The Reaction of Tetra(μ-trifluoroacetato)dimolybdenum with Trimethylchlorosilane and Propionitrile: Products with Novel Stereochemistries[†]

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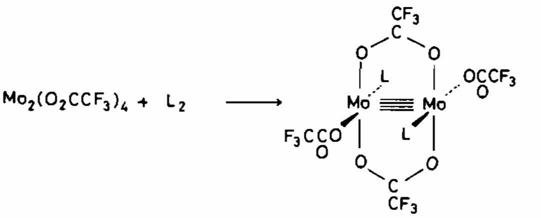
Treatment of a solution of $Mo_2(O_2CCF_3)_4$ in toluene with $(CH_3)_3SiCl$ and C_2H_5CN at $-78°$ to 0 °C affords red-orange crystals of composition $Mo_2(O_2CCF_3)_2(C_2H_5CN)_2Cl_2 \cdot Mo_2(O_2CCF_3)_3(C_2H_5CN)Cl$. This compound contains two different dinuclear molecules linked by three Cl···Mo bridges (2.894–3.005 Å) and one O···Mo bridge (3.053 Å) into infinite chains in which the two dinuclear units alternate. It crystallizes in space group Cc *with the following unit cell dimensions:* a = *22.324(5)* Å, b = *12.640(4)* Å, c = *17.547(8)* Å, β = *113.41(5)*°, V = *4543(6)* Å^3. *With Z = 4, no crystallographic symmetry is imposed. Molecule **a**. $Mo_2(O_2CCF_3)_2(C_3H_5CN)_2Cl_2$, has an Mo–Mo distance of 2.127(2) Å, while that in molecule **b**, $Mo_2(O_2CCF_3)_3(C_2H_5CN)Cl$, is 2.134(2) Å. The CF_3CO_2 groups in **a** are* cis *and the other ligands alternate around the rectangle they define so that the symmetry of **a** is C_2. Molecule **b** has a virtual mirror plane containing one CF_3CO_2 ligand, two Mo atoms and the C_2H_5CN and Cl ligands.*

Introduction

The $Mo_2(O_2CR)_4$ molecules are moderately reactive and this is especially well established in the case of the trifluoroacetate [1–6], which is a convenient material to work with because of its solubility in various organic solvents. Among the most interesting reactions are those in which carboxylate bridges are opened up, allowing new ligands to enter equatorial sites and leaving two carboxyl groups attached as monodentate ligands, eqn. (1).



(1)

In this paper we report a new type of reaction in which the reagent $(CH_3)_3SiCl$ has been used to attack and esterify the $CF_3CO_2^-$ group while transferring Cl^- to the dimolybdenum unit. This study was conceived in anticipation that *one* of the relatively simple reactions shown as eqn. (2) would occur.

$$Mo_2(O_2CCF_3)_4 + nMe_3SiCl \xrightarrow{RCN} Mo_2(O_2CCF_3)_{4-n}(RCN)_nCl_n + nMe_3SiO_2CCF_3 \quad (2)$$

$(1 \leqslant n \leqslant 4)$

Instead, the isolated material contains two of the possible products, namely those with $n = 1$ and $n = 2$.

Experimental Section

Molybdenum(II) trifluoroacetate, 0.080 g (0.12 mmol), was dissolved in 10 ml of toluene. The temperature was lowered to −78 °C and 0.1 ml of propionitrile followed by 0.05 ml (0.63 mmol) of trimethylchlorosilane were added. The cold mixture was put in the refrigerator and as it warmed up the color became red. In a few days the solution was almost colorless and red-orange crystals had been

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[†] No reprints available.

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TABLE I. Crystallographic Data.

FORMULA	$Mo_2(O_2CCF_3)_2(NCC_2H_5)_2Cl_2 \cdot Mo_2(O_2CCF_3)_3(NCC_2H_5)Cl$
Formula weight	1220.44
Space group	*Cc* #9
a, Å	22.324(5)
b, Å	12.640(4)
c, Å	17.547(8)
α, degrees	90.00
β, degrees	113.41(5)
γ, degrees	90.00
V, Å^3	4543(6)
Z	4
d_{calc}, g/cm^3	1.784
Crystal size, mm	0.3 × 0.25 × 0.15
μ(MoKα), cm^{-1}	13.316
Data collection instrument	Enraf-Nonius CAD-4
Radiation	Mo-Kα
Scan method	$\theta - 2\theta$
Data collection range	$5° \leqslant 2\theta \leqslant 50$
No. unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	2659
Numbers of parameters refined	375
R^a	0.0586 (0.0589)^d
R_w^b	0.0730 (0.0739)^d
Quality-of-fit indicator^c	1.873 (1.880)^d
Largest shift/esd, final cycle	0.19 (0.24)^d

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/N_{obs} - N_{parameters})]^{1/2}$. [d] Figures in parentheses are for the opposite enantiomorph.

deposited. These were mostly very small needles (*ca.* 60 mg) but among them were a few larger orange crystals (*ca.* 10 mg). We have not yet identified the substance forming needle crystals.

X-ray Diffraction Data Collection

An orange crystal of dimensions 0.30 × 0.25 × 0.15 mm was covered with epoxy cement and mounted at the end of a glass fiber. Geometric and intensity data were obtained on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo-radiation*. The unit cell was determined by indexing 25 reflections found by the automatic search procedure and reducing it to the conventional unit cell of highest symmetry, which was *C*-centered monoclinic. The 25 reflections were reindexed, recentered and the unit cell parameters were refined by a least-squares procedure.

A preliminary data collection of 789 reflections indicated systematic absences of the classes, hkl, h + k = 2n + 1 and 00l, l = 2n + 1. These indicated that the space group was either *Cc* or *C*2/*c*. Data collection was continued but the reflections of classes hkl, h + k = 2n + 1 and h0l, l = 2n + 1 were skipped. A total of 4484 reflections including three intensity standards, which were measured after every hour of exposure to X-rays, were measured in the range $5.0 \leqslant 2\theta \leqslant 50$.

The intensities were corrected for Lorentz and polarization effects. No absorption corrections were thought to be necessary because of the low absorption coefficient and since the three standard reflections gave constant intensities throughout the 67.7 hours X-ray exposure time, decay corrections were also unnecessary.

Structure Solution and Refinement

A three-dimensional Patterson map did not yield a correct solution for the heavy atom position when the space group was assumed to be *C*2/*c*. However, in the space group *Cc* the second highest vector yielded the correct position for one molybdenum

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*The general procedures used for data collection and processing have been given in earlier papers, *e.g.*, A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem.*, *18*, 3558 (1979).

TABLE II. Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B (Å^2)
Mo1	0.100	0.1036(1)	0.100	0.0
Mo2	0.01416(8)	0.1107(1)	−0.0114(1)	3.45(4)
Mo3	0.32431(9)	0.3177(1)	0.3691(1)	3.65(4)
Mo4	0.23583(9)	0.2885(2)	0.2636(1)	3.87(4)
Cl1	−0.0748(2)	0.1384(5)	0.0325(3)	4.5(1)
Cl2	0.4075(3)	0.3568(5)	0.3195(3)	5.0(1)
Cl3	0.2269(2)	0.1023(4)	0.2365(3)	4.4(1)
F1′	−0.025(2)	−0.259(3)	0.023(2)	12(1)*
F1	0.077(2)	−0.269(3)	0.114(2)	11(1)*
F2	0.008(1)	−0.264(2)	−0.023(1)	4.5(5)*
F2′	0.025(2)	−0.237(3)	0.132(2)	8.9(9)*
F3	−0.012(1)	−0.242(2)	0.083(2)	7.2(7)*
F3′	0.092(1)	−0.274(2)	0.081(1)	4.7(5)
F4	0.038(1)	0.481(2)	−0.015(1)	5.6(6)*
F4′	0.060(1)	0.470(2)	−0.050(2)	6.2(6)*
F5	0.131(1)	0.478(2)	0.080(2)	6.3(6)*
F5′	0.083(2)	0.493(3)	0.072(2)	9.6(9)*
F6′	0.153(1)	0.441(2)	0.042(2)	6.3(6)*
F6	0.128(1)	0.430(2)	−0.026(2)	7.9(8)*
F7	0.197(1)	0.165(2)	−0.096(1)	5.6(6)*
F7′	0.188(2)	−0.019(3)	−0.099(2)	10(1)*
F8	0.225(1)	0.004(2)	−0.059(2)	6.1(6)*
F8′	0.146(1)	0.136(2)	−0.160(2)	7.6(8)*
F9	0.136(1)	0.050(2)	−0.171(2)	7.6(8)*
F9′	0.226(2)	0.100(3)	−0.072(2)	9.3(9)*
F10	0.220(2)	0.210(3)	0.548(2)	9.7(9)*
F10′	0.121(1)	0.343(2)	0.433(2)	7.2(7)*
F11	0.135(1)	0.187(2)	0.454(2)	6.2(6)*
F11′	0.212(1)	0.304(2)	0.548(2)	6.0(6)*
F12	0.179(2)	0.359(3)	0.510(2)	10(1)*
F12′	0.169(2)	0.175(3)	0.492(2)	8.7(9)*
F13	0.271(1)	0.687(2)	0.355(1)	4.9(5)*
F13′	0.284(2)	0.690(3)	0.306(3)	12(1)*
F14	0.257(2)	0.660(4)	0.224(3)	13(1)*
F14′	0.197(2)	0.656(3)	0.222(2)	9.5(9)*
F15	0.172(2)	0.653(3)	0.261(2)	8.6(8)*
F15′	0.203(2)	0.653(4)	0.327(3)	13(1)*
O1	0.1585(5)	0.082(1)	0.0323(7)	4.0(3)
O2	0.1179(6)	0.267(1)	0.0988(9)	4.5(4)
O3	0.0909(6)	−0.060(1)	0.1087(8)	4.0(3)
O4	0.0008(6)	−0.055(1)	−0.0107(8)	4.2(4)
O5	0.0279(6)	0.278(1)	−0.0188(8)	4.4(4)
O6	0.0669(7)	0.085(1)	−0.0832(8)	4.6(4)
O7	0.3016(6)	0.481(1)	0.3661(9)	5.3(4)
O8	0.2737(6)	0.296(1)	0.4495(8)	4.8(4)
O9	0.2104(7)	0.448(1)	0.257(1)	6.2(4)
O10	0.1827(6)	0.273(1)	0.3422(8)	4.7(4)
N1	0.0571(7)	0.123(1)	0.187(1)	4.1(4)
N2	0.3574(9)	0.164(1)	0.394(1)	5.2(5)
N3	0.2685(8)	0.314(2)	0.166(1)	6.0(6)
C1	0.0412(9)	−0.100(2)	0.047(1)	4.0(4)*
C2	0.0774(9)	0.318(1)	0.035(1)	3.7(4)*
C3	0.127(1)	0.077(2)	−0.046(1)	4.2(4)*
C4	0.215(1)	0.282(2)	0.415(1)	5.3(5)*
C5	0.251(1)	0.507(2)	0.301(1)	5.5(5)*
C6	0.033(1)	−0.223(2)	0.052(2)	6.9(7)*
C7	0.090(1)	0.429(2)	0.022(1)	5.4(5)*

(continued overleaf)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C8	0.168(1)	0.076(2)	−0.099(1)	5.9(6)*
C9	0.175(2)	0.267(3)	0.474(2)	8.9(8)*
C10	0.236(2)	0.641(3)	0.285(2)	11(1)*
C11	0.031(1)	0.122(2)	0.230(1)	5.5(5)*
C12	−0.004(1)	0.123(2)	0.289(2)	7.6(7)*
C13	0.374(1)	0.075(2)	0.409(2)	6.4(6)*
C14	0.390(2)	−0.044(3)	0.425(2)	11(1)*
C15	0.292(2)	0.328(3)	0.118(2)	9.3(9)*
C16	0.328(2)	0.399(4)	0.065(3)	15(2)*
C17	−0.067(2)	0.138(3)	0.254(2)	9.0(8)*
C18	0.369(2)	−0.109(3)	0.365(2)	13(1)*
C19	0.395(4)	0.378(6)	0.144(4)	25(3)*

*Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)^* \, [a^{2*}\beta(1,1) + b^{2*}\beta(2,2) + c^{2*}\beta(3,3) + ab(\cos \text{gamma})^*\beta(1,2) + ac(\cos \text{beta})^*\beta(1,3) + bc(\cos \text{alpha})^* \beta(2,3)]$.

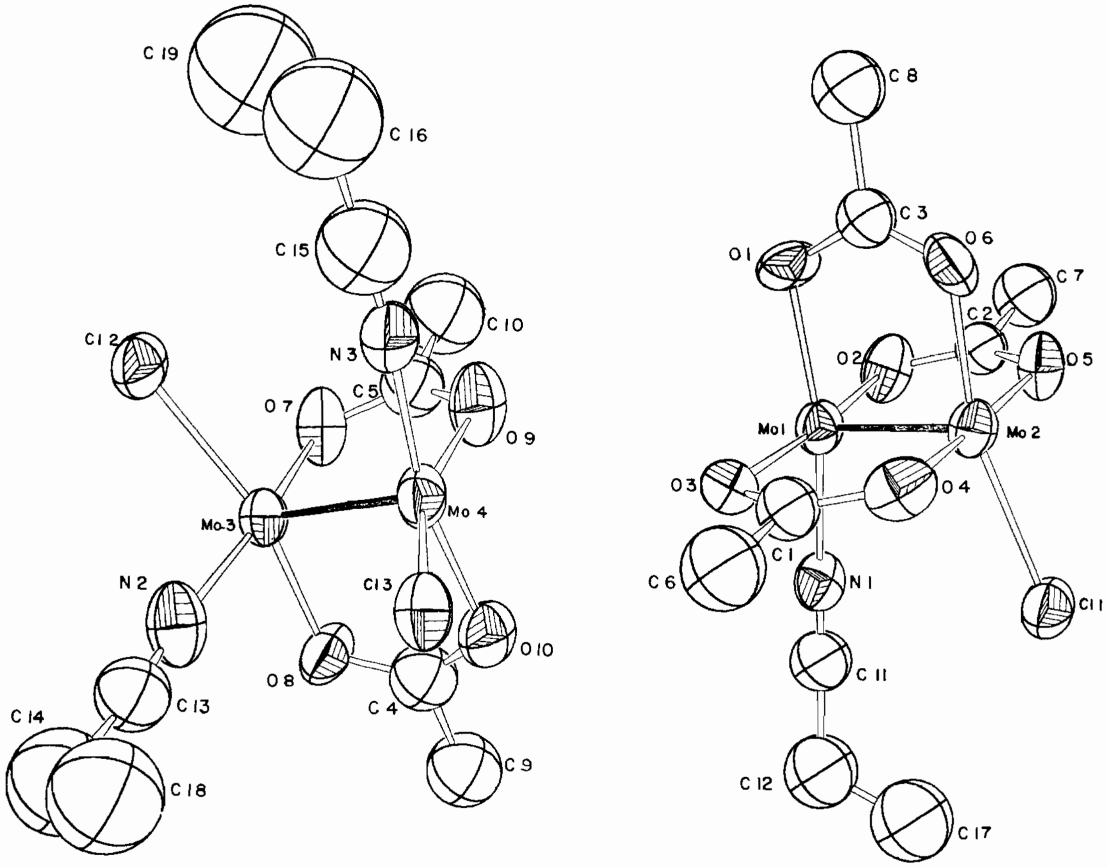


Fig. 1. ORTEP drawings of molecules a (left) and b (right). The atom labeling scheme is defined. Each atom is represented by its ellipsoid of thermal vibration at the 50% probability level. Flourine atoms have been omitted for clarity.

atom. The positions of three other molybdenum atoms were obtained rapidly from difference Fourier maps followed by least squares refinement. The distances between them clearly indicated that there were two independent dinuclear species in the asymmetric unit.

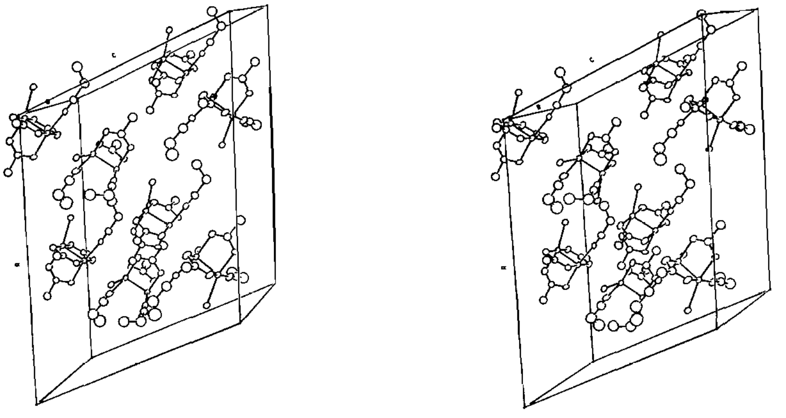


Fig. 2. An ORTEP stereographic representation of the unit cell contents. The atoms are represented by their ellipsoids of vibration at the 20% probability level.

The process of finding and refining the positions of the remaining atoms established that one of the dinuclear species had two trifluoroacetate, two chloride and two propionitrile ligands, while the other one had three trifluoroacetate, one chloride and one propionitrile ligand.

A model of disorder in the positions of the fluorine atoms had to be used to refine the structure. The dampening factor also had to be reduced to less than one. However, after 14 low-angle reflections with $\sin \theta/\lambda \leqslant 0.09$ were assigned zero weights the structure could be satisfactorily refined (with a dampening factor of one). The largest shifts (0.1–0.19) involved only a few positional parameters of some fluorine atoms. The isotropic thermal parameters for the carbon atoms could not be converted to anisotropic parameters.

The final refined model thus included 30 fluorine atoms with multiplicity of 0.5. Anisotropic thermal parameters were used for the 4 molybdenum atoms, and the atoms directly bonded to them. Isotropic thermal parameters were used for the remaining atoms. Figures of merit are given in Table I. The atomic coordinates are listed in Table II along with isotropic thermal parameters. A tabulation of the anisotropic tensor components and a table of the final calculated and observed structure factors are available as supplementary material.

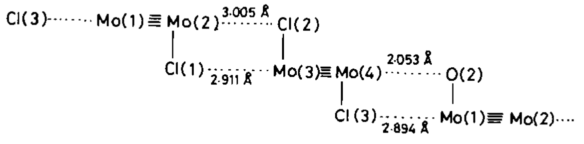
After the final refinement the enantiomorph was changed and the structure again refined to convergence. This produced essentially insignificant changes in the figures of merit (See Table I) and did not alter any bond distances or angles by amounts greater than 3σ.

Results

The crystal consists of a regular, alternating packing of two different molecules, $Mo_2(O_2CCF_3)_2(C_2H_5CN)_2Cl_2$ (molecule **a**) and $Mo_2(O_2CCF_3)_3(C_2H_5CN)Cl$ (molecule **b**). These two molecules jointly comprise the crystallographic asymmetric unit and no rigorous symmetry is imposed on either of them. The molecules are shown in Fig. 1, where the atom labeling scheme is defined. Table III gives selected bond lengths and angles.

In molecule **a** the average distances are as follows: Mo–O, 2.13(3) Å; Mo–N, 2.10(4) Å; Mo–Cl, 2.394(5) Å. The average angles are: Mo–Mo–O, 90.7(5)°; Mo–Mo–N, 99(1)°; Mo–Mo–Cl, 108.1(5)°. In molecule **b** the distances are: Mo–O. (av), 2.10(3) Å, Mo–N, 2.12(2) Å; Mo–Cl, 2.425(5) Å. The angles are: Mo–Mo–O(av), 91(1)°; Mo–Mo–N, 99.1(4)°; Mo–Mo–Cl, 105.4(1)°.

The packing, to form infinite chains of alternating **a** and **b** molecules, is shown in detail in the stereoview of the unit cell, Fig. 2. The molecules are linked together by weak bridging through chlorine atoms and one oxygen atom. The contacts that merit discussion are those shown schematically below (in Å); further details are found in Table IV.



Discussion

There has previously been evidence [2–5] that $Mo_2(O_2CCF_3)_4$ in solution is subject to attack by donor molecules so as to open the CF_3CO_2 bridges and leave unidentate CF_3CO_2 groups. The present investigation shows that the reagent Me_3SiCl can replace these by Cl atoms and sequester the CF_3CO_2 groups by forming $CF_3CO_2SiMe_3$.

TABLE III. Selected Bond Distances (Å), Bond Angles (Deg.).[a]

Bond Distances (Å)	
Mo(1)–Mo(2)	2.127(2)
Mo(1)–O(1)	2.105(11)
Mo(1)–O(2)	2.105(13)
Mo(1)–O(3)	2.087(11)
Mo(1)–N(1)	2.12(2)
Mo(2)–Cl(1)	2.425(5)
Mo(2)–O(4)	2.112(11)
Mo(2)–O(5)	2.142(12)
Mo(2)–O(6)	2.063(14)
Mo(3)–Mo(4)	2.134(2)
Mo(3)–Cl(2)	2.395(5)
Mo(3)–O(7)	2.126(14)
Mo(3)–O(8)	2.146(14)
Mo(3)–N(2)	2.07(2)
Mo(4)–Cl(3)	2.394(5)
Mo(4)–O(9)	2.080(14)
Mo(4)–O(10)	2.154(13)
Mo(4)–N(3)	2.13(2)
N(1)–C(11)	1.11(3)
N(2)–C(13)	1.18(3)
N(3)–C(15)	1.17(3)
Bond Angles (Deg.)	
Mo(1)–Mo(2)–Cl(1)	105.4(1)
Mo(1)–Mo(2)–O(4)	91.8(3)
Mo(1)–Mo(2)–O(5)	89.9(3)
Mo(1)–Mo(2)–O(6)	91.7(4)
Mo(2)–Mo(1)–O(1)	91.2(3)
Mo(2)–Mo(1)–O(2)	93.1(4)
Mo(2)–Mo(1)–O(3)	91.8(4)
Mo(2)–Mo(1)–N(1)	99.1(4)
Mo(3)–Mo(4)–Cl(3)	108.5(1)
Mo(3)–Mo(4)–O(9)	91.2(4)
Mo(3)–Mo(4)–O(10)	90.9(3)
Mo(3)–Mo(4)–N(3)	100.1(4)
Mo(4)–Mo(3)–Cl(2)	107.8(1)
Mo(4)–Mo(3)–O(7)	91.0(3)
Mo(4)–Mo(3)–O(8)	90.0(3)
Mo(4)–Mo(3)–N(2)	98.7(4)
N(1)–C(11)–C(12)	179(2)
N(2)–C(13)–C(14)	175(3)
N(3)–C(15)–C(16)	156(3)
Mo(1)–N(1)–C(11)	172(2)
Mo(3)–N(2)–C(13)	177(2)
Mo(4)–N(3)–C(15)	174(2)

It is not common for two different molecules to crystallize together in the same solid phase, but cases are known [7]. We have found here another clear example. There is no obvious reason why it happens here since the weak intermolecular interactions that occur are of types that might well have occurred in crystals consisting entirely of one type of molecule or the other.

TABLE IV. Bond Distances (Å), Bond Angles (Deg.) Defining Axial Interactions.[a]

Bond Distances (Å)	
Mo(1)–Cl(3)	2.894(5)
Mo(2)–Cl(2)	3.005(5)
Mo(3)–Cl(1)	2.911(5)
Mo(2)–Cl(1)	2.425(5)
Mo(3)–Cl(2)	2.395(5)
Mo(4)–Cl(3)	2.394(5)
Mo(4)–O(2)	3.053(13)
Mo(1)–O(2)	2.105(13)
Bond Angles (Deg.)	
Cl(1)–Mo(3)–Mo(4)	166.9(1)
Cl(2)–Mo(2)–Mo(1)	169.8(1)
Cl(3)–Mo(1)–Mo(2)	171.6(1)
Mo(2)–Cl(1)–Mo(3)	97.2(2)
Mo(3)–Cl(2)–Mo(2)	95.4(2)
Mo(1)–Cl(3)–Mo(4)	97.8(2)
Mo(3)–Mo(4)–O(2)	171.6(3)
Mo(1)–O(2)–Mo(4)	100.0(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Only very recently has the first example of a molecule of type **a** with C_2 symmetry been reported. Andersen and coworkers [8] obtained $Mo_2(O_2CCMe_3)_2(PEt_3)_2Cl_2$ in this isomeric form by the reaction of $Mo_2Cl_4(PEt_3)_4$ with two equivalents of pivalic acid. There are several interesting differences between their molecule and ours. The bulkier neutral ligand, PEt_3, is apparently responsible for considerably enlarging the Mo–Mo–L and Mo–Mo–Cl angles which in their case are *ca.* 104° and *ca.* 115° respectively, as compared to corresponding values of *ca.* 99° and *ca.* 108° in our molecule **a**. In spite of this evidence of greater end-against-end repulsive forces, their Mo–Mo distance 2.113(1) Å is significantly shorter than ours, 2.134(2) Å and 2.127(2) Å. While several electronic reasons for this can be envisaged, none can be supported or disproved experimentally.

It is interesting that when Andersen *et al.* [8] carried out a reaction similar to ours, namely, that of $Mo_2(O_2CCMe_3)_4$ with Me_3SiCl in presence of PEt_3, they obtained the *trans* isomer (C_{2h} symmetry) of $Mo_2(O_2CCMe_3)_2(PEt_3)_2Cl_2$. There have, of course, been a number of other examples of this type of $Mo_2(O_2CR)_2L_2X_2$ compound.

Molecule **b** in our structure is of a type that we do not believe has previously been reported; in any case no such structure has been determined X-ray crystallographically. It is interesting that even though there are three bridging carboxyl groups in **b** it has an Mo–Mo bond length appreciably greater than that in $Mo_2(O_2CCF_3)_4$, 2.090(4) Å [1]. Moreover, the molecule in our crystal that has three bridging carboxyl groups (**b**) perhaps has a longer Mo–Mo bond than the one with two bridging carboxyl groups (**a**), although the difference, 0.007(3) Å, may not be significant.

Acknowledgements

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Supplementary Material Available

Tables of structure factors, anisotropic thermal parameters and complete lists of bond lengths and angles (17 pages). These are available upon request from F.A.C.

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