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Preparation and Structures of Two Compounds Containing the Tetra(μ-salicylato)-dimolybdenum(II) Unit

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Reactions of $Mo(CO)_6$ with salicylic acid, o-C_6H_4-$(OH)COOH$, in diglyme and o-$C_6H_4Cl_2$ give rise to $Mo_2(O_2CC_6H_4OH)_4 \cdot 2$(diglyme), 1 and $Mo_2(O_2CC_6H_4OH)_4 \cdot$o-$C_6H_4Cl_2$, 2 respectively. In 1 the $Mo_2(O_2CC_6H_4OH)_4$ molecule resides on a center of inversion and is coordinated in the axial positions by molecules of diglyme. Some important dimensions are: Mo–Mo, 2.101(1) Å, Mo–O(carboxylate), 2.112[4] Å (av), Mo–O (diglyme), 2.588(2) Å. The salicylate OH groups do not interact with the metal atoms at all. The compound crystallizes in space group C2/c with unit cell dimensions of a = *19.028(2) Å;* b = *13.230(1) Å;* c = *18.330(2) Å; β = 110.44(1)°;* V *= 4324(1) Å^3;* Z *= 4. In compound 2 there are two independent $Mo_2(O_2CC_6H_4OH)_4$ units each residing on a center of inversion and these two dinuclear units (which are essentially identical in their dimensions) are linked into infinite chains with some of the salicylato OH groups of each one serving as axial ligands to its neighbors. The o-$C_6H_4Cl_2$ molecules are located between the chains with which they have only van der Waals contacts. Key dimensions are: Mo–Mo, 2.092(1), 2.094(1) Å; Mo–O(carboxylato), 2.109[5] Å (av.), Mo–O (axial), 2.601(3), 2.645(3) Å. The compound crystallizes in space group $P\bar{1}$ with the following unit cell dimensions:* a = *12.441(3) Å;* b = *14.479(2) Å,* c = *10.353(3) Å; α = 99.30(2)°; β = 97.50(2)°; γ = 111.94(1)°;* V *= 1670(1) Å^3;* Z *= 2.*

Introduction

By now a considerable number of compounds in which the quadruply bonded dimolybdenum unit, Mo_2^{4+}, is encircled by four bridging ligands, especially carboxylato anions, have been described [1]. However, there has been little reported for any dimetal unit, including Mo_2^{4+}, concerning compounds in which the R group in $M_2(O_2CR)_4$ bears a donor functionality. In this paper we describe the preparation and structures of two compounds of the $Mo_2(O_2CR)_4$ type in which the acid used is salicylic acid, *i.e.*, R = *o*-(OH)C_6H_4. In one case we used a good donor solvent, diglyme, $CH_3OC_2H_4OC_2H_4OCH_3$, as the reaction medium, while in the other we used a suitably high-boiling solvent with low, though not entirely non-existent donor properties, *ortho*-dichlorobenzene. Since the carboxylato group itself offers two possibilities for linking the $Mo_2(O_2CR)_4$ units together (using additional lone pairs of the carboxyl groups or the OH groups), and there is also the possibility that the reaction solvents (which in both cases were incorporated into the crystalline products) might form axial donor bonds to the $Mo_2(O_2CR)_4$ units, the question of how these crystalline solids, $Mo_2(O_2CC_6H_4OH)_4 \cdot 2$(diglyme), 1, and $Mo_2(O_2CC_6H_4OH)_4 \cdot$*o*-$C_6H_4Cl_2$, 2 would be organized structurally was of interest.

Experimental

Preparation

Mo_2(salicylate)$_4 \cdot 2$diglyme, 1, and Mo_2(salicylate)$_4 \cdot$*o*-$C_6H_4Cl_2$, 2 were prepared by reaction of $Mo(CO)_6$ and salicylic acid in refluxing diglyme and *ortho*-dichlorobenzene respectively [2]. In both cases good quality yellow crystals were obtained in large quantities by slow cooling of the reaction mixture.

X-Ray Crystallography. Collection of Data

Diffraction data for compounds 1 and 2 were collected at room temperature on an Enraf-Nonius CAD-4F autodiffractometer using Mo Kα radiation ($\lambda\alpha$ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. The final unit cell parameters for 1 were determined from a least-squares fit of 25 reflections in the range 26° $\leqslant 2\theta \leqslant$ 35° and are presented in Table I along with other

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TABLE I. Crystallographic Data and Data Collection Procedures.

Formula	$Mo_2O_{18}C_{40}H_{48}$, **1**	$Mo_2Cl_2O_{12}C_{34}H_{24}$, **2**
M	1008.70	887.35
Space Group	C2/c	$P\bar{1}$
a, Å	19.028(2)	12.441(3)
b, Å	13.230(1)	14.479(2)
c, Å	18.330(2)	10.353(3)
α, deg.	90.00(0)	99.30(2)
β, deg.	110.44(1)	97.50(2)
γ, deg.	90.00(0)	111.94(1)
V, $Å^3$	4324(1)	1670(1)
Z	4	2
ρ_c (g/cm^3)	1.549	1.765
μ(Mo Kα) (cm^{-1})	6.364	9.569
Crystal size (mm)	0.5 × 0.2 × 0.1	0.4 × 0.4 × 0.3
Diffractometer	Enraf-Nonius CAD-4	
Radiation; graphite monochromated Mo Kα ($\lambda\alpha$ = 0.71073 Å)		
Collection Range	$+h +k \pm l\ 0 \leqslant 2\theta \leqslant 55°$	$+h \pm k \pm l\ 0 \leqslant 2\theta \leqslant 47°$
Scan type	$\omega-2\theta$	$\omega-2\theta$
Scan width	$0.65 + 0.35 \tan\theta$	$0.69 + 0.35 \tan\theta$
Maximum Counting Time (s)	60	45
X-Ray Exposure Time (h)	61	58
Crystal Decomposition	0	0
No. Unique Data	4386	5024
No. Data with $I \geqslant 3\sigma(I)$	3446	3886
p	0.05	0.05
No. Variables	290	547
R_1	0.035	0.028
R_2	0.050	0.037
Esd	1.622	1.173
Largest Shift[a]	0.52	0.15
Largest Peak[b]	0.80	0.77

[a] Largest parameter shift in final refinement cycle. [b] Large peak in a final difference Fourier $e/Å^3$.

pertinent crystallographic data. The final lattice constants for compound 2 were determined from a least-squares fit to 25 reflections in the range $16° \leqslant 2\theta \leqslant 27°$ and these and other data are also given in Table I. Additional details concerning the data collection technique have appeared elsewhere [3]. The data for 1 and 2 were corrected for Lorentz and polarization effects but not absorption.

Solution and Refinement of Structures

Mo_2(salicylate)$_4$·2diglyme, 1

A three-dimensional Patterson map gave the position of the unique molybdenum atom (the other molybdenum atom being related by inversion symmetry). Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.38$ and $R_2 = 0.46$ where the R_i are defined as

$$R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$$

Subsequent least-squares cycles and difference Fourier maps located all remaining nonhydrogen atoms and indicated a 3:1 disorder of the –OH and –H groups *ortho* to the carboxylate function on the salicylate ligands. All hydrogen atoms except those on methyl carbon atoms and –OH groups were included at calculated positions and their contributions included in F_c values, but they were not refined. With the inclusion of these atoms in the refinement and anisotropic thermal parameters assigned to all nonhydrogen atoms, the refinement converged at $R_1 = 0.035$ and $R_2 = 0.050$. A final difference synthesis showed random fluctuations not exceeding ±0.80 $e/Å^3$.

Mo_2(salicylate)$_4$·o-$C_6H_4Cl_2$, 2

The positions of the two independent molybdenum atoms were obtained from a Patterson map,

TABLE II. Table of Positional Parameters and Their Estimated Standard Deviations for Nonhydrogen Atoms in $Mo_2(salicylate)_4 \cdot 2Diglyme$, **1**.[a]

Atom	x	y	z
Mo(1)	0.75239(1)	0.17219(2)	0.48974(1)
O(1)	0.6706(1)	0.3483(2)	0.3955(1)
O(2)	0.6757(1)	0.1832(2)	0.3747(1)
O(3)	0.6641(1)	0.1405(2)	0.5302(1)
O(4)	0.6585(1)	0.3048(2)	0.5526(1)
O(5A)	0.5597(2)	0.3686(3)	0.6079(2)
O(5B)	0.4270(5)	0.9730(7)	0.4296(6)
O(6A)	0.6030(2)	0.4689(2)	0.2817(2)
O(6B)	0.5943(8)	0.118(1)	0.2410(7)
C(11)	0.6352(2)	0.2148(3)	0.5544(2)
C(12)	0.5740(2)	0.1961(3)	0.5849(2)
C(13)	0.5416(2)	0.2765(3)	0.6117(2)
C(14)	0.4854(2)	0.2554(3)	0.6417(2)
C(15)	0.4610(2)	0.1605(4)	0.6455(3)
C(16)	0.4929(2)	0.0803(4)	0.6181(3)
C(17)	0.5481(2)	0.0981(3)	0.5886(2)
C(21)	0.6517(2)	0.2706(2)	0.3501(2)
C(22)	0.6040(2)	0.2862(3)	0.2688(2)
C(23)	0.5801(2)	0.2030(3)	0.2187(2)
C(24)	0.5390(2)	0.2180(3)	0.1406(2)
C(25)	0.5209(2)	0.3137(3)	0.1121(2)
C(26)	0.5424(2)	0.3965(3)	0.1599(2)
C(27)	0.5836(2)	0.3843(3)	0.2385(2)
O(S1)	0.7831(2)	−0.0186(2)	0.4912(1)
O(S2)	0.7900(2)	−0.1667(2)	0.6134(2)
O(S3)	0.8036(2)	−0.3556(3)	0.6989(2)
C(S1)	0.8556(3)	−0.0584(4)	0.5016(3)
C(S2)	0.7272(3)	−0.0908(3)	0.4915(3)
C(S3)	0.7257(3)	−0.1125(4)	0.5700(3)
C(S4)	0.8003(4)	−0.1794(4)	0.6948(3)
C(S5)	0.7726(3)	−0.2691(4)	0.7142(2)
C(S6)	0.7749(3)	−0.4429(5)	0.7207(3)

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

consistent with the presence of two independent dimers situated on inversion centers at 0, 0, 0 and ½, ½, 0. The refinement was begun in the space group P$\bar{1}$ and several least-squares cycles followed by difference Fourier maps rapidly led to the location of all atoms (including hydrogen atoms) of the two independent molybdenum dimers and one molecule of *ortho*dichlorobenzene of crystallization per dimolybdenum molecule. Anisotropic thermal parameters were assigned to all nonhydrogen atoms and subsequent least-squares refinement gave the final discrepancy indices shown in Table I. The final difference Fourier map was devoid of significant features.

TABLE III. Table of Positional Parameters and Their Estimated Standard Deviations for Nonhydrogen Atoms in $Mo_2[salicylate]_4 \cdot o\text{-}ClC_6H_4Cl$, **2**.[a]

Atom	x	y	z
Mo(1)	0.48723(2)	0.44064(2)	0.04995(3)
Mo(2)	−0.04071(3)	−0.03581(2)	0.07135(3)
Cl(1)	0.5530(2)	0.8557(1)	0.1023(2)
Cl(2)	0.3695(1)	0.9582(1)	0.1224(2)
O(1)	0.3381(2)	0.3409(2)	−0.1045(2)
O(2)	0.3689(2)	0.4688(2)	−0.2092(2)
O(3)	0.3992(2)	0.6083(2)	0.0463(2)
O(4)	0.3717(2)	0.4831(2)	0.1542(2)
O(5)	−0.1029(2)	0.0779(2)	0.1285(2)
O(6)	−0.0134(2)	0.1562(2)	−0.0205(2)
O(7)	0.1972(2)	0.1260(2)	0.0742(2)
O(8)	0.1101(2)	0.0484(2)	0.2257(2)
O(17)	0.8369(2)	0.8317(2)	0.2014(2)
O(27)	0.2356(3)	0.4619(2)	0.3282(3)
O(37)	0.0377(3)	0.3544(2)	0.0127(3)
O(47)	0.3966(2)	0.2799(2)	0.1463(3)
C(11)	0.3090(3)	0.3763(2)	−0.2042(3)
C(12)	0.7934(3)	0.6903(2)	0.3109(3)
C(13)	0.8209(3)	0.6567(3)	0.4256(4)
C(14)	0.0878(3)	0.2809(3)	0.4705(4)
C(15)	0.0196(3)	0.1814(3)	0.4787(4)
C(16)	0.9556(3)	0.8538(3)	0.4103(4)
C(17)	0.8617(3)	0.7907(3)	0.3067(3)
C(21)	0.3513(3)	0.5607(3)	0.1301(3)
C(22)	0.2747(3)	0.5948(3)	0.2045(4)
C(23)	0.2556(3)	0.6804(3)	0.1824(4)
C(24)	0.1858(4)	0.7147(3)	0.2507(5)
C(25)	0.1357(4)	0.6653(4)	0.3447(6)
C(26)	0.1539(4)	0.5828(4)	0.3692(5)
C(27)	0.2220(3)	0.5453(3)	0.2990(4)
C(31)	−0.0724(3)	0.1538(3)	0.0738(3)
C(32)	−0.1040(3)	0.2401(3)	0.1175(4)
C(33)	−0.1905(4)	0.2285(3)	0.1947(4)
C(34)	−0.2210(4)	0.3079(3)	0.2375(5)
C(35)	−0.1671(4)	0.4000(3)	0.2050(5)
C(36)	−0.0814(4)	0.4140(3)	0.1314(5)
C(37)	−0.0486(3)	0.3342(3)	0.0861(4)
C(41)	0.1977(3)	0.1165(2)	0.1967(3)
C(42)	0.2992(3)	0.1877(2)	0.3016(3)
C(43)	0.3038(3)	0.1779(3)	0.4346(4)
C(44)	0.3962(3)	0.2441(3)	0.5335(4)
C(45)	0.4850(4)	0.3248(3)	0.5051(4)
C(46)	0.4826(4)	0.3354(3)	0.3747(4)
C(47)	0.3920(3)	0.2668(3)	0.2734(4)
C(51)	0.4957(4)	−0.0025(3)	0.2433(5)
C(52)	0.5180(4)	0.0751(4)	0.3511(6)
C(53)	0.6166(5)	0.1083(4)	0.4508(6)
C(54)	0.6950(4)	0.0643(4)	0.4416(5)
C(55)	0.6784(4)	0.9871(3)	0.3369(5)
C(56)	0.5768(4)	0.9534(3)	0.2355(5)

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

The positional parameters for nonhydrogen atoms are listed in Table II and Table III for compounds 1 and 2, respectively. Tables of hydrogen atom positions, thermal parameters for all atoms and lists of observed and calculated structure factors for both compounds are available as supplementary material.

TABLE IV. Bond Distances (Å) and Angles (°) for Nonhydrogen Atoms in Mo_2(salicylate)$_4$·2Diglyme, **1**.[a]

Distances

Mo(1)–Mo(1)′	2.101(1)	C(14)–C(15)	1.349(5)
–O(1)	2.119(2)	C(15)–C(16)	1.400(6)
–O(2)	2.108(2)	C(16)–C(17)	1.359(5)
–O(3)	2.102(2)	C(21)–C(22)	1.465(4)
–O(4)	2.118(2)	C(22)–C(23)	1.403(4)
–O(S1)	2.588(2)	–C(27)	1.412(4)
O(1)–C(21)	1.293(3)	C(23)–C(24)	1.385(4)
O(2)′–C(21)	1.266(3)	C(24)–C(25)	1.367(5)
O(3)–C(11)	1.279(3)	C(25)–C(26)	1.372(4)
O(4)′–C(11)	1.276(3)	C(26)–C(27)	1.388(4)
O(5A)–C(13)	1.274(5)	O(S1)–C(S1)	1.426(4)
O(5B)–C(17)	1.153(8)	–C(S2)	1.431(5)
O(6A)–C(27)	1.347(4)	O(S2)–C(S3)	1.400(5)
O(6B)–C(27)	1.19(1)	–C(S4)	1.445(6)
C(11)–C(12)	1.479(4)	O(S3)–C(S5)	1.361(5)
C(12)–C(13)	1.400(4)	–C(S6)	1.394(6)
–C(17)	1.397(4)	C(S2)–C(S3)	1.477(6)
C(13)–C(14)	1.391(5)	C(S4)–C(S5)	1.395(7)

Angles

Mo(1)′–Mo(1)–O(1)	90.35(5)	C(13)–C(14)–C(15)	122.2(3)
–O(2)	93.04(5)	C(14)–C(15)–C(16)	119.2(3)
–O(3)	92.44(5)	C(15)–C(16)–C(17)	120.3(4)
–O(4)	90.87(5)	O(5B)–C(17)–C(12)	123.8(5)
–O(S1)	167.82(5)	–C(16)	115.3(5)
O(1)–Mo(1)–O(2)	176.60(6)	C(12)–C(17)–C(16)	120.9(3)
–O(3)	89.13(7)	O(1)–C(21)–O(2)′	120.8(2)
–O(4)	90.98(7)	–C(22)	118.5(2)
–O(S1)	77.84(7)	O(2)′–C(21)–C(22)	120.6(2)
O(2)–Mo(1)–O(3)	90.43(7)	C(21)–C(22)–C(23)	120.0(3)
–O(4)	89.26(7)	–C(27)	121.2(3)
–O(S1)	98.79(6)	C(23)–C(22)–C(27)	118.8(3)
O(3)–Mo(1)–O(4)	176.68(6)	O(6B)–C(23)–C(22)	122.1(6)
–O(S1)	90.39(7)	C(24)	117.9(6)
O(4)–Mo(1)–O(S1)	86.40(7)	C(22)–C(23)–C(24)	120.1(3)
Mo(1)–O(1)–C(21)	118.5(2)	C(23)–C(24)–C(25)	120.2(3)
–O(2)–C(21)′	117.2(2)	C(24)–C(25)–C(26)	121.1(3)
–O(3)–C(11)	117.5(2)	C(25)–C(26)–C(27)	120.3(3)
–O(4)–C(11)′	118.3(2)	O(6A)–C(27)–C(22)	123.5(3)
O(3)–C(11)–O(4)′	120.9(2)	–C(26)	117.0(3)
–C(12)	119.6(3)	C(22)–C(27)–C(26)	119.5(3)
O(4)′–C(11)–C(12)	119.5(3)	Mo(1)–O(S1)–C(S1)	124.5(2)
C(11)–C(12)–C(13)	120.4(3)	–C(S2)	119.1(2)
C(11)–C(12)–C(17)	120.7(3)	C(S1)–O(S1)–C(S2)	115.9(3)
C(13)–C(12)–C(17)	118.9(3)	C(S3)–O(S2)–C(S4)	115.0(4)
O(5A)–C(13)–C(12)	123.2(3)	C(S5)–O(S3)–C(S6)	113.4(4)
–C(14)	118.2(3)	O(S1)–C(S2)–C(S3)	113.6(3)
C(12)–C(13)–C(14)	118.6(3)	O(S2)–C(S3)–C(S2)	110.0(3)
		O(S2)–C(S4)–C(S5)	115.8(5)
		O(S3)–C(S5)–C(S4)	115.7(4)

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

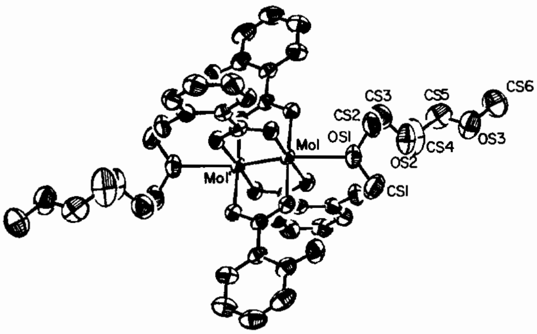

Fig. 1. The $Mo_2(O_2CC_6H_4OH)_4 \cdot 2(CH_3OCH_2CH_2OCH_2CH_2OCH_2)$ unit in compound **1**. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of its electron density. The atom labeling for the diglyme molecule is defined. The atoms in the two independent salicylate ions are numbered in a manner that is evident from Table IV.

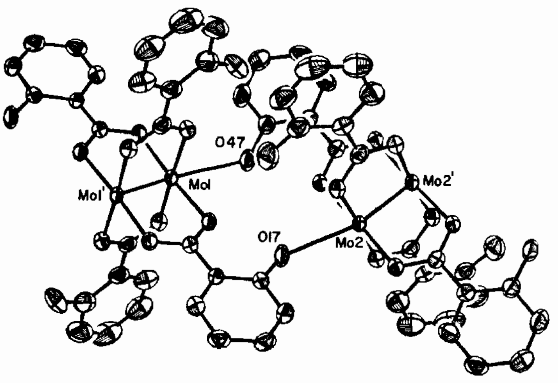

Fig. 2. The repeat unit, Mo_4(salicylato)$_8$, in the infinite chain found in compound **2**, with atoms represented by 30% thermal ellipsoids.

Results

In compound **1** the $Mo_2(O_2CC_6H_4OH)_4$ unit resides on a center of inversion and each axial position, as shown in Fig. 1, is occupied by one oxygen atom of a diglyme molecule. The OH groups of the salicylate ligands have no interaction with any metal atoms. The $Mo_2(O_2CR)_4$ unit has quite conventional dimensions [1] with an Mo–Mo bond length of 2.101(1) Å and a mean Mo–O distance for the carboxylato oxygen atoms of 2.112[4] Å. The axial Mo–O distances are 2.588(2) Å. A complete set of bond lengths and bond angles is presented in Table IV.

The OH groups are disordered; in a given molecule there are always two in each direction, but for each one there is a 3:1 preference for one direction *vs.* the other. Regardless of which location a given OH group finds itself in, it forms a hydrogen bond to the adjacent carboxyl oxygen atom and this maintains essential coplanarity of each $-CO_2$ group and its attached C_6H_4OH group. These hydrogen bonds have lengths in the range 2.550(11) Å to 2.586(4) Å. It may be that this internal hydrogen bonding lessens the tendency of both the OH and the carboxyl oxygen atoms to be available for intermolecular association, thus helping to favor the diglyme oxygen atoms as axial ligands.

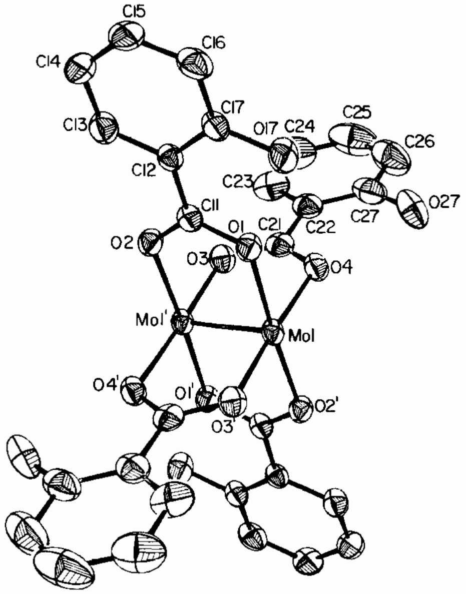

Fig. 3. A representative dinuclear unit in compound **2**, showing the atom labeling pattern. The labeling in the Mo(2)–Mo(2)' unit follows a similar pattern with advancement of numerical indices.

Compound 2 presents a novel and interesting structural situation. For the first time we find $M_2(O_2CR)_4$ units linked through intermolecular axial donor bonds in which a donor functionality of the R group provides the connecting atom. In Fig. 2 we see the two crystallographically independent $Mo_2(O_2CC_6H_4OH)_4$ units that, together, constitute the repeating motif in the infinite chain of such units. Each $Mo_2(O_2CC_6H_4OH)_4$ subunit resides on a crystallographic inversion center, the Mo(1)–Mo(1)' unit at the 0, 0, 0 position and the Mo(2)–Mo(2)' unit at the-½, ½, 0 position. Figure 3 shows the complete Mo(1)–Mo(1)' unit and its atom numbering scheme. The labeling in the Mo(2)–Mo(2)' follows an analogous pattern as is made evident in Table V, where the bond lengths and angles in compound 2 are listed. The o-$C_6H_4Cl_2$ molecules are located between the chains and make only van der Waals contacts.

The two independent, centrosymmetric $Mo_2(O_2CC_6H_4OH)_4$ units are essentially identical to each other and have dimensions similar to those previously

TABLE V. Bond Distances (Å) and Angles (°) Involving Nonhydrogen Atoms in Mo_2[salicylate]$_4$·o-$C_6H_4Cl_2$, 2.[a]

Distances			
Molecule 1		Molecule 2	
Mo(1)–Mo(1)′	2.092(1)	Mo(2)–Mo(2)′	2.094(1)
–O(1)	2.136(3)	–O(5)	2.101(2)
–O(2)	2.102(2)	–O(6)	2.108(2)
–O(3)	2.093(2)	–O(7)	2.113(2)
–O(4)	2.112(2)	–O(8)	2.107(2)
–O(47)	2.601(3)	–O(17)	2.645(3)
O(1)–C(11)	1.293(4)	O(5)–C(31)	1.273(4)
O(2)–C(11)	1.279(4)	O(6)–C(31)	1.293(4)
O(3)–C(21)	1.267(4)	O(7)–C(41)	1.297(4)
O(4)–C(21)	1.294(4)	O(8)–C(41)	1.275(4)
O(17)–C(17)	1.377(4)	O(47)–C(47)	1.365(4)
O(27)–C(27)	1.354(6)	O(37)–C(37)	1.366(5)
C(11)–C(12)	1.465(5)	C(31)–C(32)	1.466(5)
C(12)–C(13)	1.403(5)	C(32)–C(33)	1.400(6)
–C(17)	1.395(5)	–C(37)	1.392(6)
C(13)–C(14)	1.365(5)	C(33)–C(34)	1.367(7)
C(14)–C(15)	1.395(6)	C(34)–C(35)	1.369(8)
C(15)–C(16)	1.375(6)	C(35)–C(36)	1.363(8)
C(16)–C(17)	1.381(5)	C(36)–C(37)	1.397(6)
C(21)–C(22)	1.471(5)	C(41)–C(42)	1.464(5)
C(22)–C(23)	1.393(6)	C(42)–C(43)	1.403(5)
–C(27)	1.394(6)	–C(47)	1.392(5)
C(23)–C(24)	1.368(7)	C(43)–C(44)	1.357(6)
C(24)–C(25)	1.377(9)	C(44)–C(45)	1.379(6)
C(25)–C(26)	1.352(9)	C(45)–C(46)	1.381(6)
C(26)–C(27)	1.384(7)	C(46)–C(47)	1.369(5)
Solvent Molecule			
	Cl(1)–C(56)	1.715(5)	
	Cl(2)–C(51)	1.716(5)	
	C(51)–C(52)	1.366(8)	
	–C(56)	1.385(7)	
	C(52)–C(53)	1.367(8)	
	C(53)–C(54)	1.355(8)	
	C(54)–C(55)	1.358(8)	
	C(55)–C(56)	1.402(7)	
Mo(1)′–Mo(1)–O(1)	90.48(6)	Mo(2)′–Mo(2)–O(5)	92.70(7)
–O(2)	93.30(6)	–O(6)	91.01(7)
–O(3)	92.25(7)	–O(7)	91.13(6)
–O(4)	91.30(7)	–O(8)	92.72(6)
–O(47)	164.71(8)	–O(17)	165.37(7)
O(1)–Mo(1)–O(2)	176.19(9)	O(5)–Mo(2)–O(6)	176.13(9)
–O(3)	91.22(9)	–O(7)	92.45(9)
O(1)–Mo(1)–O(4)	89.04(9)	O(5)–Mo(2)–O(8)	87.76(9)
–O(47)	76.73(9)	–O(17)	97.5(1)
O(2)–Mo(1)–O(3)	89.11(9)	O(6)–Mo(2)–O(7)	86.39(9)
–O(4)	90.40(9)	–O(8)	93.15(9)
–O(47)	99.47(9)	–O(17)	78.68(9)
O(3)–Mo(1)–O(4)	176.44(9)	O(7)–Mo(2)–O(8)	176.13(9)
–O(47)	96.3(1)	–O(17)	78.00(9)
O(4)–Mo(1)–O(47)	80.3(1)	O(8)–Mo(2)–O(17)	98.14(9)
Mo(1)–O(1)–C(11)	118.2(2)	Mo(2)–O(5)–C(31)	117.3(2)
–O(2)–C(11)	117.6(2)	–O(6)–C(31)	118.0(2)

(continued on facing page)

TABLE V. *(continued)*

–O(3)–C(21)	118.4(2)	–O(7)–C(41)	117.9(2)
–O(4)–C(21)	117.6(2)	–O(8)–C(41)	117.3(2)
Mo(1)–O(47)–C(47)	132.9(2)	Mo(2)–O(17)–C(17)	136.7(2)
O(1)–C(11)–O(2)	120.3(3)	O(5)–C(31)–O(6)	120.8(3)
–C(12)	119.3(3)	–C(32)	120.1(3)
O(2)–C(11)–C(12)	120.4(3)	O(6)–C(31)–C(32)	119.1(3)
C(11)–C(12)–C(13)	120.5(3)	C(31)–C(32)–C(33)	119.4(4)
–C(17)	121.7(3)	–C(37)	121.7(4)
C(13)–C(12)–C(17)	117.8(3)	C(33)–C(32)–C(37)	118.9(4)
C(12)–C(13)–C(14)	121.6(4)	C(32)–C(33)–C(34)	120.6(5)
C(13)–C(14)–C(15)	119.3(4)	C(33)–C(34)–C(35)	120.2(5)
C(14)–C(15)–C(16)	120.5(4)	C(34)–C(35)–C(36)	120.6(5)
C(15)–C(16)–C(17)	119.8(4)	C(35)–C(36)–C(37)	120.5(5)
O(17)–C(17)–C(12)	121.6(3)	O(37)–C(37)–C(32)	123.9(4)
–C(16)	117.4(3)	–C(36)	116.9(4)
C(12)–C(17)–C(16)	121.0(3)	C(32)–C(37)–C(36)	119.3(4)
O(3)–C(21)–O(4)	120.4(3)	O(7)–C(41)–O(8)	120.7(3)
–C(22)	120.5(3)	–C(42)	118.6(3)
O(4)–C(21)–C(22)	119.1(4)	O(8)–C(41)–C(42)	120.7(3)
C(21)–C(22)–C(23)	119.4(4)	C(41)–C(42)–C(43)	120.0(3)
–C(27)	122.1(4)	–C(47)	121.6(3)
C(23)–C(22)–C(27)	118.5(4)	C(43)–C(42)–C(47)	118.4(3)
C(22)–C(23)–C(24)	120.9(5)	C(42)–C(43)–C(44)	120.9(4)
C(23)–C(24)–C(25)	119.5(6)	C(43)–C(44)–C(45)	120.2(4)
C(24)–C(25)–C(26)	120.8(6)	C(44)–C(45)–C(46)	119.9(4)
C(25)–C(26)–C(27)	120.7(6)	C(45)–C(46)–C(47)	120.4(4)
O(27)–C(27)–C(22)	123.1(4)	O(47)–C(47)–C(42)	122.3(3)
–C(26)	117.4(5)	–C(46)	117.5(4)
C(22)–C(27)–C(26)	119.6(5)	C(42)–C(47)–C(46)	120.2(4)

Solvent Molecule

Cl(2)–C(51)–C(52)	119.4(4)
–C(56)	122.2(4)
C(52)–C(51)–C(56)	118.4(5)
C(51)–C(52)–C(53)	121.6(6)
C(52)–C(53)–C(54)	119.2(6)
C(53)–C(54)–C(55)	122.2(6)
C(54)–C(55)–C(56)	118.1(5)
Cl(1)–C(56)–C(51)	120.3(4)
–C(55)	119.2(4)
C(51)–C(56)–C(55)	120.5(5)

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

found in other $Mo_2(O_2CR)_4$ compounds [1]. The two Mo–Mo bond lengths are identical within the errors, with values of 2.092(1) Å and 2.094(1) Å. This is slightly but significantly shorter (in a statistical sense, *i.e.*, 0.008(1.4) Å) than that in compound 1. This is consistent with the axial Mo–O bonds being longer, *i.e.*, 2.601(3) Å and 2.645(3) Å, than those in 1, which are 2.588(2) Å. The mean value of the eight equatorial Mo–O bond lengths is 2.109[5] Å, which is not significantly different from that in 1, which is 2.112[4] Å.

In compound 2 also, hydrogen bonds exist between the OH groups and carboxyl oxygen atoms and, again, this leads to essential planarity of the entire $HOC_6H_4CO_2^-$ ligand. The four independent hydrogen bonds have O····O distances in the range 2.554(3) Å to 2.648(4) Å.

Taking the structural results for both 1 and 2 together, they suggest some tentative conclusions about the relative probabilities of different types of axial ligation. In compound 1 we find separate axial ligands, in the shape of the diglyme molecules derived from the reaction solvent. The preference for such independent axial ligands, when they are available, may in this case owe something to the fact that hydrogen-bonded interactions with the OH groups of the salicylate ligands help to hold them in place.

In the absence of any good donor molecules, *i.e.,* when only *o*-$C_6H_4Cl_2$ molecules are available, the $Mo_2(O_2CR)_4$ molecules, as always, resort to self-coordination. In this case, however, the phenolic OH groups are used instead of carboxylate oxygen atoms, as in simple compounds such as the acetate, formate or trifluoroacetate. Whether this result is due simply to superior donor ability of the OH group or has other causes is a moot point. The observed structure does demonstrate for the first time that when potential donor groups are available in the RCO_2^- ligands and there is no competition from separate donor molecules, the use of these 'intramural' donor functionalities must be considered in anticipating possible structures.

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Supplementary Material Available

Tables S1 and S2, thermal parameters for **1** and **2** (4 pages); tables S3 and S4, positional and thermal parameters for hydrogen atoms in **1** and **2** (2 pages); a table of bond distances and angles involving hydrogen in **2** (Table S5, 2 pages); tables of observed and calculated structure factors for **1** (Table S6, 15 pages) and **2** (Table S7, 17 pages). This material is available from F. A. C. on request.

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