined in previous studies with other copper(II) β-diketonates: 37 ± 3 kcal mol^{-1} for bis(tropolonato)copper(II)* and 41 ± 3 kcal mol^{-1} for bis(benzoylacetonato)copper(II).[24]

Kakolowicz and Giera,[19] using an estimated value of 15 kcal mol^{-1} for the heat of sublimation of $[\mathrm{Cu(acac)_2}]$, based on experimentally determined values for analogous compounds,[25] calculated the Cu–O homolytic bond energy as 43.5 kcal mol^{-1}. The experimental values which form the basis of this estimation are now suspected to be far too low: that for $[\mathrm{Al(acac)_3}]$ for instance being quoted [25] as 4.58 kcal mol^{-1} and $[\mathrm{Be(acac)_2}]$ as 8.51 kcal mol^{-1}, whereas more recent experiments [20] give values of 28.7 and 22.5 kcal mol^{-1} respectively. Recently,[26] a selected value of 28.4 ± 1.9 kcal mol^{-1} has been proposed for the sublimation enthalpy of $[\mathrm{Al(acac)_3}]$.

If Kakolowicz and Giera's value for the enthalpy of sublimation of $[\mathrm{Cu(acac)_2}]$ is replaced by that presented in this paper, a recalculation of their bond energy for Cu–O gives a value of 39 kcal mol^{-1}, in agreement with our value.

For the process (5) $\Delta H_{\mathrm{f.r.}} = -193.0 \pm 8$ kcal mol^{-1} and hence the homolytic Co–O bond energy is 48 ± 2 kcal.

$$\mathrm{Co(g)} + 2\mathrm{acac\cdot(g)} \longrightarrow [\mathrm{Co(acac)_2}](\mathrm{g}) \qquad (5)$$

One can obtain some information on the relative strengths of the bridging and non-bridging Co–O bonds by considering the molecule to exist as a tetramer in the gaseous state. Its enthalpy of formation will be [7] four times that of the monomer plus an assumed value of 20 kcal for the tetramerisation energy: $\Delta H_{\mathrm{f.r.}} = -792 \pm 13$ kcal mol^{-1} for equation (6). The total energy of 792 kcal has to be divided amongst 24 Co–O bonds, 16 of them bridging and eight non-bridging. Consideration of a large number of metal β-diketonates shows that, within the necessarily large experimental error, the nature of the ligand has no effect on the bond strength.[7,8,23] Accordingly the terminal, or non-bridging, Co–O bonds are assigned the value 48 ± 2 kcal as in the monomer. The total bond energy assigned to the bridging oxygens is 408 kcal and this leads to a value of 25.5 kcal for each bridging Co–O bond. It should be noted that both the terminal and bridging Co–O bond energies have almost the same values as the corresponding Ni–O bonds,[7] but of course the same proviso with respect to lattice forces must be taken into account.

$$4\mathrm{Co(g)} + 8\mathrm{acac\cdot(g)} \longrightarrow [\{\mathrm{Co(acac)_2}\}_4](\mathrm{g}) \qquad (6)$$

Kakolowicz and Giera [17] calculated the Co–O bond energy as 55.3 kcal based on the low estimate of 15 kcal mol^{-1} for the enthalpy of sublimation, and furthermore took no account of the fact that cobalt(II) acetylacetonate is tetrameric in the solid but monomeric in the gaseous state.[6] Jones *et al.*[18] have reported a value of 63.7 kcal mol^{-1} for the Co–O bond energy. This is based on an inexplicably high value of the enthalpy of formation of the crystalline solid ($\Delta H_f^{\ominus} = -367$ kcal mol^{-1}) derived from the heat of combustion. Again no account was taken of the tetrameric nature of the crystalline solid.

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* Recalculated from ref. 8; tropolone = 2-hydroxycyclohepta-2,4,6-trien-1-one.

X-Ray analysis of tetrameric cobalt(II) acetylacetonate [27] shows an average Co-O distance of 2.24 Å for the bridging acetylacetonates and 2.06 Å for the terminal ligands. The O–Co–O angle for terminal ligands is 90° but this is reduced to 73° for bridging ligands.

The difference in strength between the terminal and bridging Co-O bonds obviously depends on a number of factors which cannot be evaluated quantitatively but all of which qualitatively point to the bridging bonds being weaker than the terminal. There is the possibility of d_π–p_π bonding in the planar ring system associated with the terminal oxygens, but this augmentation of bond strength is precluded for the bridging oxygens which lie in a plane at right angles. Furthermore the distortion of the bridging O–Co–O angles must lead to less effective overlap of the appropriate orbitals.

In a terminal acetylacetone ligand the two oxygens are equivalent [28] so there is effectively half a negative charge associated with each donor O–Co bond. In the case of the bridging ligands this charge must be shared between two cobalt atoms with consequent reduction in the bond strength. The ease with which the bridging bonds are broken in solution is consistent with the considerable weakening of bridging Co–O bonds demonstrated by the thermochemical studies.

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