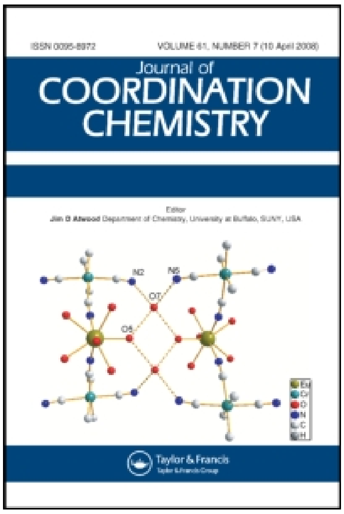

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F. A. Cotton[a]; J. G. Norman Jr.[a]
[a] Department of Chemistry Massachusetts, Institute of Technology, Cambridge, Massachusetts

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MOLYBDENUM(II) TRIFLUOROACETATE DIMER[1]

F. A. COTTON* and J. G. NORMAN, JR.[2]

Contribution from the Department of Chemistry Massachusetts, Institute of Technology, Cambridge, Massachusetts, 02139

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Molybdenum(II) trifluoroacetate dimer, $Mo_2(O_2CCF_3)_4$, has been prepared by reaction of $Mo_2(O_2CCH_3)_4$ with a 10:1 mixture of CF_3COOH and $(CF_3CO)_2O$ under nitrogen. An X-ray structure determination shows that the compound has the dinuclear, carboxylate-bridged configuration of essentially D_{4h} symmetry previously established for a number of other transition metal carboxylates. The Mo-Mo and average Mo-O distances of 2.090(4) and 2.06 (2) A are not significantly different from those found in molybdenum(II) acetate dimer [2.11(1) and 2.10(2) A]. The Mo-Mo stretching frequencies in the Raman spectrum are also similar for the two compounds: 406 cm^{-1} for the acetate and 393 cm^{-1} (389 in Et_2O soln.) for the trifluoroacetate. The mass spectrum of the trifluoroacetate shows a strong molecular-ion peak, and a fragmentation pattern characterized by successive net loss of CF_2CO_2 units. The infrared, Raman, electronic and mass spectra are discussed. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 8.392(8)$, $b = 9.209(9)$, $c = 5.568(5)$ A; $\alpha = 91.18(4)$, $\beta = 100.561(7)$, $\gamma = 89.670$ (7) deg.; $V = 423.0(8)$ A^3; $\rho_{calc} = 2.528(5)$ g/cm^3 for $Z = 1$; $\rho_{obs} = 2.48(5)$ g/ml. The structure was determined from the intensities of 630 unique reflections collected with a counter diffractometer; it was solved by direct methods and refined by full matrix least squares to a conventional R = 0.093. and weighted R = 0.080. The molecule lies on an inversion center in the crystal. There is one intermolecular contact less than the sum of van der Waals radii: Mo-O = 2.72(1) A; Mo-Mo-O = 161.0(4)°.

INTRODUCTION

The dimeric carboxylates of formula $M_2(O_2CR)_4L_2$ (M = V,[3] Cr,[4] Mo,[5] Re,[6] Ru,[7] Rh,[4], Cu[8] and L = H_2O, Cl, NCS, h^5-C_5H_5, etc.), with the general structure shown in Figure 1, constitute a uniquely useful series of transition-metal complexes with respect to the study of metal-metal interaction. Their uniqueness lies in two characteristics: (1) the four bridging carboxylates provide an ideal framework for such interaction, within which the two metals are free to reach an equilibrium separation consistent with their particular bonding requirements. (2) They have proved to be easily preparable, and quite stable once prepared, for a large number of transition metals. The first conclusion is based on a large amount of X-ray structural data: thus metal–metal distances from 2.11 $[Mo_2(OAc)_4]$[5] to 2.72 A $[Cu_2(O_2CH)_4(NCS)_2{}^{2-}]$[8] have been observed, and comparison of results for isoelectronic systems with and without bridging carboxylates (e.g., $Mo_2(OAc)_4$, 2.11(1) A; $Mo_2Cl_8{}^{4-}$, 2.139(4) A)[9] shows that the bridging configuration does not constrain the metals to a significantly different separation than they would otherwise prefer.

Because of these two features, the carboxylates have proved most useful in demonstrating the ability of an essentially qualitative molecular orbital (MO) treatment of metal–metal bonding in D_{4h} symmetry[10, 11] to rationalize the variations in bond length which occur across a given transition-metal row. The MO picture predicts that the strongest bonds (of order 4) should occur for the d^4 configuration, where all bonding MO's should be just filled, and that a steady decrease in bond order is to be expected as electrons are added past the d^4 level. Indeed, the shortest distances known for the carboxylate series occur for the d^4 species $Mo_2(OAc)_4$(2.11 A) and $Re_2(O_2CPh)_4Cl_2$ (2.24 A),[6] and the longest ones are observed near the right side of the transition metal group, for $Rh_2(OAc)_4(H_2O)_2$ (d^7, 2.39 A),[4] and various $Cu_2(O_2CR)_4L_2$ complexes (d^9, ex. $Cu_2(OAc)_4(NCS)_2{}^{2-}$, 2.64 A).[8] In the last example, even though metal–metal bonding is symmetry-allowed, it probably does not occur to any significant extent, because of poor overlap of the relevant orbitals.[12] Such overlap is expected to be usually, though perhaps not invariably, better in the second and third rows than in the first.[10]

While there is now a reasonable body of theoretical and experimental results concerning the variation of metal–metal bond strength with *M* for the dimeric carboxylates, much less information is available about the effect of varying the donor

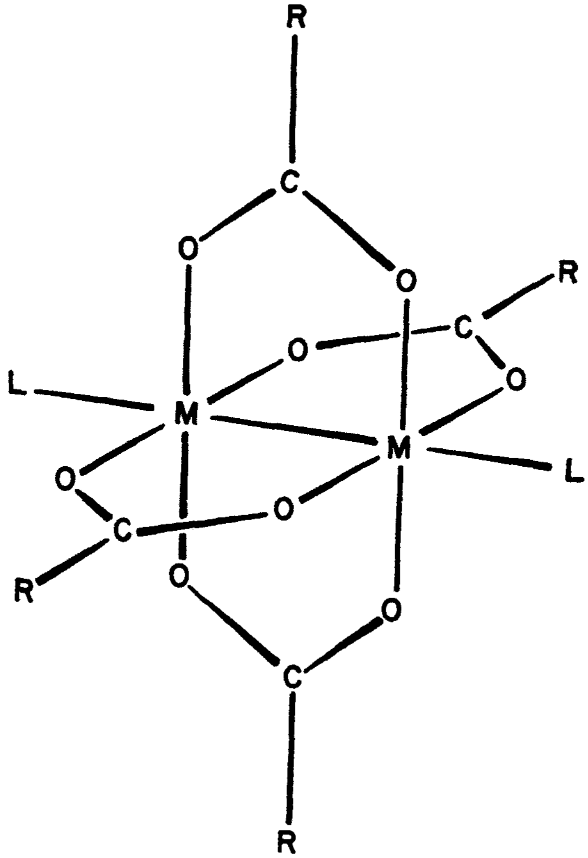

FIGURE 1 The general structure adopted by the compounds of formula $M_2(O_2CR)_4L_2$, M=V, Cr, Mo, Re, Ru, Rh, Cu.

strength of the axial ligants *L* or the carboxylate groups themselves. In all cases where the strong metal–metal bonding has been found by X-ray methods (namely, for *M* = Cr, Mo, Re, Ru and Rh), the axial ligands (H_2O or Cl) have either not been present or are rather weakly bonded to the metals, and the carboxylates (acetate, butyrate or benzoate) have differed little in acidity. If one is to study the second phenomenon experimentally, it is desirable to have it separated from the first—i.e. for there to be no axial ligands—and to have available carboxylates differing as widely in acidity as possible, so that any trends present may be clearly seen. As yet, only the molybdenum(II) carboxylates, $Mo_2(O_2CR)_4$, have been crystallized without axial donors,[13] and the ligand with closest structure to but most different acidity from the one which occurs in a known structure (acetate, $pK_a(AcOH) = 4.76$)[14] is perhaps trifluoroacetate ($pK_a(CF_3COOH) = 0.23$).[14] For these reasons we set out to prepare the previously unknown molybdenum(II) trifluoroacetate dimer, with the intention of determining its crystal structure if the synthesis were successful. The compound, if typical of complexes with perfluoro ligands, should have the secondary advantages of being volatile and easily soluble in a variety of organic solvents, allowing determination of its mass spectrum and solution-phase vibrational spectra. This paper summarizes the synthetic, crystallographic and spectroscopic results obtained for $Mo_2(O_2CCF_3)_4$.

EXPERIMENTAL

Preparation of $Mo_2(O_2CCF_3)_4$ All manipulations were carried out under dry nitrogen. A solution of 2.0 g molybdenum(II) acetate[13] in 30 ml trifluoroacetic acid and 3 ml trifluoroacetic anhydride was heated to boiling, cooled to room temperature and allowed to stand two hours at —20° C. The yellow crystals which formed were filtered, washed with pentane, and dried in a stream of nitrogen. A second crop was isolated by concentration of the filtrate and further cooling. *Yield*: 2.2 g, 73%. For purification, the product may be sublimed at 85° C/0.05 Torr to give a yellow powder. Crystals suitable for X-ray investigation may be grown by sublimation at 180° C/760 Torr nitrogen. *Anal.*: Calc. for $Mo_2C_8F_{12}O_8$: C, 14·92; H, none; F, 35.4; MW, 644. Found: C, 15.07; H, none; F, 39.6; MW, 644 (mass spectrum). Elemental analyses were performed at Spang Microanalytical Laboratory, Ann Arbor, Michigan.

The compound is soluble to varying degrees in almost all organic solvents, most readily in alcohols, ether and acetone. It may be easily recrystallized from a variety of solvents, but the crystals invariably contain solvent molecules which are lost when they are removed from solution, resulting in conversion of the material to a powder. The compound may be handled in air for a few hours without appreciable decomposition, but over prolonged periods it is not stable. Solutions are much more air-sensitive. It appears to be stable indefinitely in vacuum over P_4O_{10}.

Spectral Measurements Infrared spectra were recorded from 4000–400 cm^{-1} on a Perkin Elmer 337 spectrometer using fluorolube and Nujol mulls. Raman spectra were taken on the solid (150–1250 cm^{-1}) and a 1.0 M ether solution

(250–925 cm^{-1}) with a Cary 81 spectrometer using a Spectra-Physics helium-neon laser as the source of 6328 A exciting radiation. The ir and Raman frequencies are accurate to ± 5 and $\pm 2\,\text{cm}^{-1}$, respectively. Mass spectra in the range $m/e = 0\text{–}800$ were obtained at 200 and 70 eV using a Hitachi-Perkin Elmer RMU-6E single-focusing magnetic sector instrument.

Collection and Reduction of X-Ray Data Crystals of $Mo_2(O_2CCF_3)_4$ are somewhat soft and fragile; it was only with difficulty that a block-like specimen approximately $0.03 \times 0.07 \times 0.4$ mm was successfully sealed intact in a Lindemann glass capillary under nitrogen. Weissenberg (hkO, hk1, hk4) and precession (hO*l*, Ok*l*) photographs using Cu Kα and Mo Kα radiation, respectively, suggested that the crystals belong to the tricilinic system, implying space groups Pl ($C_1{}^1$, no. 1) or P$\bar{1}$ ($C_i{}^1$, no. 2). The crystal was transferred to a General Electric XRD-5 manual diffractometer and aligned so that c* was coincident with the ϕ axis. Unit-cell dimensions were determined using Mo Kα radiation ($\lambda = 0.71069$ A) by least squares refinement based on the accurately measured settings of 22 reflections; they are $a = 8.392(8)$, $b = 9.209(9)$, $c = 5.568(5)$ *A*; $\alpha = 91.18(4)$, $\beta = 100.561(7)$, $\gamma = 89.670(7)$ deg.; $V = 423.0(8)$ A^3. These values lead to $\rho_{calc} = 2.528(5)$ g/cm^3 for $Z = 1$; $\rho_{obs} = 2.48(5)$ *g*/ml (flotation, $CHBr_2CHBr_2$-heptane). With $Z = 1$ the molecule must lie on the inversion center in P$\bar{1}$. The crystal dimensions were carefully measured and the major faces were identified from their diffraction positions and relations to each other as (100), (010) and (001).

Intensities were measured by a scintillation counter using Nb-filtered Mo Kα radiation with a takeoff angle of 1°. The pulse-height analyzer was set to admit 91% of the Mo Kα peak. Scans were of the θ–2θ type with a scan rate of 4°/min and a fixed scan width of 2.66°, thereby accumulating the peak counts, P. Background counts, B_1 and B_2, were taken for 20 sec. at each end of the scan range. The intensites of 630 unique reflections within the range $2\theta = 0\text{–}40°$ were collected. Three reflections (100, $\bar{1}$01 and 001) were remeasured at regular intervals throughout as a check on crystal and instrument stability. They showed no systematic deviation from their initial values; the largest variation from the mean, for $\bar{1}$01, was 3.1%. This stability was somewhat surprising since, in the two months which elapsed between the beginning of film work and data collection, respectively, some darkening of the crystal and broadening of the diffraction peaks had occurred. The problem was judged to be tolerable since moving scans were to be taken and in view of the difficulty which would be involved in mounting a new crystal (see above). Apparently the compound decomposes slowly even under nitrogen, but the process is not appreciably hastened by exposure to X-rays.

Statistical analysis of the data showed that more than 50% had $I > 3\sigma_i$, where $\sigma_i = (P + B_1 + B_2)^{1/2}$, in every five-degree interval of 2θ; hence all 630 reflections were accepted, those with $I < \sigma_I/2$ being assigned $I = \sigma_I/2$. The intensities were converted to structure-factor amplitudes $|F_0| = (I/Lp)^{1/2}$, where Lp = Lorentz-polarization factor, and their e.s.d.'s, $\sigma_F = [4ILp]^{-1/2} [\sigma_I{}^2 + (0.032I)^2]^{1/2}$.

Solution and Refinement Atomic scattering factors used were those of Cromer and Waber.[15] All were corrected for the effects of anomalous dispersion using the values of $\Delta f'$ and $\Delta f''$ given by Cromer and Liberman.[16]

The structure was solved in space group P$\bar{1}$ by the symbolic addition procedure.[17] Normalized structure factors (E's) were calculated for the 200 largest $|F_0|$'s by the relationship

$E^2 = |F_0|^2 \exp 2B (\sin \theta/\lambda)^2/\epsilon k^2 \Sigma f_i{}^2$, where

B = overall temperature factor; k = overall scale factor between $|F_0|$ and $|F_c|$; ϵ = integer to correct for extinct reflections in special zones; and f_i = scattering factor for atom *i*. B and k were obtained from a Wilson plot. The phases of 156 E's were determined in terms of 7 symbols by an iterative process. The probability level required for phase determination was 0.995, and no inconsistencies were allowed. The "best" combination of signs derived for the symbols was approximately 7200 times more probable than any other combination.

An *E*-map was computed using the most probable sign combination and from it positions were derived for all 15 atoms in the asymmetric unit, $Mo(O_2CCF_3)_2$. The two carbon atoms in each CF_3CO_2 group gave a common peak; their positions were estimated from those of neighboring atoms and the peak location. Three cycles of least-squares refinement using isotropic temperature factors for all atoms gave

$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.177$ and

$R_2 = \Sigma w_F||F_0| - |F_c||^2/\Sigma w_F|F_0|^2 = 0.167$, where the weights were $w_f = \sigma_F{}^{-2}$. A difference Fourier synthesis was computed; no new atoms were found, but there was considerable evidence for anisotropic motion of those present.

The data were corrected for absorption ($\mu = 16.36\ \text{cm}^{-1}$); calcd. transmission factors ranged from 0.889 to 0.958. Three cycles of isotropic refinement using the corrected data did not change the R values, but a slight overall decrease in thermal parameters was noted. All atoms were now given anisotropic temperature factors; three cycles of refinement gave $R_1 = 0.096$; $R_2 = 0.073$.

An empirical weighting scheme $\sigma = 0.87|F_0|^{1/4}\sigma_F$ was introduced to remove an observed $|F_0|$ dependence in the quantity $w_F||F_0| - |F_c||^2$, in accordance with Cruickshank's criterion[18] (inspection of the data indicated that the dependence was not due to extinction). Three cycles of refinement using the new weights were carried out. The final R_1 and R_2 were 0.093 and 0.080, respectively. The e.s.d. of a unit-weight observation was 1.14, and the quantity $w_F||F_0| - |F_c||^2$ was now essentially independent of both $|F_0|$ and $\lambda^{-1} \sin\theta$, indicating the correctness of the weighting scheme. Inspection of the final correlation matrix revealed a number of sizable correlations between both positional and thermal parameters on different atoms. The largest correlation coefficient had the value $b_{ij} = 0.51$. The effects of all $b_{ij} \geqslant 0.2$ between positional parameters, all those between unit cell parameters, and those due to non-orthogonality of cell axes were included in calculating e.s.d.'s for interatomic distances and angles. A difference Fourier synthesis was computed using the final parameters. The largest peak, in the vicinity of the Mo atom, had a density of 1.87 electrons/A^3.

The final thermal parameters for atoms in the CF_3 groups are in several cases unreasonably large, particularly for the group (C4, F4–6). A difference Fourier synthesis was computed with the parameters for C3, C4, F4, F5 and F6 removed. There were only five significant peaks in the map, corresponding to the five removed atoms in positions essentially identical to those given them by the least-squares process. It thus appears that the large B_{ij}'s are due to a slight disorder (not uncommon for CF_3 groups)[19] and not to any misplacement of the atoms involved.

Computer Programs Programs used in the structure determination include PICK2 (J. A. Ibers) for cell-constant refinement and generation of data settings; FAME and MAGIC (R. Dewar, A. Stone) for calculation of E's and phase determination; SFIX (local version of C. T. Prewitt's SFLS–5) for full-matrix least-squares refinement based on minimization of the function $D = \Sigma w_F||F_0| - |F_c||^2$; FORDAP (A. Zalkin) for difference Fourier syntheses; DRAB70 (B. G. DeBoer) for data reduction and the absorption correction; STAN1 (B. G. DeBoer) for interatomic distances and angles; MGEOM (J. S. Wood) for least-squares planes; and ORTEP (C. K. Johnson) for intermolecular contacts and diagrams.

TABLE II

Final positional and thermal parameters[a]

Atom	X	Y	Z	B[b], Å^2
Mo	0.0578(3)	0.4668(2)	0.3570(3)	3.6(1)
O1	0.252(2)	0.372(2)	0.598(3)	4.6(8)
O2	0.133(2)	0.440(2)	0.904(2)	4.5(8)
O3	0.175(2)	0.651(2)	0.363(3)	6.2(9)
O4	0.057(2)	0.726(2)	0.682(3)	5.5(9)
C1	0.247(3)	0.382(3)	0.825(5)	4.(1)
C2	0.370(3)	0.307(4)	0.997(6)	6.(2)
C3	0.150(4)	0.739(3)	0.529(6)	6.(2)
C4	0.229(4)	0.867(6)	0.535(5)	9.(3)
F1	0.312(2)	0.204(2)	1.119(4)	10.(1)
F2	0.488(2)	0.260(2)	0.913(3)	12.(1)
F3	0.442(2)	0.395(2)	1.175(3)	10.(1)
F4	0.384(2)	0.892(2)	0.566(5)	14.(2)
F5	0.204(3)	0.985(2)	0.683(6)	17.(2)
F6	0.199(3)	0.961(2)	0.346(7)	15.(2)

TABLE II—*contd.*

Anisotropic thermal parameters,[c] Å^2

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	5.2(1)	4.9(1)	0.8(1)	0.14(9)	1.04(7)	0.39(8)
O1	6.5(9)	4.7(9)	2.7(8)	1.5(7)	1.4(7)	−0.3(7)
O2	4.7(8)	8.(1)	0.9(7)	−0.3(8)	0.5(6)	1.1(7)
O3	8.(1)	9.(1)	1.3(7)	0.5(9)	1.1(7)	0.5(8)
O4	5.1(9)	8.(1)	3.6(9)	0.4(8)	1.2(7)	1.2(8)
C1	3.(1)	5.(1)	4.(2)	0.(1)	1.(1)	−0.(1)
C2	2.(1)	11.(3)	5.(2)	−0.(2)	1.(1)	−2.(2)
C3	8.(2)	3.(2)	5.(2)	−4.(1)	−2.(2)	3.(2)
C4	7.(2)	17.(4)	3.(2)	4.(3)	3.(2)	1.(2)
F1	9.(1)	9.(1)	11.(1)	1.(1)	−0.2(9)	5.(1)
F2	10.(1)	21.(2)	5.6(9)	9.(1)	2.5(9)	5.(1)
F3	11.(1)	12.(1)	6.(1)	−1.(1)	−2.8(9)	0.8(9)
F4	6.(1)	9.(1)	27.(3)	−1.4(9)	−0.(1)	4.(1)
F5	20.(2)	11.(2)	22.(3)	−10.(2)	12.(2)	−7.(2)
F6	18.(2)	7.(1)	19.(2)	−5.(1)	0.(2)	4.(2)

[a] Numbers in parentheses represent e.s.d.'s in the last figure quoted for all tables.

[b] Effective isotropic B's for the anisotropically refined atoms.

[c] The form of the temperature factor expression is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

RESULTS AND DESCRIPTION OF STRUCTURE

The final values of $|F_c|$ and $|F_0|$ scaled to $|F_c|$ are given in Table I. This table is not included here, but a copy may be obtained from the Editor. Fractional coordinates and thermal parameters for the 15 unique atoms appear in Table II. Tables III–V present data on interatomic distances, angles and least-squares planes, respectively. Table VI contains the vibrational and electronic spectral data, and Table VII the mass spectral data. Figures 2 and 3 depict the molecular structure and a portion of the crystal structure, respectively, and illustrate the atom numbering scheme.

TABLE III

Interatomic distances

Atoms	Distance	Atoms	Distance
Bond lengths and intramolecular contacts, Å			
Mo—Mo	2.090(4)	C2—F1	1.32(3)
Mo—O1	2.11(2)	C2—F2	1.24(3)
Mo—O2	2.14(2)	C2—F3	1.33(3)
Mo—O3	1.97(2)	C4—F4	1.31(4)
Mo—O4	2.01(2)	C4—F5	1.39(5)
C1—O1	1.28(3)	C4—F6	1.37(4)
C1—O2	1.23(3)	O1 .. O2	2.20(2)
C3—O3	1.26(3)	O3 .. O4	2.28(2)
C3—O4	1.26(3)	F1 .. F2	2.10(3)
C1—C2	1.46(4)	F1 .. F3	2.06(3)
C3—C4	1.35(5)	F2 .. F3	1.99(3)
		F4 .. F5	1.94(3)
		F4 .. F6	1.91(4)
		F5 .. F6	1.87(4)
Intermolecular contact, Å			
Mo–O2	2.72(1)		

TABLE IV

Interatomic angles

Atoms	Angle	Atoms	Angle
Bond angles, deg.			
O1—Mo—O2	176.9(6)	C1—C2—F1	114.(2)
O3—Mo—O4	174.4(7)	C1—C2—F2	116.(3)
O1—Mo—O3	91.8(6)	C1—C2—F3	112.(3)
O2—Mo—O4	90.5(6)	C3—C4—F4	130.(4)
O1—Mo—O4	89.6(6)	C3—C4—F5	124.(3)
O2—Mo—O3	87.8(6)	C3—C4—F6	122.(3)
Mo—O1—C1	117.(2)	F1—C2—F2	110.(3)
Mo—O2—C1	118.(2)	F1—C2—F3	102.(3)
Mo—O3—C3	114.(2)	F2—C2—F3	101.(2)
Mo—O4—C3	112.(2)	F4—C4—F5	92.(4)
O1—C1—O2	123.(2)	F4—C4—F6	91.(3)
O3—C3—O4	129.(3)	F5—C4—F6	86.(4)
O1—C1—C2	118.(2)		
O3—C3—C4	115.(3)		
Contact angle, deg.			
Mo—Mo—O2	161.0(4)		

TABLE V

Weighted least squares planes[a]

Plane	Equation	Angles between planes, deg.		
1. $O_1O_2C_1C_2$	$0.511x + 0.853y + 0.103z = 3.983$	87(2)		
2. $O_3O_4C_3C_4$	$0.653x - 0.404y + 0.641z = -0.417$		90(1)	
3. $O_1O_2'O_3O_4'$	$-0.592x + 0.270y + 0.759z = 2.489$			90(1)

Distances of atoms from planes,[b] A

1. O_1, −0.01; O_2, −0.01; C_1, 0.04; C_2, −0.03; Mo, −0.086; Mo′, −0.080
2. O_3, −0.00; O_4, −0.00; C_3, 0.02; C_4, −0.01; Mo, 0.028; Mo′, −0.025
3. O_1, 0.02; O_2', 0.02; O_3, −0.02; O_4', −0.02; Mo, 0.075

[a] The orthogonal coordinates (x, y, z) are directed along the crystal axes $c^* \times a$, b and c^*, respectively, and are in Angstroms. The weight given to each atom i in forming the planes is $w_i = [a\sigma_{x_i} b\sigma_{y_i} c\sigma_{z_i}]^{-2/3}$. Primed atoms are related by an inversion center to those appearing in the atom parameter table.

[b] Average e.s.d.'s of atomic positions are (A): Mo, 0.002; O, 0.02; C, 0.03; F, 0.02.

TABLE VI

Spectroscopic data for $Mo_2(O_2CCF_3)_4$

Infrared:[a] 3035w, 3020w, 2920w, 2900w, 1592s, 1572s, 1459s, 1251m, 1192br, 858s, 781m, 777m, 730s, 516br, 492m, cm^{-1}.

Raman:[a] 877m(877), 746m(748), 518m(517), 501m(501), 397s(383), 201m, cm^{-1}.

Assignments and comparison with $Mo_2(O_2CCH_3)_4$

Assignment	Position, $Mo_2(O_2CCF_3)_4$	Position, $Mo_2(OAc)_4$[b]
$\upsilon_{as}(CO)_2$	1592, 1572	1512, 1494
$\upsilon_s(CO)_2$	1459	1409
υ(C—F)	1251, 1192	—(1180 in CF_3CO_2Na)
υ(Mo—Mo)	397	406

Electronic: $\tilde{\upsilon}_{max}$ = 23.0(ϵ120), 32.7(6300), 44.2(1500)kK [$Mo_2(O_2CCF_3)_4$]
22.7(ϵ 60), 34.0(7500), 42.9(3500) [$Mo_2(O_2CCH_3)_4$][c]
23.0(ϵ100), 29.4(3000), 43.9(800) [$Mo_2(O_2CC_3F_7)_4$][c]

[a] Band positions in 1.0M ether solution are given in parentheses. Other positions are from solid state spectra.

[b] Reference 25.

[c] Reference 20.

As anticipated, the structure of $Mo_2(O_2CCF_3)_4$ had idealized D_4h symmetry with the molybdenum atoms bridged by the trifluoroacetate groups. The molecule lies on an inversion center in the crystal and as a result only the unit $Mo(O_2CCF_3)_2$ is unique. The four carboxylate oxygen atoms surrounding molybdenum lie in one plane, but the Mo atom is displaced from this plane toward the other metal atom by 0.075 A, resulting in a very short Mo–Mo distance of 2.090(4) A. The two CCO_2 groups are planar and perpendicular both to each other and to the O_4 coordination sphere around Mo within experimental error. The Mo atoms deviate from the carboxylate planes by

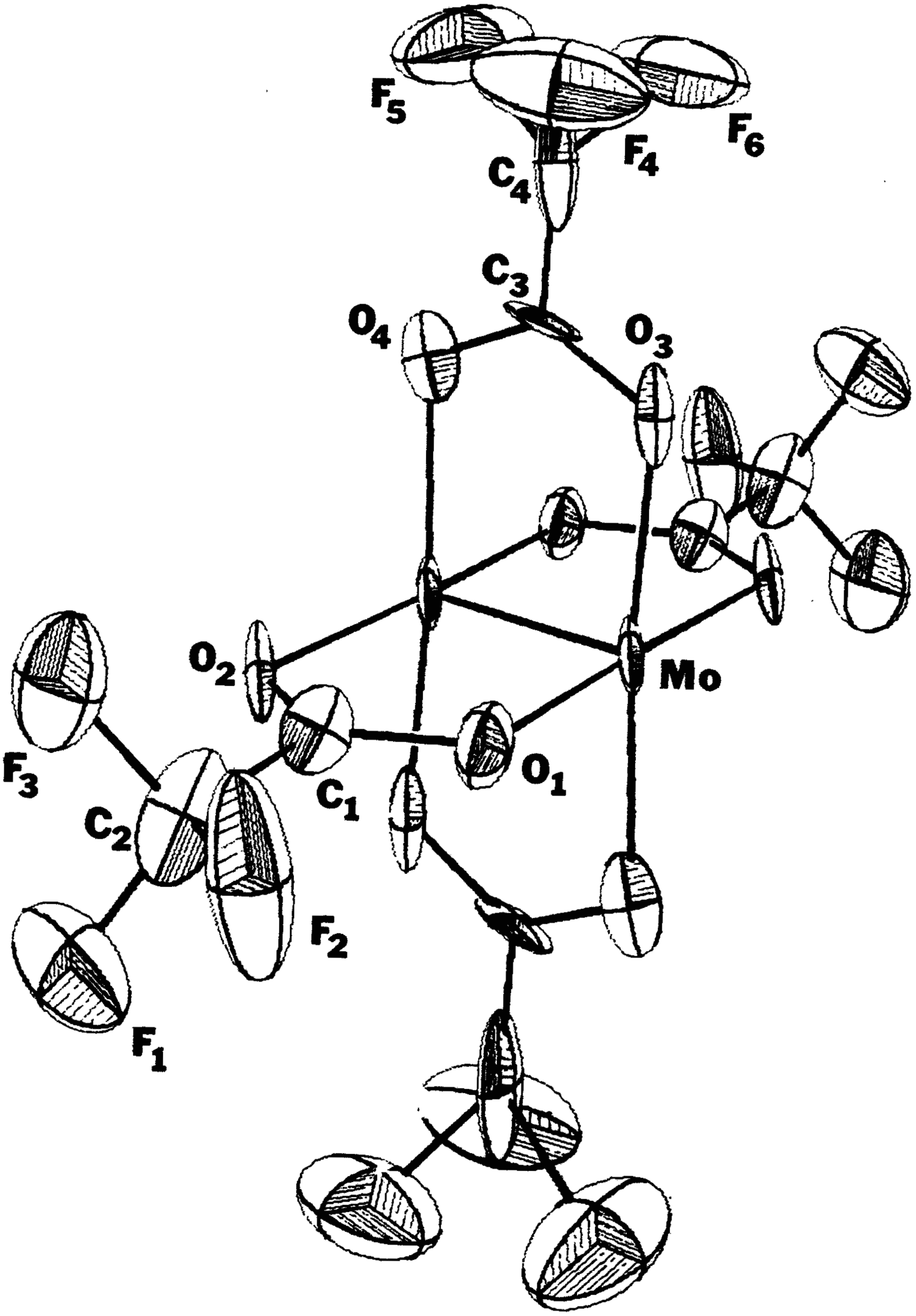

FIGURE 2 A perspective view of the molecular structure. The ellipsoids enclose 30% probability of thermal motion.

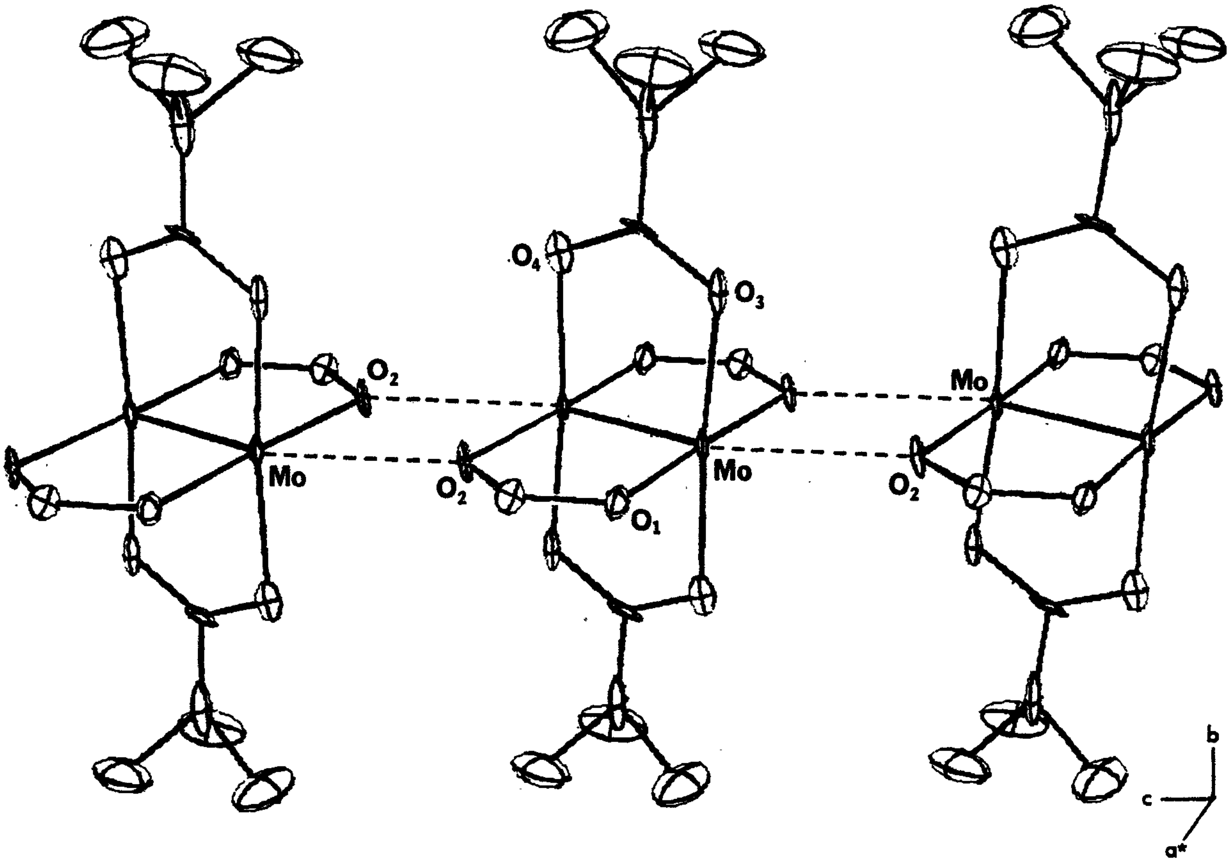

FIGURE 3 A view of the *bc* plane showing one molecule and the two with which it makes contacts less than the sum of van der Waals radii. The contacts are indicated by dotted lines. The ellipsoids enclose 10% probability of thermal motion.

0.08–0.09 A for one plane and 0.03 A for the other. The configuration of the two ligands differs significantly in quantitative detail, the average Mo–O distance, O . . . O contact, and F . . . F contacts in one being definitely shorter, longer, and shorter, respectively, than in the other.

As discussed in the Experimental section, the abnormally large thermal parameters found in the CF_3 groups are apparently due to a slight disorder. The possibility of such a problem had been anticipated from the observed softness of the crystals. The shape of the thermal ellipsoids, as illustrated by Figure 2, suggest that the nature of the disorder is at least partially rotational, around the C–CF_3 axis. Because of this phenomenon the distances and angles involving the CF_3 groups should be interpreted with caution, as the derived e.s.d.'s probably do not fully reflect the inadequacy of the model being employed.

There is only one intermolecular contact shorter than the sum of van der Waals radii, namely, that between the atoms Mo and O2. The nature of the contact is indicated by Figure 3. The oxygen atom lies close to, but not exactly along, the Mo—Mo axis ($\angle$Mo—Mo—O2 = 161.0(4)°). The Mo—O2 distance of 2.72(1) A is about 0.4 A longer than expected for even a fairly weak bonding interaction (compare the Rh—OH_2 distance of 2.310(3) A in $Rh_2(OAc)_4(H_2O)_2$)[4] but is still significantly shorter than a normal van der Waals distance. The presence of this contact, and the absence of others, provides a natural explanation for the tendency of the crystals to elongate—sometimes quite dramatically—along the *c* direction.

TABLE VII

Positive-ion mass spectrum of $Mo_2(O_2CCF_3)_4$, 70 eV[a]

m/e[b]	Intensity	Assignment[c]
644	30	$Mo_2(O_2CCF_3)_4$
625	21	$Mo_2(O_2CCF_3)_3(O_2CCF_2)$
550	48	$Mo_2F(O_2CCF_3)_3$
531	14	$Mo_2(O_2CCF_3)_3$
456	100	$Mo_2F_2(O_2CCF_3)_2$
437	14	$Mo_2F(O_2CCF_3)_2$
362	43	$Mo_2F_3(O_2CCF_3)$
195	24	$MoOC_2F_3$
133	24[d]	MoOF
114	18[e]	MoO
98	32	Mo
69	83	CF_3
44	16	CO_2
28	22	CO, N_2

[a] All peaks above m/e = 350 are listed. Below that point only peaks with intensity ≥15 are listed, as there are measurable peaks at almost every value of m/e down to 92.

[b] For peaks due to Mo-containing fragments, only the value of m/e for the most intense peak in the isotopic grouping is listed. This peak will result from the ^{98}Mo- and $^{192}Mo_2$-containing fragments for ions with one and two Mo's, respectively.

[c] Single positive charges are implied for all fragments. Isomers of the formulas listed are, of course, also possible assignments.

[d] Corrected for observed overlap with peaks due to MoF_2^+, MoO_2^+ and MoF^+.

DISCUSSION

Synthesis A number of molybdenum(II) carboxylates have been prepared by reacting $Mo(CO)_6$ with carboxylic acid–anhydride mixtures (for liquid acids) or with carboxylic acids in diglyme (for solid acids).[13] An unsuccessful attempt to prepare the trifluoroacetate by this method has been reported.[20] We were also unable to isolate $Mo_2(O_2CCF_3)_4$ from this reaction, apparently because the transformation proceeds much more slowly in CF_3COOH than other acids, since CF_3COOH boils some 30° lower than any of those previously employed. However, the compound was readily synthesized by carboxylate exchange using $Mo_2(OAc)_4$ and a CF_3COOH—$(CF_3CO)_2O$ mixture. It is easily purified by sublimation.

Crystal Structure As was expected, the trifluoroacetate adopts the familiar carboxylate-bridged configuration illustrated in Figure 1. The extremely short Mo—Mo distance of 2.090(4) A is not significantly different from that found in $Mo_2(OAc)_4$, 2.11(1) A;[5] the average Mo—O distances (2.06(2) and 2.10(2) A, with the e.s.d.'s as well as bond lengths averaged) are also the same within experimental error. One may use the Mo—O distance, and the value 0.66 A for the covalent radius of oxygen,[21] to estimate the covalent radius of molybdenum in the two compounds as ~1.42 A. The metal–metal bonds, in accord with their proposed multiple character, are thus about 0.7 A shorter than expected for an Mo—Mo single bond.

Before the X-ray results were known, we had expected that, if there were to be a significant difference between the bond lengths in the acetate and trifluoroacetate, the latter distance would be the longer one. It was felt that the higher effective charge of Mo in the supposedly more polar Mo—O bonds of the trifluoroacetate would lead to a contraction of the valence orbitals involved in metal–metal bond formation, resulting in poorer overlap of these orbitals between the two metals, at a given distance. Hence the attractive interaction between the metals would be reduced in magnitude, while the repulsive interaction of their cores would remain relatively unchanged, leading on balance to a longer and weaker bond. Whatever the *sign* of the difference in bond strength between the acetate and trifluoroacetate may be, however, it is now clear that its *magnitude* is very small and not sufficient for unambiguous detection with the present X-ray results. In retrospect, this is hardly surprising, since the rate of change of bond length with bond order is well known to decrease rapidly with increasing formal bond order. For the closely similar case of Re—Re multiple bonds it has been found[22] that a change in bond order from 4 to 3 increases the bond length by only 0.054 ± 0.006 A, which is in good accord with general graph of M—M distance against bond order.[23] A better assessment of the influence of ligand acidity on metal–metal bond strength in the carboxylates might therefore be obtained using a metal toward the right of the transition group, where the bond order should be considerably less than the value of four in the Mo compounds. As mentioned earlier, however, the Mo carboxylates are currently the only ones which have been crystallized without the complicating feature of axial ligands.

Vibrational Spectra Relatively small changes in bond order, which may be undetectable from comparison of bond lengths, are usually reflected with far greater sensitivity by shifts in vibrational stretching frequencies of the bond involved. For instance, in metal carbonyls, a decrease in formal C—O bond order of 0.5 in the range 2–3, which is barely detectable by X-ray methods, may result in a decrease in C—O stretching frequencies of 100–200 cm^{-1}.[24] (The quantitative correlation between vibrational spectra and bond orders is, of course, best made using force constants rather than stretching frequencies.) We have previously carried out an approximate normal-coordinate analysis on $Mo_2(OAc)_4$, resulting in assignment of the strong Raman band at 406 cm^{-1} to the A_{1g} mode consisting predominantly of Mo—Mo stretching (the mode contains no significant contribution from Mo—O stretching, and only a minor contribution due to Mo—Mo—O angle bending.)[25] The Mo—Mo force constant of *ca.* 3.7 derived from this analysis is as expected for a bond order of 3–4; providing strong independent support for the proposal[10] that the bond has order 4. The strongest band in the Raman spectrum of $Mo_2(O_2CCF_3)_4$—indeed, the only significant band in the region 200–500 cm^{-1}—occurs at 397 cm^{-1} in the solid and 383 cm^{-1} in the ether solution; this band may be rather confidently assigned to ν(Mo—Mo) by comparison with the acetate spectrum. The decrease of about 10 cm^{-1} in going from the acetate to the trifluoroacetate perhaps indicates a slight weakening of the metal–metal bond, but by comparison with the sort of shifts usually observed in vibrational spectra (see above), the difference seems very small indeed. The Raman results are therefore in line with those from the X-ray analysis. The slightly lower value for ν(Mo—Mo) observed in ether solution may be attributed to weak coordination of ether molecules as axial ligands, which should decrease the metal–metal bond strength by a very small amount.[26] No solution measurements were possible on $Mo_2(OAc)_4$ because of its low solubility.

The bands in the solid state infrared spectrum of $Mo_2(O_2CCF_3)_4$ due to carboxylate and C—F stretching may be assigned by comparison with the spectra of $Mo_2(OAc)_4$[25] and CF_3CO_2 Na. The entire spectrum of the complex from 1250 and 640 cm^{-1} qualitatively resembles that of CF_3CO_2Na.

Mass Spectrum The high volatility of $Mo_2(O_2CCF_3)_4$ has made it possible to obtain the first mass spectral data for the dimeric carboxylates. A strong peak is observed for the molecular ion, $Mo_2(O_2CCF_3)_4^+$, which as expected increases markedly in intensity to the other peaks when the electron energy is lowered from 70 to 20 eV. The molecule breaks down by successive loss of three CF_2CO_2 units, the third fluorine from trifluoroacetate becoming bonded to Mo in each fragmentation process. When the unit $Mo_2F_3(O_2CCF_3)^+$ is reached, the breakdown process becomes less systematic, resulting finally in the fragments $MoOF^+$, MoO^+ and Mo^+. There is no evidence for the Mo_2^+ ion; rather some oxygen and/or fluorine remains bonded to Mo until the metal–metal bond is cleaved. Overall, the mass spectrum supports the view that the same basic structure found for the trifluoroacetate in the crystal is retained in the gas phase.

The large number of stable molybdenum isotopes (92, 94–98, 100, all with natural abundance in the range 10–24%) complicates the spectrum, since each fragment containing Mo gives rise to a group of peaks. However, this feature allows ready recognition and differentiation of peaks containing one and two Mo's, since the characteristic isotopic "fingerprint" for each case is different and easily identified. For example, one can positively characterize the grouping near $m/e = 195$ as due to $MoOC_2F_3^+$ ($m/e = 189$–197) rather than Mo_2^+ ($m/e = 184$–200) because the isotopic intensity pattern is essentially identical to that observed for Mo^+ rather than $Mo_2(O_2CCF_3)_4^+$. In the same way, overlap of peak groups due to $MoOF^+$ and MoO^+ with less intense groups from MoF_2^+, MoO_2^+ and MoF^+ can be detected and corrected for.

Electronic Spectrum The solution electronic spectrum of $Mo_2(O_2CCF_3)_4$ closely resembles that reported previously for other molybdenum(II) carboxylates.[20] The previous workers attempted to assign the two lower-energy transitions in the acetate using the results of a semi-empirical MO calculation as a guide. They concluded that the band at 34.0 kK is due to the allowed $B_{2g} \rightarrow B_{1u}$ transition between δ and δ^* orbitals involved in the metal–metal bond. We have no particular quarrel with this assignment, but we feel that a completely reliable analysis of the electronic structure of the dimeric carboxylates could only be made with the aid of single crystal polarized spectra. From a structural point of view, molybdenum(II) trifluoroacetate seems a particularly attractive candidate for such work, since all molecules in the lattice are oriented in the same direction, roughly along *c*, and a symmetry analysis in D_{4u} shows that the $B_{2g} \rightarrow B_{1u}$ transition should be the only low-lying allowed band which is *z*-polarized. Unfortunately, the high intensity of the transition would make its observation virtually impossible using crystals of the pure compound.

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26. *Note Added in Proof:* We have recently observed that V(Mo–Mo) = 343 cm^{-1} For $Mo_2(O_2CCF_3)_4$ in pyridine, indicating a significant weakening of the metal-metal bond by comparison to the solid-state and ether solution spectra.