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Synthesis and Characterization of Bis(neopentyl)-tetrakis(acetato)dimolybdenum. A Notably Short Metal–Metal Distance for a d^3–d^3 Dinuclear Compound Containing a M–M Triple Bond of Valence Molecular Orbital Configuration $\pi^4\delta^2$

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The tetracarboxylates of dimolybdenum, $Mo_2(O_2CR)_4$, [1] are amongst the best known examples of compounds which contain quadruple bonds between metal atoms having the M–M MO description $\sigma^2\pi^4\delta^2$. We describe here the synthesis and characterization of a closely related compound, $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$, which retains the $Mo_2(O_2CMe)_4$ core and has two neopentyl ligands, one bonded to each molybdenum along the Mo–Mo axis. Remarkably the Mo–Mo distance is 2.1302(6) Å, only slightly longer than that in $Mo_2(O_2CMe)_4$, 2.0934(8) Å [2], and is the shortest yet seen for a d^3–d^3 Mo_2^{6+} containing compound.

The reaction between $Mo_2(CH_2Bu^t)_2(NMe_2)_4$ [3] and acetic anhydride proceeds quite rapidly in methylene chloride at –78 °C according to eqn. (1). (Note the use of dry and oxygen free solvents and atmospheres is required.) Upon removal of the solvent and organic amide by dynamic vacuum, a yellow–orange powder is formed. Recrystallization from toluene gives orange, hexagonal plates, $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$, which is thermally quite stable and sublimes *in vacuo*, 100–120 °C, 10^{-4} torr.

$$Mo_2(CH_2Bu^t)_2(NMe_2)_4 + 4(MeCO)_2O \xrightarrow[CH_2Cl_2]{-78\ ^\circ C} Mo_2(O_2CMe)_4(CH_2Bu^t)_2 + 4MeCONMe_2 \qquad (1)$$

The ^1H NMR spectrum and infrared spectrum are virtually identical to those of the related ditungsten compound, $W_2(CH_2Bu^t)_2(O_2CMe)_4$, [4, 5] which suggested a similar structure and this was confirmed by a single crystal X-ray study**. A view of the centrosymmetric molecule is given in Fig. 1 which reveals the typical $Mo_2(O_2C)_4$ core found in $Mo_2(O_2CR)_4$ compounds supplemented by axially ligated neopentyl ligands. The Mo–Mo distance, 2.1302(6) Å, is shorter than the Mo–C distance 2.192(2) Å and is shorter than any previously reported Mo–Mo distance in a d^3–d^3 Mo_2^{6+}-containing compound [6]. Typically in Mo_2X_6 compounds ($X = CH_2SiMe_3$ [7], CH_2Ph [8], NMe_2 [9], OCH_2Bu^t [10] and SAr [11, 12]), which have ethane-like cores, the Mo–Mo distance is close to 2.20 Å. Indeed the Mo–Mo distance is only slightly longer than those seen for the Mo_2^{4+}-containing compounds of formula $Mo_2(O_2CR)_4$ [1] *cf.* Mo–Mo = 2.0934(8) Å in $Mo_2(O_2CMe)_4$ [2].

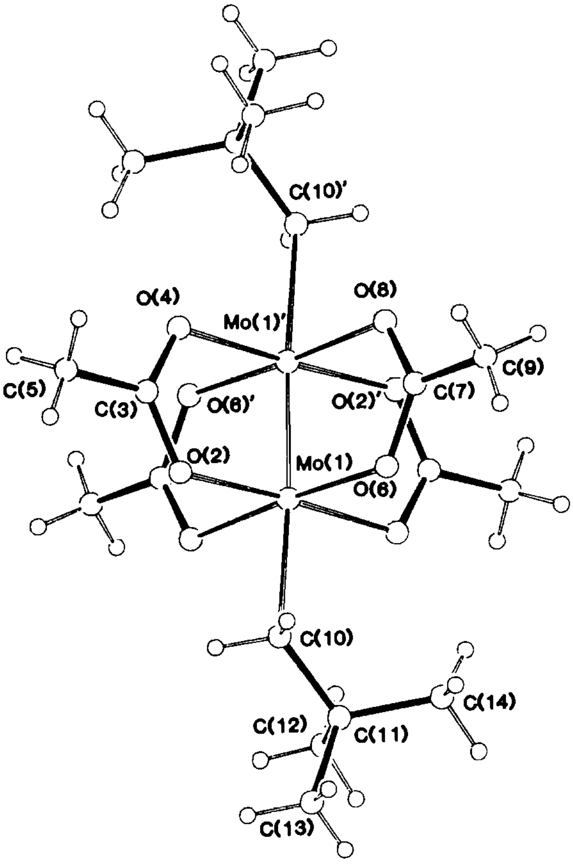

Fig. 1. A ball and stick view of the centrosymmetric molecule $Mo_2(CH_2Bu^t)_2(O_2CMe)_4$. Mo–Mo = 2.1302(6) Å; Mo–C = 2.1923(17) Å; Mo–O (average) = 2.1029 Å; Mo–Mo–C = 174.50(4)°; Mo–Mo–O (average) = 91.35°; Mo–O–C = 117.79°.

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**Crystal data for $Mo_2(CH_2Bu^t)_2(O_2CMe)_4$ at –157 °C: $a = 9.400(2)$, $b = 7.745(2)$, $c = 8.782(2)$, $\alpha = 112.54(1)$, $\beta = 107.64(1)$, $\gamma = 77.47(1)$, $Z = 1$, $D_c = 1.694$ g cm^{-3}, space group $P\bar{1}$. Of the 4932 unique reflections collected using Mo Kα radiation ($6° < 2\theta < 45°$), the 4785 having $F > 3\sigma(F)$ were used in a full-matrix least-squares refinement. The hydrogen atoms were located and refined and no absorption or extinction corrections were used. Final residual values are $R = 0.0288$ and $R_w = 0.0322$.

**See left-hand column.

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The electronic structure of the Mo–Mo quadruple bond is now well established in $Mo_2(O_2CR)_4$ compounds [1, 13–18] and the valence MO description $\sigma^2\pi^4\delta^2$ is commonly accepted. The bonds between tungsten atoms in $W_2R_2(O_2CR')_4$ compounds have [4, 5, 19] a valence MO configuration $\pi^4\delta^2$ and it seems likely that a similar valence MO configuration is present in the new dimolybdenum compound. A comparison of the UV–Vis absorption spectra of the compounds $Mo_2(O_2CMe)_4$ [17], $W_2(O_2CMe)_4$ [20], $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$ and $W_2(O_2CMe)_4(CH_2Bu^t)_2$ [5] reveals great similarities. Of particular note is the lowest energy transition assignable to the $\delta \rightarrow \delta^*$ transition [5, 17, 20]. This relatively weak absorption occurs at 23 000 cm^{-1} for $Mo_2(O_2CMe)_4$ [17] and is shifted to lower energy, 21 800 cm^{-1}, for $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$ consistent with the slight lengthening of the Mo–Mo distance and an increase in formal positive charge on the metal in the latter compound. The $\delta \rightarrow \pi^*CO_2$ of the carboxylate ligand transition occurs at higher energy in $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$ relative to the same transition in $W_2(O_2CMe)_4(CH_2Bu^t)_2$ [5] and is seen as a shoulder at 325 nm (3.08×10^4 cm^{-1} with $\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}) on the intense $\sigma_{M-C} \rightarrow \sigma_{M-C}{}^*$ transition at 285 nm (3.51×10^4 cm^{-1}, $\epsilon = 2.8 \times 10^4$ M^{-1} cm^{-1}). The valence MO description $\pi^4\delta^2$ which is reliably established for $W_2R_2(O_2CR')_4$ compounds on both the basis of theoretical work [20] and experimental data derived from UV–Vis spectra, photoelectron spectra and cyclic voltammetry [5] may thus well apply to the present $Mo_2{}^{6+}$-containing compound. It should be noted, however, that whereas the W–W distance in $W_2(O_2CR')_4$ and $W_2R_2(O_2CR')_4$ compounds are identical within experimental error, *ca.* 2.18–2.19 Å [4, 5, 21–23], the Mo–Mo distance in the related $Mo_2(O_2CMe)_4(CH_2Bu^t)_2$ compound is *ca.* 0.04 Å longer than that in $Mo_2(O_2CMe)_4$ [2]. It seems that this difference between molybdenum and tungsten chemistry can be related to relativistic effects and the role of the W 6s orbital contributions to W–W and W–C bonding relative to Mo 5s contributions [19]. In this context it will be interesting to see whether or not a $Cr_2R_2(O_2CR')_4$ compound can be synthesized and what structural features such a compound will exhibit.

Finally, it should be noted that the lack of a formal M–M σ component to the triple bond in $M_2R_2(O_2CR')_4$ compounds is a result of a formal cancellation of M–M σ and σ^* bonding components and has a direct parallel with the chemistry of carbon. The diatomic molecule C_2 is unique in having a double bond lacking a formal σ component [24, 25]. The valence MO description for C_2 is π^4 and C_2 has a shorter (1.24 Å) [24] double bond than ethylene (1.34 Å [26] which may loosely be described in terms of the valence MO description $\sigma^2\pi^2$.

Supplementary Material

Tables of atomic coordinates, thermal parameters, bond lengths and bond angles are available from the authors on request.

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