Standard Enthalpies of Formation of the Tetra-μ-acetato-derivatives of Dimolybdenum(II), Chromium(II)–Molybdenum(II), Dichromium(II), and Dichromium(II) Dihydrate, and Di-μ-acetato-bis(pentane-2,4-dionato)dimolybdenum(II), and their Metal–Metal Bond Enthalpy Contributions

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The following standard enthalpies (kJ mol^{-1}) of formation of the crystalline solids at 298.15 K have been determined using solution reaction calorimetry: $\Delta H_f^{\ominus}[\mathrm{Mo_2(O_2CMe)_4,c}] = -1\,970.7 \pm 8.4$, $\Delta H_f^{\ominus}[\mathrm{CrMo(O_2CMe)_4,c}] = -2\,113.9 \pm 6.4$, $\Delta H_f^{\ominus}[\mathrm{Cr_2(O_2CMe)_4,c}] = -2\,297.5 \pm 6.6$, $\Delta H_f^{\ominus}[\mathrm{Cr_2(O_2CMe)_4.2H_2O,c}] = -2\,875.4 \pm 6.7$, and $\Delta H_f^{\ominus}[\mathrm{Mo_2(O_2CMe)_2(pd)_2,c}]$ (pd = pentane-2,4-dionate) = $-1\,805.0 \pm 8.9$. The corresponding metal–metal bond enthalpy contributions in the gaseous species have been assessed as $\bar{D}$(Mo–Mo) = 334, $\bar{D}$(Cr–Mo) = 249, and $\bar{D}$(Cr–Cr) = 205 kJ mol^{-1}. The bond enthalpy contribution for the co-ordination of each water molecule in $[\mathrm{Cr_2(O_2CMe)_4}]\cdot 2\mathrm{H_2O}$ has been estimated as 44 kJ mol^{-1}.

THE preparation and characterisation of compounds which contain two metal atoms directly linked by a multiple bond has attracted considerable interest during the past 15 years.[1] Recently, attention has been focused on the strengths of these bonds. From studies of the photolytic cleavage of $[\mathrm{Re_2Cl_8}]^{2-}$ it was suggested [2] that the dissociation energy of this Re–Re quadruple bond is *ca.* 300 kJ mol^{-1}. Subsequent discussions, however, raised this estimate to become more consistent with the bond dissociation energies, D(Mo–Mo) = 480—550 and D(Re–Re) = 460—670 kJ mol^{-1} obtained [3] by applying the Birge–Sponer extrapolation to resonance-Raman data for $[\mathrm{Mo_2Cl_8}]^{4-}$ and $[\mathrm{Re_2Cl_8}]^{2-}$. Further studies of this type were made by Clark and D'Urso,[4] which led to estimates of *ca.* 500 kJ mol^{-1} for the Mo–Mo and Re–Re quadruple bond-dissociation energies in their octachloro- and octabromo-complexes. Thermochemical investigations by solution-reaction calorimetry of $[\mathrm{M_2(NMe_2)_6}]$ (M = Mo or W), $[\mathrm{Mo(NMe_2)_4}]$, and $[\mathrm{W(NMe_2)_6}]$ were interpreted as indicating that $\bar{D}$(Mo≡Mo) and $\bar{D}$(W≡W) are within the ranges 592 ± 196 and 775 ± 218 kJ mol^{-1} respectively.[5]

This paper reports the enthalpies of formation of $[\mathrm{Mo_2(O_2CMe)_4}]$, $[\mathrm{CrMo(O_2CMe)_4}]$, $[\mathrm{Cr_2(O_2CMe)_4}]$, $[\mathrm{Cr_2(O_2CMe)_4}]\cdot 2\mathrm{H_2O}$, and $[\mathrm{Mo_2(O_2CMe)_2(pd)_2}]$ (pd = penta-2,4-dionate); these were determined to permit assessment of the contribution of the metal–metal bond to the chemical binding energy in the corresponding $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ (M = Cr or Mo) species. This study is also of interest in relation to the discussions [6-10] of differences between the electronic structures of the Cr–Cr and Mo–Mo interactions in these molecules.

EXPERIMENTAL

Analytically pure samples of $[\mathrm{Mo_2(O_2CMe)_4}]$,[11] $[\mathrm{CrMo(O_2CMe)_4}]$,[12] $[\mathrm{Cr_2(O_2CMe)_4}]$,[13] $[\mathrm{Cr_2(O_2CMe)_4}]\cdot 2\mathrm{H_2O}$,[14] and $[\mathrm{Mo(O_2CMe)_2(pd)_2}]$ [15] were prepared and purified as previously described. Sodium chromate(VI) was prepared as described by Kusnetsova *et al.*[16] Acetic acid (B.D.H., AnalaR) was distilled prior to use, and the remaining compounds in the reaction schemes were prepared and purified as previously described.[17]

The solution-reaction calorimetric method was chosen for determination of the enthalpies of formation of these compounds since each is quantitatively hydrolysed and molybdenum(II) is oxidised to molybdenum(VI) and/or chromium(II) oxidised to chromium(III) in a strongly acidic aqueous solution of iron(III) chloride. The calorimeter and auxiliary equipment have been described.[17] The accuracy was checked by measuring the enthalpy of solution of tris(hydroxymethyl)methylamine in hydrochloric acid (0.1 mol dm^{-3}): the result, -245.77 ± 0.37 J g^{-1}, agrees with that of Kilday and Prosen,[18] -245.76 ± 0.26 J g^{-1}.

RESULTS

The thermochemical reactions for determining the enthalpies of formation of $[\mathrm{Mo_2(O_2CMe)_4}]$, $[\mathrm{CrMo(O_2CMe)_4}]$, $[\mathrm{Cr_2(O_2CMe)_4}]$, $[\mathrm{Cr_2(O_2CMe)_4}]\cdot 2\mathrm{H_2O}$, and $[\mathrm{Mo_2(O_2CMe)_2(pd)_2}]$ were (1)—(5) respectively.

$$[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{c}) + 8\mathrm{FeCl_3}(\mathrm{c}) + 8\mathrm{H_2O}(\mathrm{l}) + 4\mathrm{NaCl}(\mathrm{c}) \longrightarrow 2\mathrm{Na_2[MoO_4]}(\mathrm{c}) + 8\mathrm{FeCl_2}(\mathrm{c}) + 12\mathrm{HCl}(\text{in } 7.97\mathrm{H_2O})(\mathrm{l}) + 4\mathrm{MeCO_2H}(\mathrm{l}) \quad (1)$$

$$[\mathrm{CrMo(O_2CMe)_4}](\mathrm{c}) + 8\mathrm{FeCl_3}(\mathrm{c}) + 8\mathrm{H_2O}(\mathrm{l}) + 4\mathrm{NaCl}(\mathrm{c}) \longrightarrow \mathrm{Na_2[MoO_4]}(\mathrm{c}) + \mathrm{Na_2[CrO_4]}(\mathrm{c}) + 8\mathrm{FeCl_2}(\mathrm{c}) + 12\mathrm{HCl}(\text{in } 7.97\mathrm{H_2O})(\mathrm{l}) + 4\mathrm{MeCO_2H}(\mathrm{l}) \quad (2)$$

$$[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{c}) + 8\mathrm{FeCl_3}](\mathrm{c}) + 8\mathrm{H_2O}(\mathrm{l}) + 4\mathrm{NaCl}(\mathrm{c}) \longrightarrow 2\mathrm{Na_2[CrO_4]}(\mathrm{c}) + 8\mathrm{FeCl_2}(\mathrm{c}) + 12\mathrm{HCl}(\text{in } 7.97\mathrm{H_2O})(\mathrm{l}) + 4\mathrm{MeCO_2H}(\mathrm{l}) \quad (3)$$

$$[\mathrm{Cr_2(O_2CMe)_4}]\cdot 2\mathrm{H_2O}(\mathrm{c}) + 8\mathrm{FeCl_3}(\mathrm{c}) + 6\mathrm{H_2O}(\mathrm{l}) + 4\mathrm{NaCl}(\mathrm{c}) \longrightarrow 2\mathrm{Na_2[CrO_4]}(\mathrm{c}) + 8\mathrm{FeCl_2}(\mathrm{c}) + 12\mathrm{HCl}(\text{in } 7.97\mathrm{H_2O})(\mathrm{l}) + 4\mathrm{MeCO_2H}(\mathrm{l}) \quad (4)$$

$$[\mathrm{Mo_2(O_2CMe)_2(pd)_2}](\mathrm{c}) + 8\mathrm{FeCl_3}(\mathrm{c}) + 8\mathrm{H_2O}(\mathrm{l}) + 4\mathrm{NaCl}(\mathrm{c}) \longrightarrow 2\mathrm{Na_2[MoO_4]}(\mathrm{c}) + 8\mathrm{FeCl_2}(\mathrm{c}) + 2\mathrm{MeCO_2H}(\mathrm{l}) + 12\mathrm{HCl}(\text{in } 7.97\mathrm{H_2O})(\mathrm{l}) + 2\mathrm{Hpd}(\mathrm{l}) \quad (5)$$

The standard enthalpy of each of these reactions $[\Delta H_r^{\ominus}(1)$—$\Delta H_r^{\ominus}(5)]$ was determined by measuring the enthalpy of solution of each reactant and product successively in the calorimetric solvent. The concentrations were chosen so that the final solution resulting from the dissolution of all the reactants approached the same composition and was of the same enthalpy as the corresponding solution from the dissolution of all the products. The molar enthalpies of solution of $\mathrm{Na_2[MoO_4]}$(c) and of $\mathrm{Na_2[CrO_4]}$(c) were independent of concentration over a range five times that required for the reaction scheme; moreover, the molar enthalpy of solution of $\mathrm{Na_2[CrO_4]}$(c)

TABLE 1

Enthalpies of reaction and solution at 298.15 K

	Reaction	Solution	Number of experiments	ΔH (298 K)/kJ mol^{-1}
(1)	$H_2O(l)$ + initial solvent	A_1	4	-0.05 ± 0.00
(2)	$NaCl(c)$ + solution A_1	A_2	5	$+5.27 \pm 0.05$
(3)	$FeCl_3$ + solution A_2	A_3	5	-117.46 ± 0.37
(4)	$[Mo_2(O_2CMe)_4](c)$ + solution A_3	F_1	8	-200.88 ± 0.49
(5)	$[CrMo(O_2CMe)_4](c)$ + solution A_3	$(F_1 + F_2)$	3	-220.93 ± 0.38
(6)	$[Cr_2(O_2CMe)_4](c)$ + solution A_3	F_2	5	-200.66 ± 0.71
(7)	$[Cr_2(O_2CMe)_4]\cdot 2H_2O(c)$ + solution A_3	F_2	7	-194.47 ± 1.00
(8)	$[Mo_2(O_2CMe)_2(pd)_2](c)$ + solution A_3	F_1	4	-246.61 ± 0.79
(9)	$MeCO_2H(l)$ + initial solvent	B_1	5	-0.56 ± 0.01
(10)	HCl (in $7.97H_2O$)(l) + solution B_1	B_2	4	-2.52 ± 0.01
(11)	$FeCl_2(c)$ + solution B_2	B_3	5	-69.43 ± 0.15
(12)	Hpd(l) + solution B_3	B_4	3	-1.08 ± 0.05
(13)	$Na_2[MoO_4](c)$ + solution B_4	F_1	5	-53.62 ± 0.69
(14)	$Na_2[CrO_4](c)$ + solution B_3	F_2	5	-340.50 ± 0.44

was independent of the presence of $Na_2[MoO_4]$ in the solvent and *vice versa*. Similarly, the molar enthalpy of solution of Hpd(l) was unaffected by the presence of acetic acid in the solvent.

The initial solvent was composed of $FeCl_3$, HCl, $HClO_4$, and H_2O in the mol ratio 1 : 15 : 30 : 1 000. The enthalpies of reaction and solution are listed in Table 1 where, in accordance with normal thermochemical practice, the errors assigned are uncertainty intervals,[19] *i.e.* twice the standard deviation of the mean.

The standard enthalpies of the thermochemical reactions (1)—(5) are given by (6)—(10) respectively.

$$\begin{aligned}\Delta H_r^{\ominus}(1) &= 103.64\Delta H_1 + 4\Delta H_2 + 8\Delta H_3 + \Delta H_4 - \\ &\quad 4\Delta H_9 - 12\Delta H_{10} - 8\Delta H_{11} - 2\Delta H_{13} \\ &= -429.5 \pm 3.5 \text{ kJ mol}^{-1}\end{aligned} \tag{6}$$

$$\begin{aligned}\Delta H_r^{\ominus}(2) &= 103.64\Delta H_1 + 4\Delta H_2 + 8\Delta H_3 + \Delta H_5 - 4\Delta H_9 - \\ &\quad 12\Delta H_{10} - 8\Delta H_{11} - \Delta H_{13} - \Delta H_{14} \\ &= -162.7 \pm 3.3 \text{ kJ mol}^{-1}\end{aligned} \tag{7}$$

$$\begin{aligned}\Delta H_r^{\ominus}(3) &= 103.64\Delta H_1 + 4\Delta H_2 + 8\Delta H_3 + \Delta H_6 - \\ &\quad 4\Delta H_9 - 12\Delta H_{10} - 8\Delta H_{11} - 2\Delta H_{14} \\ &= 144.5 \pm 3.4 \text{ kJ mol}^{-1}\end{aligned} \tag{8}$$

$$\begin{aligned}\Delta H_r^{\ominus}(4) &= 101.64\Delta H_1 + 4\Delta H_2 + 8\Delta H_3 + \Delta H_7 - \\ &\quad 4\Delta H_9 - 12\Delta H_{10} - 8\Delta H_{11} - 2\Delta H_{14} \\ &= 150.8 \pm 3.5 \text{ kJ mol}^{-1}\end{aligned} \tag{9}$$

$$\begin{aligned}\Delta H_r^{\ominus}(5) &= 103.64\Delta H_1 + 4\Delta H_2 + 8\Delta H_3 + \Delta H_8 - 2\Delta H_9 - \\ &\quad 12\Delta H_{10} - 8\Delta H_{11} - 2\Delta H_{12} - 2\Delta H_{13} \\ &= -474.2 \pm 3.6 \text{ kJ mol}^{-1}\end{aligned} \tag{10}$$

The standard enthalpies of formation of the crystalline solids, given in Table 2, are derived from the above standard enthalpies of reaction and the following auxiliary data, in kJ mol^{-1} at 298.15 K: $\Delta H_f^{\ominus}(NaCl,c) = -411.00 \pm 0.01$,[20] $\Delta H_f^{\ominus}(HCl\cdot 7.97H_2O,l) = -160.00 \pm 0.01$,[20] $\Delta H_f^{\ominus}(H_2O,l) = -285.83 \pm 0.01$,[21] $\Delta H_f^{\ominus}(MeCO_2H,l) = -484.3 \pm 0.3$,[22] $\Delta H_f^{\ominus}(Hpd,l) = -423.8 \pm 1.5$,[22] $\Delta H_f^{\ominus}(FeCl_2,c) - \Delta H_f^{\ominus}(FeCl_2,c) = -57.70 \pm 0.46$,[23] $\Delta H_f^{\ominus}(Na_2[MoO_4],c) = -1\,467.6 \pm 3.3$,[24] and $\Delta H_f^{\ominus}(Na_2[CrO_4],c) = -1\,344.0 \pm 2.1$.[24, 25]

TABLE 2

Standard enthalpies (kJ mol^{-1}) of formation at 298.15 K

Compound	$\Delta H_f^{\ominus}(c)$	ΔH_f (sub.) (est.)	$\Delta H_f^{\ominus}(g)$
$[Mo_2(O_2CMe)_4]$	$-1\,970.7 \pm 8.4$	145	$-1\,826$
$[CrMo(O_2CMe)_4]$	$-2\,113.9 \pm 6.4$	145	$-1\,969$
$[Cr_2(O_2CMe)_4]$	$-2\,297.5 \pm 6.6$	145	$-2\,153$
$[Cr_2(O_2CMe)_4]\cdot 2H_2O$	$-2\,875.4 \pm 6.7$	150	$-2\,725$
$[Mo_2(O_2CMe)_2(pd)_2]$	$-1\,805.0 \pm 8.9$	145	$-1\,660$

No experimental data are available for the enthalpies of sublimation of these compounds, but from the sublimation temperatures at *ca.* 10^{-3} Torr * of $[Mo_2(O_2CMe)_4]$,[1] $[CrMo(O_2CMe)_4]$,[13] and $[Cr_2(O_2CMe)_4]$,[6] $\Delta H^{\ominus}$(sub.) is estimated to be 145 kJ mol^{-1}, similar values being found for compounds of comparable molecular mass. That for $[Cr_2(O_2CMe)_4]\cdot 2H_2O$ is estimated to be slightly larger, 150 kJ mol^{-1}, but this is hypothetical as it is improbable that this molecule would have an independent existence in the gaseous state.

DISCUSSION

To derive metal–metal bond enthalpy contributions from the data in Table 2, some assumptions must be made concerning the transferability of bond enthalpy contributions. For $[Mo_2(O_2CMe)_4](g)$, $[Mo_2(O_2CMe)_2(pd)_2](g)$, and $[Mo(pd)_3](g)$ it is assumed that: (*i*) $\bar{D}$(Mo–Mo) is the same in $[Mo_2(O_2CMe)_4](g)$ and in $[Mo_2(O_2CMe)_2(pd)_2](g)$; *r*(Mo–Mo) in the molecules in the crystalline state is 2.093(1) (ref. 1) and 2.129(1) Å (ref. 15) respectively; (*ii*) $\bar{D}(Mo–O)_{O_2CMe}$ is the same for the binding of the acetato-groups in $[Mo_2(O_2CMe)_4](g)$ and in $[Mo_2(O_2CMe)_2(pd)_2](g)$; in both molecules the acetato-groups bridge the metal centres and the dimensions within these MoOC(Me)OMo bridges are not significantly different in any respect; (*iii*) $\bar{D}(Mo–O)_{pd}$ is the same for the binding of the pentane-2,4-dionato-groups in $[Mo_2(O_2CMe)_2(pd)_2](g)$ and in $[Mo(pd)_3](g)$; in the former a bidentate pentane-2,4-dionato-group is bound to each molybdenum atom and this form of co-ordination is expected in $[Mo(pd)_3]$.[26]

The enthalpies of disruption of these molecules can be equated to the sum of the appropriate bond enthalpy contributions [equations (11)—(13)]. From (11)—(13),

$$[Mo_2(O_2CMe)_4](g) \longrightarrow 2Mo(g) + 4MeCO_2(g)$$

$$\begin{aligned}\bar{D}(Mo–Mo) + 8\bar{D}(Mo–O)_{O_2CMe} &= 2\Delta H_f^{\ominus}(Mo,g) + \\ &\quad 4\Delta H_f^{\ominus}(MeCO_2,g) - \Delta H_f^{\ominus}[Mo_2(O_2CMe)_4,g]\end{aligned} \tag{11}$$

$$[Mo_2(O_2CMe)_2(pd)_2](g) \longrightarrow 2Mo(g) + 2MeCO_2(g) + 2pd(g)$$

$$\begin{aligned}\bar{D}(Mo–Mo) &+ 4\bar{D}(Mo–O)_{O_2CMe} + 4\bar{D}(Mo–O)_{pd} \\ &= 2\Delta H_f^{\ominus}(Mo,g) + 2\Delta H_f^{\ominus}(MeCO_2,g) + \\ &\quad 2\Delta H_f^{\ominus}(pd,g) - \Delta H_f^{\ominus}[Mo_2(O_2CMe)_2(pd)_2,g]\end{aligned} \tag{12}$$

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

$$[\mathrm{Mo(pd)_3}](\mathrm{g}) \longrightarrow \mathrm{Mo(g)} + 3\mathrm{pd(g)}$$

$$6\bar{D}(\mathrm{Mo{-}O})_{\mathrm{pd}} = \Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) + 3\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{pd,g}) - \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo(pd)_3,g}] \quad (13)$$

$$\bar{D}(\mathrm{Mo{-}Mo}) = \tfrac{2}{3}\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) + \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo_2(O_2CMe)_4,g}] - 2\Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo_2(O_2CMe)_2(pd)_2,g}] + \tfrac{4}{3}\Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo(pd)_3,g}] \quad (14)$$

equation (14) can be derived. With the following auxiliary data at 298.15 K in kJ mol^{-1}, $\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) = 658.1 \pm 2.1$ [24] and $\Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo(pd)_3,g}] = -1\,198.9 \pm 6.6$,[17] then $\bar{D}(\mathrm{Mo{-}Mo}) = 334.2$ kJ mol^{-1}. To derive $\bar{D}(\mathrm{Cr{-}Mo})$ and $\bar{D}(\mathrm{Cr{-}Cr})$ in the corresponding $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ species an additional assumption is made: (*iv*) $\bar{D}(\mathrm{Mo{-}O})_{\mathrm{pd}} - \bar{D}(\mathrm{Cr{-}O})_{\mathrm{pd}} = \bar{D}(\mathrm{Mo{-}O})_{\mathrm{O_2CMe}} - \bar{D}(\mathrm{Cr{-}O})_{\mathrm{O_2CMe}}$. Considering the disruption of $[\mathrm{Cr(pd)_3}](\mathrm{g})$ similarly to $[\mathrm{Mo(pd)_3}](\mathrm{g})$, equation (13), with $\Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Cr(pd)_3,g}] = -1\,410.0 \pm 5.8$ kJ mol^{-1} [27] and $\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Cr,g}) = 396.6 \pm 2.1$ kJ mol^{-1},[24] we get equation (15), and for the disruption of $[\mathrm{CrMo(O_2CMe)_4}](\mathrm{g})$ and $[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{g})$, equations (16) and (17). Substitution of (11) and (15)

$$\bar{D}(\mathrm{Mo{-}O})_{\mathrm{pd}} - \bar{D}(\mathrm{Cr{-}O})_{\mathrm{pd}} = 8.4\ \mathrm{kJ\ mol^{-1}} \quad (15)$$

$$[\mathrm{CrMo(O_2CMe)_4}](\mathrm{g}) \longrightarrow \mathrm{Cr(g)} + \mathrm{Mo(g)} + 4\mathrm{MeCO_2(g)}$$

$$\bar{D}(\mathrm{Cr{-}Mo}) + 4\bar{D}(\mathrm{Mo{-}O})_{\mathrm{O_2CMe}} + 4\bar{D}(\mathrm{Cr{-}O})_{\mathrm{O_2CMe}} = \Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Cr,g}) + \Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) + 4\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{MeCO_2,g}) - \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{CrMo(O_2CMe)_4,g}] \quad (16)$$

$$[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{g}) \longrightarrow 2\mathrm{Cr(g)} + 4\mathrm{MeCO_2(g)}$$

$$\bar{D}(\mathrm{Cr{-}Cr}) + 8\bar{D}(\mathrm{Cr{-}O})_{\mathrm{O_2CMe}} = 2\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Cr,g}) + 4\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{MeCO_2,g}) - \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{g}) \quad (17)$$

$$\bar{D}(\mathrm{Cr{-}Mo}) - \bar{D}(\mathrm{Mo{-}Mo}) = \Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Cr,g}) - \Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) - \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{CrMo(O_2CMe)_4,g}] + \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo_2(O_2CMe)_4,g}] + 33.6 = -84.9\ \mathrm{kJ\ mol^{-1}} \quad (18)$$

$$\bar{D}(\mathrm{Cr{-}Cr}) - \bar{D}(\mathrm{Mo{-}Mo}) = 2\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Cr,g}) - 2\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{Mo,g}) - \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Cr_2(O_2CMe)_4,g}] + \Delta H_{\mathrm{f}}^{\ominus}[\mathrm{Mo_2(O_2CMe)_4,g}] + 67.2 = -128.8\ \mathrm{kJ\ mol^{-1}} \quad (19)$$

into (16) and (17) yields (18) and (19). Combination of (14), (18), and (19) yields the values $\bar{D}(\mathrm{Mo{-}Mo}) = 334$, $\bar{D}(\mathrm{Cr{-}Mo}) = 249$, and $\bar{D}(\mathrm{Cr{-}Cr}) = 205$ kJ mol^{-1} for the metal–metal bond enthalpy contributions in these $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ species.

The magnitudes of the $\bar{D}(\mathrm{M{-}M})$ values depend on the estimated enthalpies of sublimation and on the assumptions (*i*)—(*iv*) that were made. In connection with assumption (*i*), $\bar{D}(\mathrm{Mo{-}Mo})$ is given, from (11)—(13) by (20). If the metal–metal bond enthalpy contribution in

$$\bar{D}(\mathrm{Mo{-}Mo}) = 2\{\bar{D}(\mathrm{Mo{-}Mo})\ \text{in}\ [\mathrm{Mo_2(O_2CMe)_2(pd)_2}](\mathrm{g})\} - \{\bar{D}(\mathrm{Mo{-}Mo})\ \text{in}\ [\mathrm{Mo_2(O_2CMe)_4}](\mathrm{g})\} \quad (20)$$

$[\mathrm{Mo_2(O_2CMe)_2(pd)_2}](\mathrm{g})$ is less than in $[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{g})$, then the $\bar{D}(\mathrm{M{-}M})$ values will be lower than the real values in $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ by twice the difference between $\bar{D}(\mathrm{Mo{-}Mo})$ in $[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{g})$ and $[\mathrm{Mo(O_2CMe)_2(pd)_2}](\mathrm{g})$. Assumptions (*ii*) and (*iii*) concern the transferability of the Mo–O bond enthalpy contributions between related molecules: (*ii*) appears reasonable because the dimensions of the acetato-group bridges are not significantly different. With respect to (*iii*), although previous studies [17] suggest that $\bar{D}(\mathrm{Mo{-}O})_{\mathrm{pd}}$ is transferable between $[\mathrm{Mo(pd)_3}](\mathrm{g})$ and $[\mathrm{MoO_2(pd)_2}](\mathrm{g})$, the assumption that $\bar{D}(\mathrm{Mo{-}O})_{\mathrm{pd}}$ is independent of the oxidation state of Mo is of critical importance and may be incorrect, hence the $\bar{D}(\mathrm{M{-}M})$ values must be considered tentative. Assumption (*iv*) is unlikely to cause large uncertainties in $\bar{D}(\mathrm{Cr{-}Mo})$ and $\bar{D}(\mathrm{Cr{-}Cr})$.

The $\bar{D}(\mathrm{M{-}M})$ values indicate that the M–M bonds in the $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ (M = Mo and/or Cr) molecules are reasonably strong in a thermochemical sense. The short Mo–Mo separation of 2.093(1) Å within the constituent molecules of $[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{c})$ is in accord with the interpretation of this intermetallic interaction as a $\sigma^2\pi^4\delta^2$ quadruple bond.[1,7-10] The thermochemical $\bar{D}(\mathrm{Mo{-}Mo}) = 334$ kJ mol^{-1} is significantly lower than the bond dissociation energies (480—550 [3] and *ca.* 500 [4] kJ mol^{-1}) suggested for the dissociation of the $[\mathrm{Mo_2X_8}]^{4-}$ (X = Cl or Br) ions, on the basis of a Birge–Sponer extrapolation of the frequencies observed for the corresponding ν(Mo–Mo) vibrational progressions. In arriving at their values the authors [3,4] acknowledged that the Birge–Sponer extrapolation tends to overestimate bond dissociation energies and a reduction of *ca.* 20% was made to compensate. Whether this reduction is sufficient is questionable, since although the Birge–Sponer extrapolation has been extensively applied to diatomic molecules little experience has been gained of more complex systems. $\bar{D}(\mathrm{Mo{-}Mo}) = 334$ kJ mol^{-1} in $[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{g})$ is of similar order of magnitude to that reported for the Mo–Mo triple bond in $[\mathrm{Mo_2(NMe_2)_6}](\mathrm{g})$, $\bar{D}(\mathrm{Mo{-}Mo}) = 398$ kJ mol^{-1} calculated by making the assumption that $\bar{D}(\mathrm{Mo{-}N})$ is the same in $[\mathrm{Mo_2(NMe_2)_6}](\mathrm{g})$ and in $[\mathrm{Mo(NMe_2)_4}](\mathrm{g})$.[5] Independent investigations have reported that, in the diatomic molecule at 298 K, $\bar{D}(\mathrm{Mo_2,g}) = 406 \pm 20$ kJ mol^{-1},[28] and theoretical discussions have suggested that $\mathrm{Mo_2(g)}$ contains a sextuple bond.[29]

The values for $\bar{D}(\mathrm{Mo{-}Mo})$, $\bar{D}(\mathrm{Cr{-}Mo})$, and $\bar{D}(\mathrm{Cr{-}Cr})$ in the $[\mathrm{M_2(O_2CMe)_4}](\mathrm{g})$ molecules are in the order expected and lead to a small enthalpy for the redistribution reaction (21), $\Delta H^{\ominus}(\text{redistribution}) = 20$ kJ mol^{-1}. This

$$\tfrac{1}{2}[\mathrm{Mo_2(O_2CMe)_4}](\mathrm{g}) + \tfrac{1}{2}[\mathrm{Cr_2(O_2CMe)_4}](\mathrm{g}) \longrightarrow [\mathrm{CrMo(O_2CMe)_4}](\mathrm{g}) \quad (21)$$

Cr–Mo bond has been suggested to be significantly weaker than this Mo–Mo one on the basis of their respective ν(M–M) frequencies [13] and theoretical treatments [7,10] have predicted that $\mathrm{Cr^{II}{-}Cr^{II}}$ interactions will be weaker than comparable $\mathrm{Mo^{II}{-}Mo^{II}}$ ones. Discussions [7,10] of the nature of $\mathrm{Cr^{II}{-}Cr^{II}}$ interactions differ in the description of the electronic structure of these bonds. From SCF-Xα-SW calculations, Cotton and Stanley [9] suggested that the $\sigma^2\pi^4\delta^2$ quadruple-bond description is appropriate for $[\mathrm{Cr_2(O_2CMe)_4}]$ molecules, whilst Benard,[7,10] Veillard,[7] and Hillier and co-workers,[8] from *ab initio* treatments, concluded that this particular configuration makes a relatively small contribution to the ground state. The former theoretical approach interprets differences between the strengths of Cr^{II}–Cr^{II} and Mo^{II}–Mo^{II} interactions in terms of differences in orbital overlaps, whilst the latter adds to this weakening of the Cr^{II}–Cr^{II} interactions by inclusion of non-bonded or weakly bonded metal–metal configurations to the ground-state wavefunction. The data presented here confirm the presence of a reasonably strong Cr^{II}–Cr^{II} interaction in $[Cr_2(O_2CMe)_4](g)$ but do not distinguish between the alternative theoretical conclusions.

Chromium(II)–chromium(II) interactions are remarkable in that the intermetallic distance is known to vary from 1.830(4) Å in $[Li_6Cr_2(C_6H_4O\text{-}o)_4Br_2]\cdot 6Et_2O(c)$ [30] to 2.541(1) Å in $[Cr_2(O_2CCF_3)_4]\cdot 2Et_2O(c)$,[31] the length being sensitive to the nature of the ligands which are equatorial and axial to the metal–metal bond. This has been shown for $[Cr_2(O_2CMe)_4]$ systems; $[Cr_2(O_2CMe)_4]\cdot 2H_2O(c)$ [32] and $[Cr_2(O_2CMe)_4](c)$ [6] have r(Cr–Cr) of 2.362(1) and 2.288(2) Å, respectively with the corresponding Cr $\cdots$ O axial separations being 2.272(3) and 2.327(4)°. Thus in these systems, it may be difficult to separate the effects of metal–metal and metal–axial ligand bonding with the latter occurring partially at the expense of the former. Therefore, the enthalpy of the dissociation (22), calculated from the data in Table 2 and

$$[Cr_2(O_2CMe)_4]\cdot 2H_2O(g) \longrightarrow [Cr_2(O_2CMe)_4](g) + 2H_2O(g) \qquad (22)$$

$\Delta H_f^{\ominus}(H_2O,g) = -241.81 \pm 0.01$ kJ mol^{-1},[21] is ΔH(dissociation) = 88.4 kJ mol^{-1}. This will give a low estimate for $\bar{D}$(Cr–OH$_2$) of 44 kJ mol^{-1} if the dissociation (22) is accompanied by a strengthening of the Cr–Cr interaction. The effect of the loss of axial ligands upon the enthalpy of sublimation of $[Cr_2(O_2CMe)_4](c)$ is expected to be partially compensated by a strengthening of the Cr–Cr interaction. Accurate determination of the enthalpies of sublimation of the tetra-μ-acetato-complexes of Cr^{II} and Mo^{II} would improve the precision of the thermochemical interpretations presented here but is not likely to alter the general conclusions.

We thank the S.R.C. for the awards of a Postdoctoral Fellowship (to K. J. C.) and a Research Studentship (to S. P.).

[9/072 *Received*, 16*th January*, 1979]

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