Molecular Structure of Tetrakis-μ-trifluoroacetato-dimolybdenum(II), $[Mo_2(O_2CCF_3)_4]$; a Gas-phase Electron-diffraction Study

By **C. David Garner,* Ian H. Hillier,** and **Ian B. Walton,** The Chemistry Department, Manchester University, Manchester M13 9PL
Brian Beagley, The Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The molecular structure and interatomic dimensions of $[Mo_2(O_2CCF_3)_4]$ in the gas phase at 150 °C have been determined by electron-diffraction measurements and shown to be similar to those obtained by *X*-ray diffraction methods; dimensions obtained include Mo–Mo 2.105(9), Mo–O 2.102(6) Å, and Mo–Mo–O 91.9(3)°.

CURRENTLY much interest is centred upon the synthesis and characterisation of compounds containing multiple metal–metal bonds.[1,2] The range of compounds which contain a quadruple bond between a pair of molybdenum(II) atoms is now quite extensive, and several discussions of the electronic structure of these metal–metal bonds have now been presented.[3-7] Gas-phase He(I) and He(II) photoelectron-spectral data have provided useful information in this respect, particularly for the dimolybdenum(II) tetra-μ-carboxylates, $[Mo_2(O_2CR)_4]$ (R = H, Me, CF_3, or Bu^t).[8-10] Although the molecular structures of several of these compounds have been determined by *X*-ray diffraction methods,[10-13] no structural characterisation has been attempted for any of these species in the gas phase. Such a study seemed necessary to confirm the nature of the gas-phase species and to determine values for the intramolecular dimensions, particularly the molybdenum–molybdenum separation in the free molecule. Therefore, we have undertaken an electron-diffraction study of $[Mo_2(O_2CCF_3)_4]$.

EXPERIMENTAL

The compound $[Mo_2(O_2CCF_3)_4]$ was prepared as previously described,[12] and purified by sublimation at 90 °C (0.05 Torr).† Diffraction patterns at nominal nozzle-to-plate distances of 100, 50, and 25 cm were collected photographically on Kodak electron-image plates, using a Balzers K.D.G.2 gas-diffraction apparatus.[14] The temperature of the sample at the diffraction point was estimated to be 150 °C, and the beam wavelength was 0.056 75 ± 0.000 03 Å. The intensities were converted into digital form using a fully automated Joyce-Loebl microdensitometer. The *s* ranges and weighting scheme are detailed in Table 1. All calculations were carried out using the CDC 7600 computer at the University of Manchester Regional Computer Centre, using established procedures.[15]

TABLE 1

s Ranges and weighting scheme

Nominal camera distance (cm)	*s* Range (Å^{-1})	Weighting scheme			
		l_a/Å^{-1}	w_a	l_b/Å^{-1}	w_b
100	1.000 by 0.025 to 8.100	2.0	0.7	7.0	2.3
50	2.00 by 0.05 to 16.25	3.0	1.05	15.4	2.3
25	8.0 by 0.1 to 27.0	8.0		25.0	2.3

where, for

$s_{\text{min.}} \leqslant s < l_a$ weight = $\exp[-w_a(l_a - s)]$
$l_a \leqslant s < l_b$ weight = 1.0
$l_b \leqslant s \leqslant s_{\text{max.}}$ weight = $\exp[-w_b(s - l_b)]$

Solution and Refinement.—A preliminary inspection showed that the basic molecular framework (Figure 1) typical of these compounds [1] was consistent with the experimental radial-distribution (r.d.) curve (Figure 5). For refinement, the Mo[OC(C)O]$_4$ moiety was taken to have D_{4h} symmetry; all the C–F bonds and F–C–F angles were assumed to be equal and each CF_3 group was placed in a special position, such that one C–F bond was coplanar with the CO_2 moiety of that group, the net molecular geometry being C_{4v}.

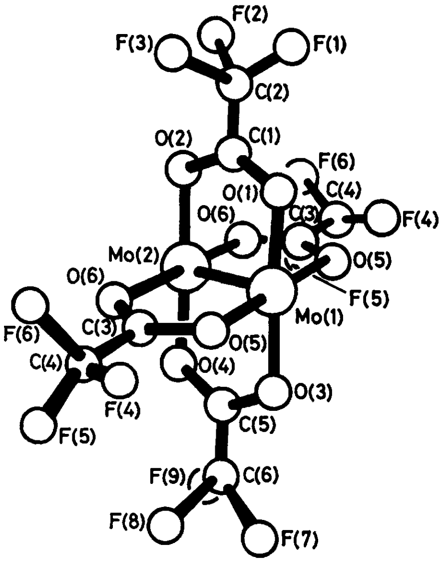

FIGURE 1 Molecular structure of $[Mo_2(O_2CCF_3)_4]$

Seven independent geometrical parameters are required to specify the 435 interatomic distances within the molecule, the ones chosen being the Mo–Mo, Mo–O, Mo $\cdots$ C(CF$_3$), C–C, and C–F separations and the Mo–Mo–O and F–C–F interbond angles. The initial values of these independent parameters were taken as the average values given in ref. 12. The value of the root-mean-square (r.m.s.) amplitude of vibration for the C–F, C–C, and C–O distances was taken as the average of those obtained in the electron-diffraction studies of $CF_3CO_2H(g)$ [16] and $(CF_3CO)_2O(g)$;[17] for the remaining amplitudes, the approximation $u = d/30$ where d = interatomic separation and u = r.m.s. amplitude of vibration (Å) was used to obtain an initial value. The

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

TABLE 2

Averaged bond lengths and certain other interatomic distances and interbond angles within the $[Mo_2(O_2CCF_3)_4]$ molecule

Atoms	Distance/Å $[Mo_2(O_2CCF_3)_4]$ (g) [a]	$[Mo_2(O_2CCF_3)_4]$ (c) [b]
Mo–Mo	2.105(9)	2.090(4)
Mo–C	2.102(6)	2.06(8)
Mo–C(CF_3)	2.86(1)	2.83(7)
C–C	1.54(1)	1.41(6)
C–F	1.335(5)	1.33(5)
C–O	1.25(2)	1.26(3)
F · · · F	2.19(2)	1.98(8)
O · · · O	2.24(2)	2.24(5)
	Angle/°	
Mo–Mo–O	91.9(3)	92(1)
O–Mo–O_{cis}	89.9(6)	90(2)
O–Mo–O_{trans}	176.2(6)	176(3)
Mo–O–C	114.6(7)	115(3)
O–C–O	126.9(7)	126(3)
O–C–C	116.5(4)	117(2)
C–C–F	109.1(5)	120(7)
F–C–F	109.8(7)	97(9)

[a] This work; values in parentheses are estimated standard deviations (three times the least-squares standard deviation). [b] Ref. 12; values in parentheses are the corresponding estimated standard deviation.

scattering factors of Cox and Bonham [18] were employed. Anharmonicities were set equal to 2.0 for bonded distances and 0.0 for non-bonded distances and were not refined. Background functions were subtracted using routine smoothness criteria.[14] A damping factor of 0.002 Å^{-2} was used in the calculation of the r.d. curve.

Because of correlation problems caused by the similar Mo–Mo and Mo–O distances, the early refinements were restricted to variations in the parameters Mo · · · C, C–C, C–F, F–C–F, and Mo–Mo–O. When convergence was achieved in these respects, the values obtained were used in separate refinements of the Mo–Mo and Mo–O distances. The refined values of all these independent geometrical parameters were then held constant whilst all the amplitudes, except those for the C–F, C–C, and C–O distances, were refined. For simplicity, the Mo–O and Mo–Mo distances were assigned the same amplitude and otherwise

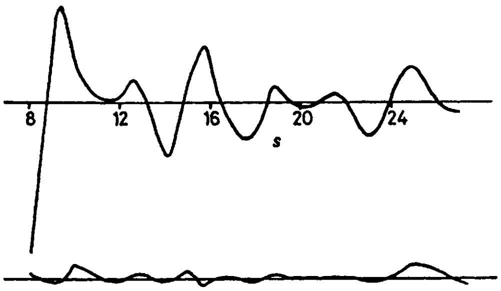

FIGURE 2 Observed and weighted-difference molecular intensities at a nozzle-to-plate distance of 25 cm

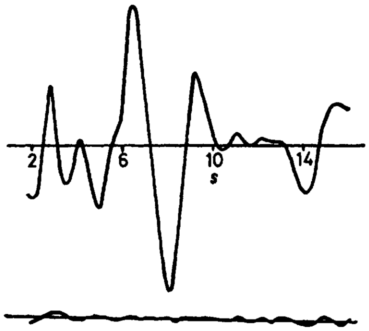

FIGURE 3 Observed and weighted-difference molecular intensities at a nozzle-to-plate distance of 50 cm

TABLE 3

Refined interatomic distance [a] and r.m.s. amplitudes of vibration (Å) for $[Mo_2(O_2CCF_3)_4]$ (g)

	Contact	Multiplicity	Distance	Amplitude [b]
(1)	O(1)–C(1)	8	1.25	0.042
(2)	C(2)–F(1)	12	1.335	0.042
(3)	C(1)–C(2)	4	1.54	0.042
(4)	Mo(1)–O(1)	8	2.102	0.055
(5)	Mo–Mo	1	2.105	0.055
(6)	F(1)–F(2)	12	2.18	0.114
(7)	O(1)–O(2)	4	2.24	0.114
(8)	C(1)–F(1)	12	2.34	0.114
(9)	O(1)–C(2)	8	2.38	0.114
(10)	O(1)–F(1)	4	2.54	0.114
(11)	O(2)–F(2)	8	2.80	0.077
(12)	Mo(1)–C(1)	8	2.86	0.077
(13)	O(1)–O(5)	8	2.97	0.077
(14)	Mo(1)–O(2)	8	3.02	0.077
(15)	O(1)–F(2)	8	3.27	0.077
(16)	O(2)–F(1)	4	3.48	0.134
(17)	O(1)–C(3)	16	3.57	0.134
(18)	O(1)–O(6)	8	3.72	0.134
(19)	C(1)–C(3)	4	3.76	0.134
(20)	O(1)–O(3)	4	4.20	0.134
(21)	Mo(1)–C(2)	8	4.33	0.134
(22)	Mo(1)–F(1)	4	4.64	0.245
(23)	O(1)–O(4)	4	4.76	0.245
(24)	O(2)–F(6)	8	4.77	0.245
(25)	Mo(2)–F(2)	8	4.78	0.245
(26)	O(1)–C(4)	16	4.83	0.245
(27)	O(2)–C(5)	8	4.89	0.245
(28)	C(1)–F(6)	8	4.94	0.245
(29)	C(1)–C(4)	8	4.97	0.245
(30)	F(3)–F(6)	4	5.01	0.245
(31)	Mo(1)–F(2)	8	5.05	0.245
(32)	O(1)–F(6)	8	5.06	0.245
(33)	O(1)–F(4)	8	5.09	0.245
(34)	Mo(2)–F(1)	4	5.18	0.245
(35)	C(1)–C(5)	2	5.32	0.264
(36)	C(1)–F(4)	8	5.49	0.264
(37)	C(2)–F(6)	8	5.62	0.264
(38)	O(2)–F(4)	8	5.62	0.264
(39)	O(2)–F(5)	8	5.65	0.264
(40)	O(1)–F(5)	8	5.90	0.264
(41)	C(4)–C(6)	4	5.94	0.264
(42)	C(1)–F(5)	8	6.00	0.264
(43)	F(1)–F(6)	8	6.14	0.264
(44)	C(2)–F(4)	8	6.38	0.264
(45)	O(1)–C(6)	8	6.40	0.264
(46)	F(1)–F(4)	4	6.56	0.264
(47)	O(1)–F(7)	4	6.74	0.264
(48)	F(3)–F(5)	8	6.74	0.264
(49)	O(2)–F(8)	8	6.84	0.264
(50)	C(1)–C(6)	4	6.86	0.181
(51)	O(1)–F(8)	8	7.05	0.181
(52)	C(2)–F(5)	8	7.07	0.181
(53)	O(2)–F(7)	4	7.15	0.181
(54)	C(1)–F(7)	12	7.41	0.181
(55)	F(1)–F(5)	8	7.61	0.181
(56)	F(2)–F(5)	4	8.10	0.283
(57)	C(2)–C(6)	2	8.40	0.283
(58)	C(2)–F(7)	12	8.93	0.283
(59)	F(1)–F(7)	6	9.28	0.283
(60)	F(1)–F(8)	12	9.53	0.283

[a] See Figure 1 for specification of the atoms. [b] Estimated errors: 0.055(5); 0.077(12); 0.114(12); 0.134(11); 0.245(6); 0.264(27); 0.181(34); 0.283(84). The amplitude for contacts (1)—(3) was not refined.

Table 4

Least-squares correlation matrix multiplied by 1 000

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
a	1 000								
b	577	1 000							
c	302	457	1 000						
d	30	28	1	1 000					
e	37	35	3	96	1 000				
f	−144	−153	−87	20	294	1 000			
g	312	272	158	23	147	409	1 000		
h	74	263	331	4	6	85	314	1 000	
i	96	169	222	4	−29	51	156	476	1 000
j	430	489	352	16	30	−65	122	25	−45
k	270	458	468	1	−1	−134	91	183	222
l	181	84	−2	4	−2	57	24	49	59
m	81	218	211	−4	15	−268	−94	−199	−431
n	−152	−119	52	−2	−42	125	56	275	735
o	326	333	108	37	20	−168	143	84	−210
p	427	437	347	2	13	−91	136	269	261
q	−116	−181	−262	−1	19	−74	−109	−411	−678
r	−60	−12	48	29	6	254	191	238	373

	j	*k*	*l*	*m*	*n*	*o*	*p*	*q*	*r*
j	1 000								
k	164	1 000							
l	275	108	1 000						
m	442	87	−493	1 000					
n	84	4	64	−327	1 000				
o	11	−12	−89	187	−335	1 000			
p	532	53	38	230	135	−148	1 000		
q	−353	−202	−431	277	−674	253	−522	1 000	
r	127	−218	−128	−213	648	205	−5	−337	1 000

a, *b*, and *c* are scale factors for 100-, 500-, and 25-cm data, *d*, *e*, *f*, *g*, *h*, *i*, *j*, and *k* are amplitudes for contacts (see Table **3**) 56—60, 50—55, 35—49, 22—34, 16—21, 11—15, 6—10, and 4.5, *l*, *m*, *n*, *o*, *p*, are Mo–Mo, Mo(1)–O(1), Mo(1)–C(1), C(1)–C(2), and C(2)–F(1), and *q* and *r* are interbond angles Mo(2)–Mo(1)–O(1) and F(1)–C(2)–F(2), respectively.

all distances in a given peak of the r.d. curve were taken to have the same amplitude. The final refinement allowed for variations in all the independent geometrical parameters and the eight amplitudes within the same cycle. The residual, $\Sigma(|I_{obs.}| - |I_{calc.}|)/\Sigma|I_{obs.}|$, was 0.089 for all the parameters refined together to final convergence.

RESULTS AND DISCUSSION

The molecular intensity data are presented in Figures 2—4 and the observed and difference radial-distribution curves in Figure 5. The values of the independent geometrical parameters, together with the consequent values for certain other intramolecular dimensions, are compared with the corresponding data for $[Mo_2(O_2CCF_3)_4]$(c) [12] in Table 2. Table 3 lists values obtained for all the intramolecular separations and their amplitudes. The final least-squares correlation matrix is given in Table 4.

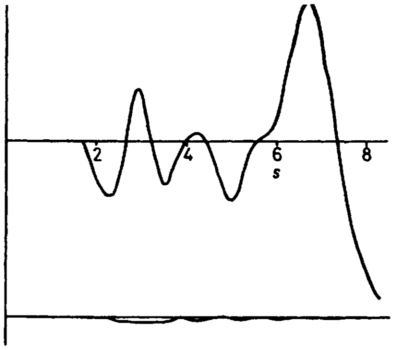

FIGURE 4 Observed and weighted-difference molecular intensities at a nozzle-to-plate distance of 100 cm

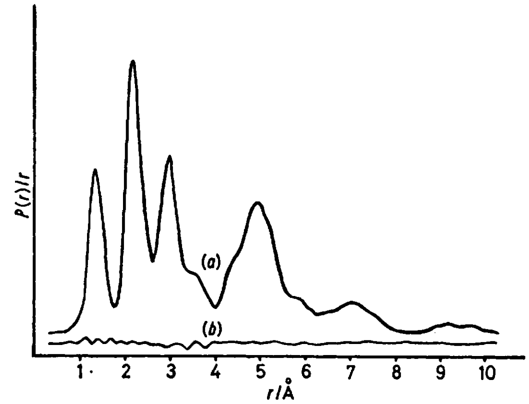

FIGURE 5 Observed (*a*) and difference (*b*) radial-distribution curves for $[Mo_2(O_2CCF_3)_4]$ (g)

Within the limits of the technique and the assumptions made in the interpretation of the data, this electron-diffraction study appears to be of higher precision than that achieved by *X*-ray diffraction.[12] Differences in the dimensions are seen particularly for the value of C–C bond length and C–C–F (and hence the F–C–F) interbond angles; the data reported here are in good accord with the corresponding details of CF_3CO_2H(g),[16] $(CF_3CO)_2O$(g),[17] and $K[X(O_2CCF_3)_2]$(c) (X = H or D) [19] which represent the most accurate structural data currently available for the trifluoroacetate group. However, there are no significant differences in the dimensions obtained for the metal's co-ordination sphere in the two structural studies of $[Mo_2(O_2CCF_3)_4]$. Therefore, the use of the dimensions obtained from crystallographic studies to interpret gas-phase photoelectron-spectral data for $[Mo_2(O_2CR)_4]$ compounds is justified. An important feature to emerge is that the length of the Mo–Mo bond is not significantly changed from the solid to gaseous phase. In $[Mo_2(O_2CCF_3)_4]$(c) each metal atom achieves a weak binding to an oxygen atom of a neighbouring molecule, Mo ··· O 2.72(1) Å. Therefore, this work has verified that the length of the quadruple bond between a pair of molybdenum(II) atoms is insensitive to the attachment of additional ligands along the metal–metal axis.[20]

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