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Di-, hexa- and poly-nuclear molybdenum(II) carboxylates containing quadruply bonded $[Mo_2]^{4+}$ units: crystal structures of $[Mo_2(O_2CCHF_2)_2(bpy)_2(MeCN)(BF_4)][BF_4]$ and $[Mo_6(O_2CCHF_2)_{12}(bpy)_4]$ (bpy = 2,2′-bipyridine)

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The reaction of $[Mo_2(O_2CMe)_4]$ with an excess of CHF_2CO_2H resulted in the formation of $[Mo_2(O_2CCHF_2)_4]\cdot MeCN$ **1**. Treatment of **1** with Et_3O^+ gave $[Mo_2(O_2CCHF_2)_2(MeCN)_4][BF_4]_2$ **2**, which was converted into $[Mo_2(O_2CCHF_2)_2(bpy)_2(MeCN)(BF_4)][BF_4]$ **3** on addition of 2,2′-bipyridine (bpy). The reaction of **1** and **3** (1 : 2) in the presence of $CHF_2CO_2^-$ gave the 'trimer-of-dimers' complex $[Mo_6(O_2CCHF_2)_{12}(bpy)_4]$ **4** in which two $[Mo_2(O_2CCHF_2)_4(bpy)_2]$ units are the two axial ligands to a central $[Mo_2(O_2CCHF_2)_4]$ unit. The related reaction of **1** and **3** at a 1 : 1 ratio in the presence of $CHF_2CO_2^-$ gave $[Mo_4(O_2CCHF_2)_8(bpy)_2]_n$ **5**, which was concluded to be a one-dimensional polymer consisting of alternating $[Mo_2(O_2CCHF_2)_4(bpy)_2]$ and $[Mo_2(O_2CCHF_2)_4]$ units identical to those in **4.**

The reactions of 2,2′-bipyridine (bpy) with dinuclear metal carboxylate complexes of formula $[M_2(O_2CR)_4]$ have been attracting interest recently as a source of complexes with interesting structures and/or physical and reactivity properties.[1–5] The structural nature of the products has depended heavily on the identity of the metal. With $Cu_2(O_2CR)_4(H_2O)_2$ the absence of metal–metal bonding has led to a variety of structural types being formed, both discrete and polymeric.[1] In contrast, reactions of bpy with $[M_2(O_2CR)_4]$ (M = Mo^{II} or Rh^{II}, R = Me or CF_3) species has led to dinuclear products such as $[Mo_2(O_2CR)_2(bpy)_2]^{2+}$,[2] $[Mo_2(O_2CR)_4(bpy)_2]$,[2] $[Rh_2(O_2CR)_4(bpy)]$[3] and $[Rh_2(O_2CR)_2(bpy)_2(MeCN)_2]^{2+}$[4] salts that retain the metal–metal bonded unit.

The one-dimensional polymer $[Cu_4(O_2CMe)_8(bpy)_2]_n$ has an interesting structure consisting of alternating $[Cu_2(O_2CMe)_4]$ and $[Cu_2(O_2CMe)_2(bpy)_2]^{2+}$ units that are linked together by *syn,anti* bridging acetate groups.[5] This linkage of *different* dinuclear units by acetate groups is one of the stimuli for the present work, directed towards the preparation of discrete and polynuclear molybdenum(II) complexes containing different types of $[Mo^{II}_2]^{4+}$ units. We herein report the preparation of di-, hexa- and poly-nuclear species, and describe their structures and selected properties. The carboxylate employed is difluoroacetate, $CHF_2CO_2^-$, chosen in order to provide a more soluble $[Mo_2(O_2CR)_4]$ starting material than $[Mo_2(O_2CMe)_4]$ while also providing a less labile system than those containing $CF_3CO_2^-$. The $CF_2HCO_2^-$ ligand has proven to be a nice compromise in these regards.

Experimental

General

All manipulations were performed under inert-atmosphere conditions using standard Schlenk and glove-box techniques. 2,2′-Bipyridine (Aldrich) and difluoroacetic acid (Lancaster) were used as received. All solvents were distilled from drying agents prior to use. The compound $[Mo_2(O_2CMe)_4]$ was prepared by a literature procedure.[6]

Preparations

$[Mo_2(O_2CCHF_2)_4]$ $\cdot$MeCN **1.** A stirred slurry of $[Mo_2(O_2CMe)_4]$ (3.60 g, 8.41 mmol) in CH_2Cl_2 (40 cm^3) was treated with an excess of difluoroacetic acid (5 cm^3, 79.5 mmol). The reaction mixture was refluxed for 2 d and the yellow product was filtered off and dried *in vacuo*. Recrystallisation from a MeCN–Et_2O layering gave complex **1** in 78% yield (4.00 g) (Found: C, 19.93; H, 1.21; N, 2.42. $C_{10}H_7F_8Mo_2NO_8$ requires C, 19.59; H, 1.15; N, 2.28%). ^1H NMR spectrum in CD_3CN: O_2CCHF_2, δ 6.65 (t).

$[Mo_2(O_2CCHF_2)_2(MeCN)_4][BF_4]_2$ 2. Treatment of a stirred, yellow slurry of complex **1** (0.97 g, 1.58 mmol) in CH_2Cl_2 (40 cm^3) with 2 equivalents of Et_3OBF_4 (1 M in CH_2Cl_2, 3.16 cm^3, 3.16 mmol) and an excess of MeCN (7 cm^3) resulted in the formation of a bright pink solid. The slurry was stirred overnight and the solid was collected by filtration and dried *in vacuo*. Recrystallisation from a MeCN–Et_2O layering gave **2** as deep pink crystals in 44% yield (0.50 g) (Found: C, 19.57; H, 2.10; N, 7.27. $C_{12}H_{14}B_2F_{12}Mo_2N_4O_4$ requires C, 20.03; H, 1.96; N, 7.78%). ^1H NMR spectrum in CD_3CN: O_2CCHF_2, δ 6.86 (t).

$[Mo_2(O_2CCHF_2)_2(bpy)_2(MeCN)(BF_4)][BF_4]$ 3. A pink solution of complex **2** (0.400 g, 0.556 mmol) in MeCN (25 cm^3) was treated with a MeCN solution containing 2 equivalents of bpy (0.174 g, 1.11 mmol) to give an immediate change from bright pink to red. Addition of Et_2O by vapour diffusion slowly resulted in red crystals of **3** in 67% yield (0.34 g) (Found: C, 34.41; H, 2.35; N, 7.60. $C_{26}H_{21}B_2F_{12}Mo_2N_5O_4$ requires C, 34.36; H, 2.33; N, 7.70%). ^1H NMR spectrum in CD_3CN: O_2CCHF_2, δ 7.23 (t, 2); bpy, 8.76 (d, 4), 8.24 (d, 4), 8.17 (t, 4), and 7.67 (t, 4).

$[Mo_6(O_2CCHF_2)_{12}(bpy)_4]$ 4. A yellow solution of complex **1** (11.2 mg, 0.018 mmol) in MeCN (2 cm^3) was treated with 2 equivalents of **3** (33.4 mg, 0.036 mmol) and 4 equivalents of $[NBu^n_4][O_2CCHF_2]$ (24.7 mg, 0.073 mmol) to give a deep red solution. Slow evaporation of this solution produced red crystals of **4**$\cdot$4MeCN in 69% yield (15.8 mg) that were suitable for crystallography; dried solid analyses as **4**$\cdot\frac{1}{2}$MeCN (Found: C, 33.35; H, 2.24; N, 4.86. $C_{65}H_{45.5}F_{24}Mo_6N_{8.5}O_{24}$ requires C, 33.06; H, 1.94; N, 5.04%).

$[Mo_4(O_2CCHF_2)_8(bpy)_2]$ 5. A yellow solution of complex **1** (16.9 mg, 0.028 mmol) in MeCN (1 cm^3) was treated with 1 equivalent of **3** (25.0 mg, 0.028 mmol) and 2 equivalents of

Table 1 Crystallographic data for compounds **3** and **4**·4MeCN

	3	**4**·4MeCN
Formula[a]	$C_{26}H_{21}B_2F_{12}Mo_2N_5O_4$	$C_{72}H_{56}F_{24}Mo_6N_{12}O_{24}$
M	908.99	2504.96
Crystal symmetry	Orthorhombic	Triclinic
Space group	$Cmc2_1$	$P\bar{1}$
a/Å	12.221(1)	12.122(3)
b/Å	16.216(2)	20.298(6)
c/Å	16.142(1)	9.346(2)
α/°	—	101.86(1)
β/°	—	108.93(1)
γ/°	—	86.03(1)
U/Å^3	3199	2129
Z	4	1
T/ °C	−171	−169
λ[b]/Å	0.71 069	0.71 069
D_c/g cm^{-3}	1.887	1.954
μ/cm^{-1}	8.742	9.667
Octants	$+h, +k, +l$	$+h, \pm k, \pm l$
Total data	8400[c]	6629[d]
Unique data	3837	5573
Observed data	3757[e]	4677[f]
R,R' (%)[g]	1.89, 2.00	5.70, 5.85

[a] Including solvate molecules. [b] Mo-Kα, graphite monochromator. [c] $6 \leqslant 2\theta \leqslant 45°$. [d] $6 \leqslant 2\theta \leqslant 55°$. [e] $F > 2.33\sigma(F)$. [f] $F > 3.0\sigma(F)$. [g] $R = 100\ \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = 100\ [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(|F_o|)$.

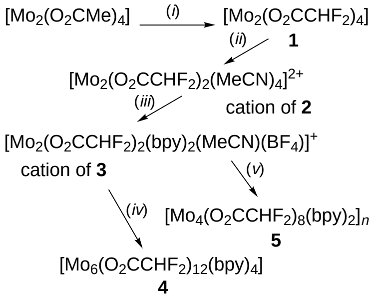
$[NBu^n_4][O_2CCHF_2]$ (18.6 mg, 0.055 mmol) to give a deep red solution, which slowly precipitated a red solid in 44% yield (18.0 mg) that analysed as **5**·2MeCN (Found: C, 31.61; H, 2.06; N, 4.88. $C_{40}H_{30}F_{16}Mo_4N_6O_{16}$ requires C, 31.23; H, 1.97; N, 5.46%).

Crystallography

Data for complexes **3** and **4**·4MeCN were collected on a Picker four-circle diffractometer by using standard low-temperature facilities; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[7] Data collection and structure solution information are listed in Table 1. The structures were solved by a combination of direct methods (SHELXS 86 or MULTAN 78)[8] and Fourier techniques, and refined on *F* by full-matrix least-squares methods.

For compound **3** a systematic search of a limited hemisphere of reciprocal space located a set of reflections with orthorhombic symmetry and systematic absences corresponding to one of the space groups $Cmc2_1$, *Cmcm*, or *C*2*cm*. Subsequent successful solution and refinement of the structure confirmed the non-centrosymmetric choice $Cmc2_1$ to be the correct space group. No crystal decay during data collection was observed, and no absorption correction was carried out. The structure was solved with no disorder or other problems being encountered. The cation lies on a mirror plane, and the BF_4^- anion also lies on a mirror plane. All non-hydrogen atoms were refined with anisotropic thermal parameters. A Fourier-difference map phased on the non-hydrogen atoms clearly located all hydrogen atoms, and these were refined isotropically in the subsequent least-squares refinement. The absolute structure of the crystal studied was determined by refinement of the two possible settings. A final Fourier-difference map was essentially featureless, the largest peak being 0.24 e Å^{-3}.

For compound **4**·4MeCN a systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than $\bar{1}$) and no systematic extinctions. The initial choice of the space group $P\bar{1}$ was confirmed by the subsequent successful solution and refinement of the structure. No crystal decay during data collection was observed and no correction for absorption was performed. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. Hydrogen atoms were included in fixed, idealised positions. The final Fourier-difference map was reasonably clean, except for some peaks of about 1.3 e Å^{-3} in the vicinity of O(60) and C(61), indicating some possible disorder in that ligand. The deepest hole was −1.0 e Å^{-3}.



Scheme 1 (*i*) CHF_2CO_2H, CH_2Cl_2, reflux, 2 d; (ii) 2 equivalents Et_3O^+, CH_2Cl_2–MeCN, room temperature, 1 d; (*iii*) 2 equivalents bpy, MeCN, room temperature; (*iv*) 0.5 equivalent complex **1**, 2 equivalents $CHF_2CO_2^-$, MeCN; (*v*) 1 equivalent complex **1**, 2 equivalents $CHF_2CO_2^-$, MeCN

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/560.

Results

Syntheses

For convenience, the compound numbering scheme and the transformations to be described in this text are summarised in Scheme 1. The complex $[Mo_2(O_2CCHF_2)_4]$ **1** can readily be prepared from $[Mo_2(O_2CMe)_4]$ by ligand exchange in CH_2Cl_2 using CHF_2CO_2H, as summarised in equation (1). The exchange is

$$[Mo_2(O_2CMe)_4] + 4\ CHF_2CO_2H \longrightarrow [Mo_2(O_2CCHF_2)_4] + 4\ MeCO_2H \quad (1)$$

facilitated by the greater acidity of CHF_2CO_2H ($pK_a = 1.33$) *vs.* $MeCO_2H$ ($pK_a = 4.76$). Compound **1** is soluble in, for example, MeCN and acetone, and slightly soluble in CH_2Cl_2.

Partial decarboxylation of complex **1** can be accomplished using the procedure previously developed to access the $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}$ species.[9] Thus, treatment of **1** with 2 equivalents of $Et_3O^+BF_4^-$ in CH_2Cl_2–MeCN led to $[Mo_2(O_2CCHF_2)_2(MeCN)_4][BF_4]_2$ **2**, which can be obtained in good overall yield (44%) and analytical purity after recrystallisation from MeCN–Et_2O. The decarboxylation is summarised in equation (2).

$$[Mo_2(O_2CCHF_2)_4] + 2\ Et_3O^+ + 4\ MeCN \longrightarrow [Mo_2(O_2CCHF_2)_2(MeCN)_4]^{2+} + 2\ CHF_2CO_2Et + 2\ Et_2O \quad (2)$$

Treatment of complex **2** with 2 equivalents of bpy led to a rapid change from bright pink to red and the subsequent isolation of red $[Mo_2(O_2CCHF_2)_2(bpy)_2(MeCN)(BF_4)][BF_4]$ **3** in 67% yield. The bpy groups replaced the co-ordinated MeCN molecules and subsequent crystallographic characterisation (see below) confirmed the *syn* orientation of the bpy groups. We saw no visual evidence during the course of this reaction or in its product for a second form that might be the *anti* isomer: for $CF_3CO_2^-$ we have earlier reported that both *syn*-$[Mo_2(O_2CCF_3)_2(bpy)_2][CF_3CO_2]_2$ and *anti*-$[Mo_2(O_2CCF_3)_4(bpy)_2]$ can be obtained with different colours in the solid state.[2]

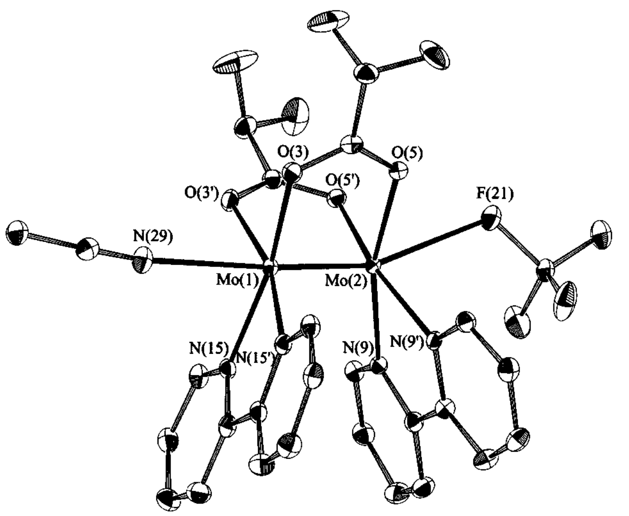


Fig. 1 An ORTEP representation of the cation of complex **3**. Thermal ellipsoids are at the 50% probability level. Primed and unprimed atoms are related by a mirror plane

The objective of preparing oligomers in which different types of $[Mo_2]^{4+}$ unit are linked together was explored and realised from the reaction of complex **1** with **3**. After consideration of the relative ratios of reagents, a reaction system was developed comprising **1**, **3** and $CHF_2CO_2^-$ in a 1:2:4 molar ratio which gave a red solution. From this were obtained well formed, large crystals of $[Mo_6(O_2CCHF_2)_{12}(bpy)_4]$ **4** on slow solvent evaporation. This product reflects the reaction stoichiometry in containing a central $[Mo_2(O_2CCHF_2)_4]$ unit linked to two $[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+}$ units by two bridging $CHF_2CO_2^-$ groups (see below), and it can thus be described conveniently (although somewhat inaccurately) as a 'trimer-of-dimers'. The formation of **4** is summarised in equation (3). The potential

$$[Mo_2(O_2CCHF_2)_4] + 2\,[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+} + 4\,CHF_2CO_2^- \longrightarrow [Mo_6(O_2CCHF_2)_{12}(bpy)_4] \quad (3)$$

formation of a one-dimensional polymer of alternating $[Mo_2(O_2CCHF_2)_4]$ and $[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+}$ units was clearly evident from the structure of **4**. Indeed, the reaction of **1**, **3** and $CHF_2CO_2^-$ in a 1:1:2 ratio was found to give a red solution which slowly precipitated a fine red solid whose analysis is consistent with the formulation $[Mo_4(O_2CCHF_2)_8(bpy)_2]_n$ expected for the chain polymer. Use of more dilute solutions yielded microcrystals, but, unfortunately, numerous attempts to obtain a crystalline sample suitable for crystallographic studies all proved in vain.

Crystal structures

The ORTEP[10] representations of the cation of **3** and complex **4** are presented in Figs. 1 and 2, respectively. Selected bond distances and angles for the two compounds are listed in Tables 2 and 3.

Compound **3** crystallises in orthorhombic space group *Cmc*2$_1$ with the cation lying on a mirror plane that contains the Mo–Mo bond and bisects the two bpy groups. The Mo(1)–Mo(2) distance [2.1431(4) Å] is typical of a $[Mo_2]^{4+}$ quadruple bond.[11] The $CHF_2CO_2^-$ groups bridge in their common *syn,syn* mode, and the two bpy groups are *syn*, which necessitates (because of the short Mo–Mo bond) unfavourably close approach of the two bpy π systems. In order to minimise the resulting repulsion, the bpy groups splay apart giving a dihedral angle of 37 ° between their two planes. Note that, as expected for a $\sigma^2\pi^4\delta^2$ quadruple bond, the cation is in an eclipsed conformation about the Mo–Mo bond (average torsional angle 0.3°). Thus, even when splayed apart, the bpy ring atoms still make several short contacts: for example, N(9)···N(15) is only 3.152(3) Å. The axial ligands are one MeCN molecule and one of the two BF_4^- anions, the other being well separated from the cation. The cation of **3** is similar to both $[Mo_2(O_2CCF_3)_2(bpy)_2]^{2+}$ and $[Mo_2(O_2CMe)_2(bpm)_2]^{2+}$ (bpm = 2,2′-bipyrimidine) reported previously.[2,12] In the former, the Mo–Mo distance [2.181(2) Å] is noticeably longer than in **3**, and the dihedral angle between the bpy planes is smaller at only ≈ 22°. In addition, both axial ligands are $CF_3CO_2^-$. In the latter, the bpm groups bind only through two N atoms and thus behave as bpy groups; the Mo–Mo distance is 2.1508(9) Å and the axial ligands are also one MeCN and one BF_4^-, as in **3**.

Table 2 Selected interatomic distances (Å) and angles (°) for $[Mo_2(O_2CCHF_2)_2(bpy)_2(MeCN)(BF_4)][BF_4]$ **3**

Mo(1)–Mo(2)	2.1431(4)	Mo(2)–O(5)	2.1030(17)
Mo(1)–O(3)	2.1091(17)	Mo(2)–N(9)	2.1665(20)
Mo(1)–N(29)	2.648(2)	Mo(2)–F(21)	2.665(2)
Mo(1)–N(15)	2.1680(21)		
Mo(2)–Mo(1)–O(3)	91.50(5)	Mo(1)–Mo(2)–O(5)	90.61(5)
Mo(2)–Mo(1)–N(15)	102.47(6)	Mo(1)–Mo(2)–N(9)	104.46(5)
O(3)–Mo(1)–O(3′)	89.89(10)	O(5)–Mo(2)–O(5′)	89.23(10)
O(3)–Mo(1)–N(15)	95.63(7)	O(5)–Mo(2)–N(9)	95.87(7)
O(3)–Mo(1)–N(15′)	164.81(8)	O(5)–Mo(2)–N(9′)	163.99(7)
N(15)–Mo(1)–N(15′)	75.70(11)	N(9)–Mo(2)–N(9′)	75.39(11)
N(29)–Mo(1)–Mo(2)	176.19(6)	F(21)–Mo(2)–Mo(1)	161.59(5)
N(29)–Mo(1)–O(3)	85.81(8)	F(21)–Mo(2)–O(5)	76.36(9)
N(29)–Mo(1)–N(15)	80.54(11)	F(21)–Mo(2)–N(9)	90.00(10)

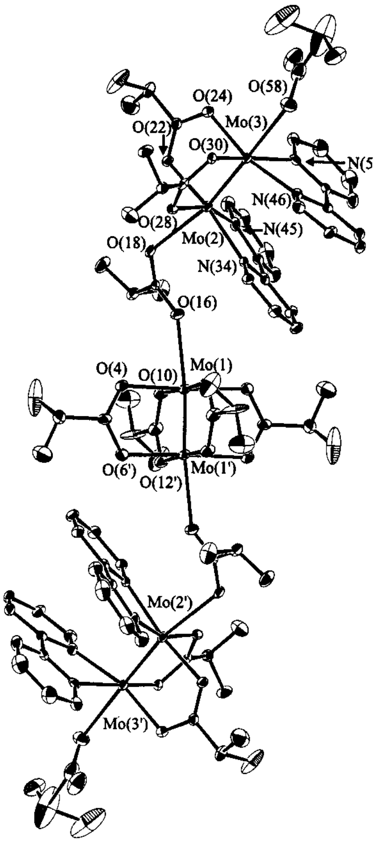


Fig. 2 An ORTEP representation of complex **4**

Compound **4** crystallises in triclinic space group $P\bar{1}$ with the molecule lying on an inversion centre located at the midpoint of the Mo(1)–Mo(1′) bond. The structure comprises a central, quadruply bonded $Mo_2(O_2CCHF_2)_4$ unit [Mo(1)–Mo(1′) 2.1234(15) Å] whose axial 'ligands' are two $[Mo_2(O_2CCHF_2)_2(bpy)_2](O_2CCHF_2)_2$ units, the linkage between the central and outer $[Mo_2]^{4+}$ units being by μ-O_2CCHF_2 groups in *syn,anti* co-

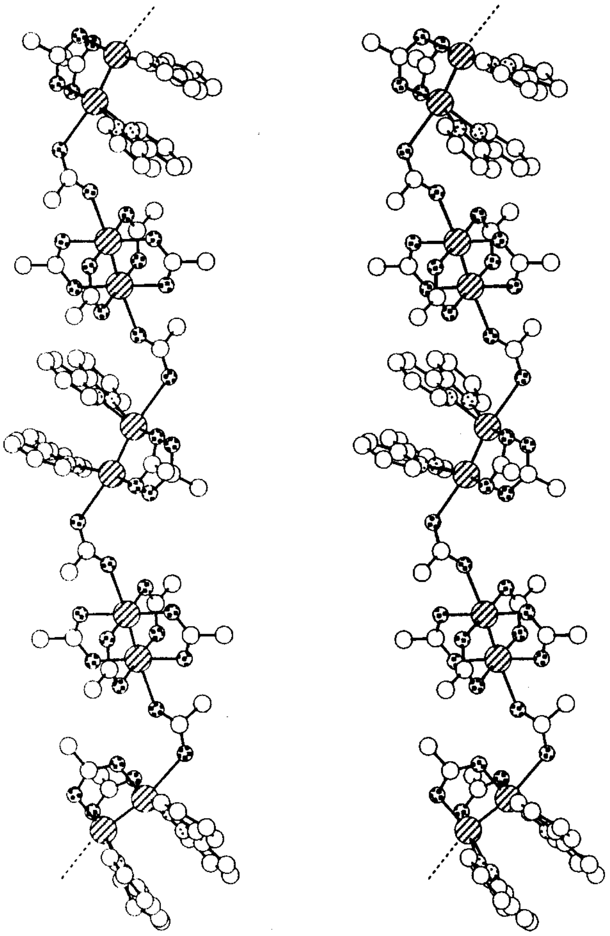


Fig. 3 A stereoview of the proposed one-dimensional zigzag chain structure of compound **5**

ordination modes. The two outer units are thus similar to that in the cation of **3** except that the axial ligands are now two $CHF_2CO_2^-$ groups. The Mo(2)–Mo(3) distance [2.1741(12) Å] is slightly longer than that in **3** but comparable with that in $[Mo_2(O_2CCF_3)_2(bpy)_2][O_2CCF_3]_2$ whose axial ligands are also carboxylate groups. Thus, the bpy planes in **4** are not as splayed as in **3** (dihedral angle 16 and 37°, respectively). The Mo–Mo vectors are not collinear, the angle between the Mo(2)–Mo(3) and Mo(1)–Mo(1′) vectors being 46.51°. The interdimer Mo · · · Mo distance, Mo(1) · · · Mo(2), is 6.036(2) Å. The bridging $CHF_2CO_2^-$ groups form relatively short contacts with the central $[Mo_2]^{4+}$ core indicating a relatively strong axial interaction, no doubt compensating partially for the electron-withdrawing nature of the four *syn,syn* bridging $CHF_2CO_2^-$ groups. Thus, Mo(1)–O(16) is only 2.435(6) Å compared with a typical axial bond in dimolybdenum carboxylates of ≈2.6 Å.[11] The Mo–Mo distances in $Mo_2(O_2CR)_4$ species are known not to be significantly influenced by the identity of R (typically 2.092 ± 0.004 Å),[13] so the Mo(1)–Mo(1′) distance of 2.1234(15) Å can be assigned as also due to the axial ligands. Although the Mo–Mo distance in $[Mo_2(O_2CMe)_4]$ species is lengthened only slightly by axial ligands (from ≈2.09 to ≈2.10 Å),[11] in $[Mo_2(O_2CCF_3)_4]$ species a greater change of as much as 0.04 Å has been observed, from 2.090(4) Å for no axial ligation to 2.129(2) Å in $[Mo_2(O_2CCF_3)_4(py)_2]$ (py = pyridine).[14] The latter distance is similar to that in **4**. We have not as yet pursued a structural characterisation of the parent complex $[Mo_2(O_2CCHF_2)_4]$.

Table 3 Selected interatomic distances (Å) and angles (°) for $[Mo_6(O_2CCHF_2)_{12}(bpy)_4]$ **4**

Mo(1)–Mo(1′)	2.1234(15)	Mo(2)–O(22)	2.119(5)
Mo(1)–O(4)	2.117(6)	Mo(2)–O(28)	2.113(5)
Mo(1)–O(6)	2.134(6)	Mo(2)–N(34)	2.174(7)
Mo(1)–O(10)	2.138(6)	Mo(2)–N(45)	2.186(7)
Mo(1)–O(12)	2.124(6)	Mo(3)–O(24)	2.117(6)
Mo(1)–O(16)	2.435(6)	Mo(3)–O(30)	2.119(5)
Mo(2)–Mo(3)	2.1741(12)	Mo(3)–O(58)	2.601(6)
Mo(2)–O(18)	2.538(6)	Mo(3)–N(46)	2.166(7)
		Mo(3)–N(57)	2.180(7)

Mo(1′)–Mo(1)–O(4)	92.11(16)	O(6)–Mo(1)–O(16)	83.43(21)
Mo(1′)–Mo(1)–O(6)	90.88(16)	O(10)–Mo(1)–O(12)	177.10(22)
Mo(1′)–Mo(1)–O(10)	91.18(16)	O(10)–Mo(1)–O(16)	87.98(22)
Mo(1′)–Mo(1)–O(12)	91.71(16)	O(12)–Mo(1)–O(16)	89.12(21)
Mo(1′)–Mo(1)–O(16)	174.26(16)	Mo(3)–Mo(2)–O(18)	168.49(13)
O(4)–Mo(1)–O(6)	177.01(22)	Mo(3)–Mo(2)–O(22)	90.04(15)
O(4)–Mo(1)–O(10)	91.01(23)	Mo(3)–Mo(2)–O(28)	91.00(14)
O(4)–Mo(1)–O(12)	89.06(23)	Mo(3)–Mo(2)–N(34)	102.04(17)
O(4)–Mo(1)–O(16)	93.58(22)	Mo(3)–Mo(2)–N(45)	106.00(18)
O(6)–Mo(1)–O(10)	88.73(23)	O(18)–Mo(2)–O(22)	78.90(19)
O(6)–Mo(1)–O(12)	91.05(22)	O(18)–Mo(2)–O(28)	86.50(20)
O(18)–Mo(2)–N(34)	89.37(21)	Mo(2)–Mo(3)–N(46)	101.21(18)
O(18)–Mo(2)–N(45)	78.24(22)	Mo(2)–Mo(3)–N(57)	97.52(17)
O(22)–Mo(2)–O(28)	93.18(21)	O(24)–Mo(3)–O(30)	91.47(21)
O(22)–Mo(2)–N(34)	165.25(23)	O(24)–Mo(3)–O(58)	92.42(21)
O(22)–Mo(2)–N(45)	94.11(24)	O(24)–Mo(3)–N(46)	166.73(23)
O(28)–Mo(2)–N(34)	95.00(23)	O(24)–Mo(3)–N(57)	98.96(24)
O(28)–Mo(2)–N(45)	161.47(23)	O(30)–Mo(3)–O(58)	79.37(20)
N(34)–Mo(2)–N(45)	74.58(26)	O(30)–Mo(3)–N(46)	92.96(23)
Mo(2)–Mo(3)–O(24)	91.25(15)	O(30)–Mo(3)–N(57)	166.76(23)
Mo(2)–Mo(3)–O(30)	90.33(14)	O(58)–Mo(3)–N(46)	76.14(23)
Mo(2)–Mo(3)–O(58)	169.15(15)	O(58)–Mo(3)–N(57)	91.99(22)
		N(46)–Mo(3)–N(57)	75.11(25)

Proposed structure of compound 5

Although a crystal structure of compound **5** has eluded all attempts to date, its stoichiometry and the structure of **4** strongly point to that proposed in Fig. 3, *i.e.* a zigzag chain structure obtained by converting the terminal $CHF_2CO_2^-$ groups of **4** (Fig. 2) into *syn,anti* bridging groups to additional $[Mo_2(O_2CCHF_2)_4]$ units. The alternation of $[Mo_2(O_2CCHF_2)_4]$ and $[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+}$ units appears the most reasonable possibility consistent with the $[Mo_4(O_2CCHF_2)_8(bpy)_2]$ formulation and the structure of **4**; it also has precedent in the related structures of $[Cu_4(O_2CMe)_8(L-L)_2]_n$ [L–L = bpy[5] or 2-(aminomethyl)pyridine[1d]] which have been determined by crystallography as zigzag chains consisting of alternating $[Cu_2(O_2CMe)_4]$ and $[Cu_2(O_2CMe)_2(L-L)_2]^{2+}$ units bridged by *syn,anti* carboxylate groups. The latter unit has no metal–metal bonding, of course, and structurally differs from the $[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+}$ unit in being doubly bridged by two η^1-O_2CMe groups.

Discussion

The 'trimer-of-dimers' structure of compound **4** is an unusual example of three covalently linked dinuclear units, and its hexanuclear structure is apparently unique in its linkage of three multiply bonded dinuclear metal units. Another hexanuclear species that can be described as three dinuclear units joined together in a chain fashion is $[Cu_6(O_2CC_6H_4Br\text{-}p)_6(dmae)_6]$ [dmae = 2-(dimethylamino)ethanolate].[15] In contrast, the complex $[Mo_6O_8(OEt)_6Cl_8]$ has a cyclic structure comprising three linked, singly bonded $[Mo^{v}_2]^{10+}$ units;[16] however, the complex $[Mo_6O_{10}(OPr^i)_{12}]$ is best described as two linked, singly bonded $[Mo^{V}_2]^{10+}$ dinuclear units with two additional Mo^{VI} atoms, one at each end.[17] Examples of two quadruply bonded $[Mo_2]^{4+}$ units linked together include $[Mo_4(O_2CBu^t)_6(2,7\text{-}O_2N_2C_8H_4)]$ (2,7-$O_2N_2C_8H_4$ = 2,7-dioxynaphthyridine)[18] and $[Mo_2(mhp)_3(MeCN)_2]^+$ (mhp = 2-hydroxy-6-methylpyridine anion).[12] The $[Mo_4Pd_2(O_2CMe)_4Cl_4(L-L)_6]$ [L–L = 2-(diphenylphosphino)-6-hydroxypyridine][19] can be described as two Mo_2Pd units linked together. Homopolymers of $[Mo_2]^{4+}$ units are more common than discrete oligomers of such units. In fact, in $[Mo_2(O_2CR)_4]$ structures, the molecules are often arranged to form infinite chains *via* weak axial interactions to the carboxylate O atoms of neighbouring molecules (Mo–O 2.6–3.0 Å).[11] Other $[Mo_2]_n$ carboxylate polymers contain bridging bidentate ligands and are of general formula $[Mo_2(O_2CR)_4L]_n$ {L = pyrazine,[20a] 4,4′-bipyridine,[20a,b] 9,10-anthraquinone,[21] 1,4-diazobicyclo[2.2.2]octane,[20a] 1,2-bis(dimethylphosphino)ethane[22] and *N,N,N′,N′*-tetramethylethane-1,2-diamine}.[22] All these contain a single repeating unit, as do many $[M_2(O_2CR)_4L]_n$ polymers with other metals, such as $[Ru_2(O_2CPh)_5]_n$[23] where $[Ru_2(O_2CPh)_4]$ units are linked by *anti,anti*-O_2CPh groups.

Conclusion

The successful preparation of compounds **4** and **5** from the assembly of preformed $[Mo_2(O_2CCHF_2)_4]$ and $[Mo_2(O_2CCHF_2)_2(bpy)_2]^{2+}$ units and $CHF_2CO_2^-$ linker groups could no doubt be extended to other hetero-oligomers and -polymers of metal–metal bonded units with $[Mo_2]^{4+}$, as in this work, or dinuclear units containing other metals. In addition, mixed-metal species should also be attainable. Judicious choice of the different dinuclear metal units employed and/or the linker group might provide species with controllable and interesting spectroscopic or physical properties. Studies along these directions are in progress.

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