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PAPER

Dicarboxylate-bridged $(Mo_2)_n$ ($n = 2, 3, 4$) paddle-wheel complexes: potential intermediate building blocks for metal–organic frameworks†

Mathias Köberl,[a] Mirza Cokoja,[b] Bettina Bechlars,[b] Eberhardt Herdtweck[b] and Fritz E. Kühn*[a,b]

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The treatment of the dimeric paddle-wheel (PW) compound $[Mo_2(NCCH_3)_{10}][BF_4]_4$ **1** with oxalic acid (0.5 equiv.), 1,1-cyclobutanedicarboxylic acid (1 equiv.), 5-hydroxyisophthalic acid (1 equiv.) (*m*-bdc–OH) or 2,3,5,6-tetrafluoroterephthalic acid (0.5 or 1 equiv.) leads to the formation of macromolecular dicarboxylate-linked $(Mo_2)_n$ entities ($n = 2, 3, 4$). The structure of the compounds depends on the length and geometry of the organic linkers. In the case of oxalic acid, the dimeric compound $[(CH_3CN)_8Mo_2(OOC–COO)Mo_2(NCCH_3)_8][BF_4]_6$ **2** is formed selectively, whereas the use of 2,3,5,6-tetrafluoroterephthalic acid affords the square-shaped complex $[(CH_3CN)_6Mo_2(OOC–C_6F_4–COO)]_4[BF_4]_8$ **3**. Bent linkers with a bridging angle of 109° and 120°, respectively, lead to the formation of the molecular loop $[(CH_3CN)_6Mo_2(OOC–C_4H_6–COO)]_2[BF_4]_4$ **4** and the bowl-shaped molecular triangle $[(CH_3CN)_6Mo_2(m\text{-bdc–OH})]_3[BF_4]_6$ **5**. All complexes are characterised by X-ray single crystal diffraction, NMR (^1H, ^{11}B, ^{13}C and ^{19}F) and UV-Vis spectroscopy.

Introduction

In the last decade, a large number of macromolecular coordination compounds and metal–organic frameworks (MOFs) containing dinuclear paddle-wheel (PW) units connected by dicarboxylate linkers have been synthesised.[1,2] This can largely be ascribed to the unique coordination behaviour of PW complexes, exhibiting an octahedral coordination environment with four bridging equatorial ligands, *e.g.* carboxylates, and one axial ligand per metal (usually solvent ligands). The angles between two *cis*-oriented equatorial ligands are usually 90°, which is why the linkage of PW units with dicarboxylates leads to well-ordered lattice structures. Thus, PW secondary building units have become important for the construction of larger coordination networks.[3–7] Yet, it has so far not been attempted to synthesise coordination polymers from molecular PW entities. The group of Cotton performed pioneering work in creating oligomeric structures such as dimers,[8,9] molecular loops,[10] triangles (Mo,[11] Rh,[12–14] Re[15]), propellers[16] and squares (Mo,[12,17] Ru,[18] Rh[19]) by connecting PW complexes with various dicarboxylate linkers to form dimeric molecules, triangular or square arrays. In Cotton's reports, at least one equatorial coordination site (per PW metal) at the M_2 centre is blocked by strongly bound bridging ligands, such as *N′N*-di-*p*-anisylformamidinate (DAniF). The remaining equatorial positions are occupied by solvent molecules and thus are available for the substitution by other ligands. The character of these accessible coordination sites determines the geometry of the product: a PW complex with two available, *cis*-oriented sites leads—dependent on the linker—either to dimeric molecular loops, or to tetrameric squares. The advantage of such precursors is their templating character, allowing the controlled design of discrete metal–organic arrays. The disadvantage, however, is the low reactivity of the product for further reaction with dicarboxylates to form larger networks. The synthesis of such coordination oligomers or polymers requires PW precursors which only exhibit labile solvent ligands, such as $[Mo_2(NCCH_3)_{10}][BF_4]_4$.[20] To date, there is only one report on the use of this compound for the synthesis of dicarboxylate-linked PW complexes. In 1997, McCann *et al.* investigated the reactivity of $[Mo_2(NCCH_3)_{10}][BF_4]_4$ with aliphatic dicarboxylic acids to create the first molecular loop with dimolybdenum units.[21] Yet, the geometry of this molecule, predetermined by the flexible dicarboxylate ligand, does not allow the formation of ordered networks.

Previously, we reported the synthesis of one-dimensional metal–organic complexes[22] and polymers[23] containing Mo_2 and Rh_2 PW complexes which are connected by various difunctional linkers *via* the axial coordination sites of the M_2 cores. This report focuses on the selective synthesis of molecular dimers, triangles and squares containing Mo_2 PW units bridged by linear or bent dicarboxylate ligands from $[Mo_2(NCCH_3)_{10}][BF_4]_4$ as intermediate building blocks for three-dimensional frameworks. Unlike Cotton's structural congeners, the complexes described here should

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[a] *Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Strasse 1, D-85747, Garching, Germany. E-mail: fritz.kuehn@ch.tum.de; Tel: +49 89 289 13081*
[b] *Chair of Inorganic Chemistry, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Strasse 1, D-85747, Garching, Germany*

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exhibit solvent molecules in the equatorial coordination sites of the PW core, allowing further controlled substitution and thus a framework growth along the coordination sphere.

Experimental

All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The solvents were dried and distilled under nitrogen following conventional methods. Chemicals were purchased from Aldrich (tetrafluoroterephthalic acid, 97%), Alfa Aesar (oxalic acid, 98% and 1,1-cyclobutanedicarboxylic acid, 99%) and Acros Organics (5-hydroxyisophthalic acid, 99%) and used as received. The precursor $[Mo_2(NCCH_3)_{10}][BF_4]_4$ **1** was prepared according to literature procedures.[20] The NMR spectra were recorded on a Bruker Avance DPX 400 spectrometer (^{1}H: 400.13 Hz, ^{11}B: 128.38 Hz, ^{13}C: 100.61 Hz and ^{19}F: 376.5 Hz). UV-Vis measurements were performed on a JASCO photometer V-550.

Synthesis of $[(CH_3CN)_8Mo_2(OOC–COO)Mo_2(NCCH_3)_8][BF_4]_6$ (2)

An acetonitrile solution (17 mL) of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (150 mg, 0.158 mmol) and 0.5 equiv. oxalic acid (7.1 mg, 0.079 mmol) is stirred for 20 h at 60 °C to yield a red solution. After solvent removal in vacuo, the residue is washed with diethyl ether (3 × 6 mL) and pentane (3 × 6 mL). Upon drying under vacuum, 122 mg (94% yield, 0.074 mmol) of compound **2** are isolated as a red solid. By slow diffusion of pentane into a concentrated acetonitrile solution of **2**, red crystals are obtained within one week. ^{1}H NMR (δ (ppm), in CD_3CN): 1.95 (s, $C\mathit{H}_3CN$). ^{11}B NMR (δ (ppm), in CD_3CN): 7.39 (s, $\mathit{B}F_4^-$). ^{19}F NMR (δ (ppm), in CD_3CN): −145.59 (s, $B\mathit{F}_4^-$) and −145.64 (s, $B\mathit{F}_4^-$). Anal. Calcd. for $C_{22}H_{30}B_6F_{24}Mo_4N_{10}O_4$ = $[(CH_3CN)_3Mo_2(OOC–COO)Mo_2(NCCH_3)_3][BF_4]_6$: C, 18.83; H, 2.15; N, 9.98. Found: C, 18.87; H, 2.20; N, 9.59. UV-Vis (CH_3CN): λ_{max} = 424 nm.

Synthesis of $[(CH_3CN)_6Mo_2(OOC–C_6F_4–COO)]_4[BF_4]_8$ (3)

A solution of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (986 mg, 1.038 mmol) and 1.1 equiv. perfluoroterephthalic acid (271 mg, 1.138 mmol) in 90 mL acetonitrile is stirred for 20 h at 60 °C. The colour of the solution changes from blue to red. After solvent removal in vacuo, a red solid is isolated and washed with diethyl ether (4 × 10 mL) until the filtrate is clear to remove any residual $HBF_4·Et_2O$. The solid is further washed with pentane (3 × 10 mL). Upon drying under vacuum, 721 mg (82% yield, 0.213 mmol) of **3** are obtained. Compound **3** can be further purified by crystallisation by overlaying a concentrated solution with pentane. ^{1}H NMR (δ (ppm), in CD_3CN): 1.95 (s, $C\mathit{H}_3CN$). ^{11}B NMR (δ (ppm), in CD_3CN): 2.04 (s, $\mathit{B}F_4^-$). ^{13}C NMR (δ (ppm), in CD_3CN): 172.1 ($\mathit{C}OO^-$) and 147.6 (C_{quat}). ^{19}F NMR (δ (ppm), in CD_3CN): −132.9 (s, 16 F, F_{ar}), −146.3 (s, 6 F, $B\mathit{F}_4^-$) and −146.4 (s, 26 F, $B\mathit{F}_4^-$). Anal. Calcd. for $C_{66}H_{51}B_8F_{48}Mo_8N_{17}O_{16}$ = $[(CH_3CN)_{4.25}Mo_2(OOC–C_6F_4–COO)]_4[BF_4]_8$: C, 25.54; H, 1.66; N, 7.67. Found: C, 24.53; H, 1.76; N, 8.19. UV-Vis (CH_3CN): λ_{max} = 432 nm.

Synthesis of $[(CH_3CN)_6Mo_2(OOC–C_4H_6–COO)]_2[BF_4]_4$ (4)

A solution of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (117 mg, 0.123 mmol) and 1 equiv. 1,1-cyclobutanedicarboxylic acid (17.8 mg, 0.123 mmol) in 10 mL acetonitrile is stirred for 24 h at room temperature, whereupon the colour of the solution changes from blue to purple. The solution is layered by a solution of hexane/diethyl ether = 4 : 1 to yield pink crystals within 72 h. The crystalline product is collected and washed with diethyl ether (3 × 4 mL) and hexane (3 × 4 mL). Upon drying in vacuo, 47 mg (51% yield, 0.031 mmol) of pink crystals of **4** are isolated. It is possible to increase the yield to 75% by precipitating **4** as a non-crystalline solid from the initial reaction solution. ^{1}H NMR (δ (ppm), in CD_3CN): 3.35 (t, $C\mathit{H}_2$, 8 H), 2.37 (m, $C\mathit{H}_2$, 4 H) and 1.95 (s, $C\mathit{H}_3CN$, *ca.* 30 H). ^{11}B NMR (δ (ppm), in CD_3CN): 7.25 (s, $\mathit{B}F_4^-$). ^{13}C NMR (δ (ppm), in CD_3CN): 187.9 ($\mathit{C}OO^-$), 147.6 (C_{quat}), 60.0 ($\mathit{C}H_2$) and 32.7 ($\mathit{C}H_2$). ^{19}F NMR (δ (ppm), in CD_3CN): −146.4 (s, $B\mathit{F}_4^-$) and −146.5 (s, $B\mathit{F}_4^-$). Anal. Calcd. for $C_{26}H_{33}B_4F_{16}Mo_4N_7O_8$ = $[(CH_3CN)_{2.5}Mo_2(OOC–C_4H_6–COO)]_2[BF_4]_4$: C, 23.97; H, 2.55; N, 7.53. Found: C, 23.90; H, 2.71; N, 7.16. UV-Vis (CH_3CN): λ_{max} = 533 nm.

Synthesis of $[(CH_3CN)_6Mo_2(\mathit{m}\text{-bdc–OH})]_3[BF_4]_6$ (5)

An acetonitrile solution (10 mL) of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (102 mg, 0.108 mmol) and 1 equiv. 5-hydroxyisophthalic acid (*m*-bdc–OH) (19.6 mg, 0.108 mmol) is stirred for 24 h at room temperature, whereupon the colour of the solution changes from blue to red. The concentrated solution is layered by a solution of hexane/diethyl ether = 4 : 1 to yield red crystals within 4 d. The crystalline product is collected and washed with diethyl ether (3 × 3 mL) and hexane (3 × 3 mL). Upon drying under vacuum, 41 mg (50% yield, 0.018 mmol) of red solid **5** are isolated. ^{1}H NMR (δ (ppm), in CD_3CN): 8.66 (s, $O\mathit{H}$), 7.99 (s, $C\mathit{H}$, 2 H), 7.82 (s, $C\mathit{H}$, 1 H) and 1.96 (s, $C\mathit{H}_3CN$, *ca.* 10 H). ^{11}B NMR (δ (ppm), in CD_3CN): 7.13 (s, $\mathit{B}F_4^-$). ^{13}C NMR (δ (ppm), in CD_3CN): 181.4 ($\mathit{C}OO^-$), 159.0 ($\mathit{C}OH$), 147.5 (C_{quat}) and 132.6 ($\mathit{C}H$). ^{19}F NMR (δ (ppm), in CD_3CN): −146.68 (s, $B\mathit{F}_4^-$) and −146.74 (s, $B\mathit{F}_4^-$). Anal. Calcd. for $C_{44}H_{42}B_6F_{24}Mo_6N_{10}O_{15}$ = $[(CH_3CN)_{3.33}Mo_2(\mathit{m}\text{-bdc-OH})]_3[BF_4]_6$: C, 25.81; H, 2.07; N, 6.84. Found: C, 25.88; H, 2.21; N, 7.17. UV-Vis (CH_3CN): λ_{max} = 416 nm.

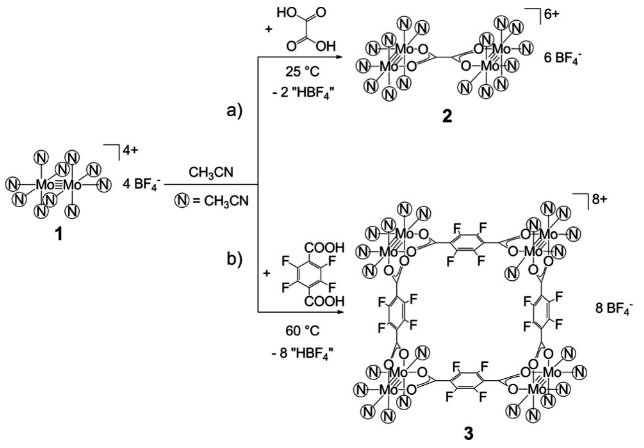
Crystallographic data

Single crystal X-ray structure determinations: **2**: red prism, $C_{50}H_{72}B_6F_{24}Mo_4N_{24}O_4$, M_r = 1977.94; monoclinic, space group $P2_1/n$ (No. 14), a = 14.9896(4), b = 18.3686(5), c = 15.5071(4) Å, β = 92.7229(14)°, V = 4264.9(2) Å^3, Z = 2, λ(Mo-Kα) = 0.71073 Å, μ = 0.680 mm^{-1}, ρ_{calcd} = 1.540 g cm^{-3}, T = 123(1) K, $F(000)$ = 1972, θ_{max}: 25.46°, R_1 = 0.0220 (7572 observed data), wR_2 = 0.0537 (all 7880 data), GOF = 1.079, 536 parameters, $\Delta\rho_{max/min}$ = 0.76/−0.56 e Å^{-3}. **3**: red prism, $C_{38}H_{33}B_4F_{24}Mo_4N_{11}O_8$, M_r = 1654.75; triclinic, space group $P\bar{1}$ (No. 2), a = 14.2639(6), b = 16.9759(8), c = 17.5316(7) Å, β = 96.067(2)°, β = 98.424(2)°, β = 99.904(2)°, V = 4099.3(3) Å^3, Z = 2, λ(Mo-Kα) = 0.71073 Å. At R_1 = 0.0571 and wR_2 = 0.1721 the refinements were aborted due to unresolvable disorder problems. **4**: red fragment, $C_{40}H_{54}B_4F_{16}Mo_4N_{14}O_8$, M_r = 1589.97; triclinic, space group $P\bar{1}$ (No. 2), a = 10.6698(4), b = 10.7944(5), c = 15.1873(6) Å, α = 89.095(2)°, β = 86.007(2)°, γ = 64.711(2)°, V = 1577.52(11) Å^3, Z = 1, λ(Mo-Kα) = 0.71073 Å, μ = 0.880 mm^{-1},

ρ_{calcd} = 1.674 g cm^{-3}, T = 123(2) K, F(000) = 788, θ_{max}: 26.01°, R_1 = 0.0231 (5979 observed data), wR_2 = 0.0628 (all 6159 data), GOF = 1.058, 395 parameters, $\Delta\rho_{max/min}$ = 0.90/−0.68 e Å^{-3}. **5**: red fragment, $C_{70}H_{78}B_6F_{24}Mo_6N_{23}O_{15}$, M_r = 2578.05; monoclinic, space group $P2_1/c$ (No. 14), a = 14.7364(6), b = 32.6112(13), c = 22.5349(9) Å, β = 104.233(2)°, V = 10497.2(7) Å^3, Z = 4, λ(Mo-Kα) = 0.71073 Å. At R_1 = 0.0658 and wR_2 = 0.1523 the refinements were aborted due to unresolvable disorder problems. CCDC-830421 (**2**) CCDC-830422 (**4**). For more details, see the ESI.†

Results and discussion

The blue dimolybdenum complex $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (**1**) selectively reacts with oxalic acid in acetonitrile to give the dimeric complex **2** in a yield of 94% (Scheme 1a). The ^{1}H NMR spectrum shows one singlet at 1.95 ppm due to free acetonitrile, which is a consequence of a fast scrambling with CD_3CN. The ^{11}B NMR spectrum shows one resonance at 7.39 (BF_4^-). According to the isotope effect of the boron atom (^{10}B, 19.9% and ^{11}B, 80.1%), two adjacent singlets in the ^{19}F NMR with an integral ratio of ~1 : 4 are observed at −145.59 and −145.64 ppm.



Scheme 1 Synthesis of (a) $[(CH_3CN)_8Mo_2(OOC–COO)Mo_2(NCCH_3)_8][BF_4]_6$ **2** and (b) $[(CH_3CN)_6Mo_2(OOC–C_6F_4–COO)]_4[BF_4]_8$ **3**.

Compound **2** is well soluble in benzonitrile (56 g L^{-1}) and dimethylformamide (50 g L^{-1}) and fairly soluble in acetonitrile (3.3 g L^{-1}). Due to the low solubility of **2**, ^{13}C NMR measurements in CD_3CN were not successful. UV-Vis experiments of the red dimer show a maximum absorbance at 424 nm. Considering the lability[20] of the coordinating acetonitrile ligands, an adequate elemental analysis is obtained for [**2** – 6 MeCN]. Attempts to synthesise a square-shaped compound by either treating **1** with an excess of oxalic acid, or reacting **2** with 1 equiv. oxalic acid were so far not successful. The molecular structure of compound **2** is presented in Fig. 1.

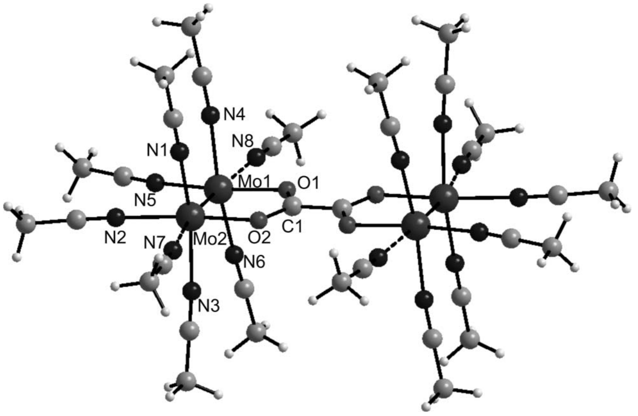


Fig. 1 Molecular structure of **2** in the solid state. The BF_4^- anions are omitted for clarity.

It crystallises in the monoclinic space group $P2_1/n$ with an inversion centre located in the middle of the oxalate C–C bond. Two dimolybdenum units are linked by the oxalate linker and the Mo_2 axes are assembled parallel to each other (torsion angle Mo1–Mo2–Mo1′–Mo2′ = 0°). The Mo_2 units and the linker atoms are all situated almost in one plane. In fact, compound **2** can be regarded as the smallest metal–organic unit, *i.e.* an 'edge' of a three-dimensional network such as $[Zn_2(bdc)_2(bipy)]$[24] or $[Zn_2(ndc)_2(dabco)]$[25] (bdc = 1,4-benzenedicarboxylate, bipy = 4,4′-bipyridine, ndc = 1,4-naphthalenedicarboxylate and dabco = 1,4-diazabicyclo[2.2.2]octane). As shown in Table 1, all molybdenum atoms exhibit an octahedral coordination environment. The Mo–Mo, Mo–N_{eq} and Mo–N_{ax} bond lengths are very similar to those found in the precursor $[Mo_2(CH_3CN)_{10}][BF_4]_4$ (deviations of ±0.01 Å).[20] The Mo–Mo bond lengths of similar dimers described by Cotton *et al.* (on average 2.09 Å),[8] which are also listed in Table 1, are shorter than those in **2**. In comparison to Cotton's oxalate-bridged dimer, the elongation of the Mo–Mo bond distance in **2** is probably due to axial coordination of electron-donating acetonitrile ligands. The Mo–O distance in **2** is about 0.05 Å shorter than in Cotton's oxalate-bridged dimer, whereas the Mo–N_{eq} bond lengths are similar. Comparing the distances d between centroids of Mo_2 units within compound **2** (d = 6.86 Å) and Cotton's dimer (d = 6.95 Å), a difference of 0.09 Å is found. The

Table 1 Comparison of bond distances (Å) in the precursor **1**,[20] compounds **2**, **4** and **5**, Cotton's (FAC) oxalate-linked dimer[8] and malonate-bridged loop[10]

$d_{min-max}$	1	2	FAC's dimer	3[a]	4	FAC's loop	5[a]
Mo–Mo	2.187(1)	2.1760(2)	2.090(1)	2.159–2.160	2.1529(2)	2.088(1)	2.145–2.152
Mo–O	—	2.075(1)–2.082(1)	2.115(3)–2.145(3)	2.072–2.093	2.079(1)–2.093(1)	2.130(6)–2.144(6)	2.053–2.106
Mo–N_{eq}	2.11(1)–2.14(1)	2.130(2)–2.151(2)	2.119(4)–2.168(5)	2.145–2.155	2.150(2)–2.159(2)	2.098(8)–2.124(7)	2.134–2.164
Mo–N_{ax}	2.60(1)	2.606(2)–2.613(2)	—	2.533–2.636	2.648(2)–2.700(1)	—	2.507–2.701
Mo–F	—	—	—	2.661	—	—	2.624
Mo–OH	—	—	—		—	—	2.902

[a] Data are taken from the aborted refinements.

Mo–N_{eq}–C bond angles in **2** and $[Mo_2(NCCH_3)_{10}]_4[BF_4]_4$ are all close to 180°, while the Mo–N_{ax}–C angles in **2** (average of 175°) are about 20° larger than in **1**. The angle Mo1–Mo2–$N7_{ax}$ is 169.6° and about 7° smaller than the angle in the starting material. Labels are given in the ESI.†

The treatment of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ with 1 equiv. perfluoroterephthalic acid (Scheme 1b) in acetonitrile at 60 °C leads to the formation of the square-shaped complex **3** in 82% yield. Below 60 °C, the reaction rate is significantly slower. Surprisingly, the treatment of 2 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ with 1 equiv. dicarboxylic acid does not afford the terephthalate-bridged analogue of compound **2**, but the tetramer **3** instead (1 equiv. of unreacted $[Mo_2(NCCH_3)_{10}][BF_4]_4$ can be isolated). The reaction of 1 equiv. of **3** with 20 equiv. perfluoroterephthalic acid at 60 °C results in the precipitation of a red solid which could not be convincingly identified. Obviously, the product structure is dependent on the length of the linker; in the case of the oxalate-bridged PW complexes, a square-shaped molecule is thermodynamically less favourable than the single-bridged complex **2**.

The purity of the compound was confirmed by ^1H NMR spectroscopy in CD_3CN. The spectrum shows only one singlet at 1.95 ppm originating from free acetonitrile. Compound **3** exhibits a higher solubility in acetonitrile (577 g L^{-1}) than the starting material **1** (11 g L^{-1}), but is barely soluble in other organic solvents such as benzonitrile (3.6 g L^{-1}) and pyridine (2.3 g L^{-1}). In the ^{13}C NMR, two shifts at 172.1 (COO^-) and 147.6 ppm (C_{quat}) can be observed. The ^{11}B NMR signal of BF_4^- is found at 2.04 ppm. The ^{19}F NMR shows one singlet at −132.9 ppm (attributed to 16 aromatic fluorine atoms of the linker) and two singlets at −146.3 and −146.4 ppm (arising from the 32 fluorine atoms of 8 BF_4^-). The ratio of integral intensities of C_6F_4 and BF_4 is 1 : 2 and confirms the *cis*-configuration of **3**. UV-Vis experiments of the red tetramer show a maximum absorbance at 432 nm. Since the coordinating acetonitrile ligands are very weakly bound to the Mo centre and thus easily removed from the complex as has been documented before,[20] elemental analysis values are not in good agreement with the calculated values.

The molecular structure of compound **3** is shown in Fig. 2. It crystallises in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell and an inversion centre located at the centre of the cationic molecule. Each dimolybdenum unit represents a corner of the square with two *cis*-arranged linking perfluoroterephthalate dianions as equatorial ligands. All remaining equatorial and most axial positions are occupied by acetonitrile molecules; BF_4^- anions occupy two of the eight axial positions. The Mo_2 axes are arranged parallel to each other. Likewise compound **2**, **3** can also be regarded as a macromolecular subunit of typical three-dimensional PW-MOFs, such as Kim's $[Zn_2(bdc)_2(dabco)]_n$.[4] The molybdenum atoms exhibit an octahedral coordination environment. The planes of the carboxylic group and the aromatic ring of the linker are twisted relative to each other. The *cis*-coordinated carboxylic groups form a right angle and enforce the square array of **3**. The coordination of BF_4^- anions raises the question whether the reactivity of **3** is influenced by axially coordinating BF_4^- anions.[26–28] This assumption is supported by the unusually poor reactivity of **3**. For instance, **3** is inert to an excess of (di)carboxylates, or to linear linkers such as 1,4-dicyanobenzene. This is contrary to the chemical intuition, a substitution of nitrile ligands by (di)carboxylates should be possible. According to ^1H NMR spectroscopy, the acetonitrile ligands can be replaced by benzonitrile. The design of cubes or 1D-tubes *via* stacking molecules of **3** along the Mo–Mo bond, however, was not yet successful. Similarly, the passivation of the equatorial coordination sites *via* replacing acetonitrile molecules by carboxylates, as well as the extension of **3** into a two-dimensional plane did so far not succeed. In the structure of compound **3**, the area of the square formed by the four Mo_2 cores is estimated to be around 11 × 11 Å^2. Cotton's tetramers have areas from 7 × 7 (oxalate-bridged square) to 15 × 15 Å^2 (4,4′-biphenyldicarboxylate square).[17] There is no substantial difference between the length of the lateral edge of **3** ($Mo_2 \cdots Mo_2$ is *ca.* 11 Å) and the distance between centroids of Mo_2 units within the perfluoroterephthalate-bridged dimer of Cotton *et al.* ($Mo_2 \cdots Mo_2$ = 11.3 Å).[8] Hence, the number of carboxylic groups coordinating to one Mo_2 unit does not seem to influence the Mo–O bond length (see Table 1). This fact is also confirmed by comparison of Mo–O bond lengths within Cotton's dimers[8] and tetramers.[17]

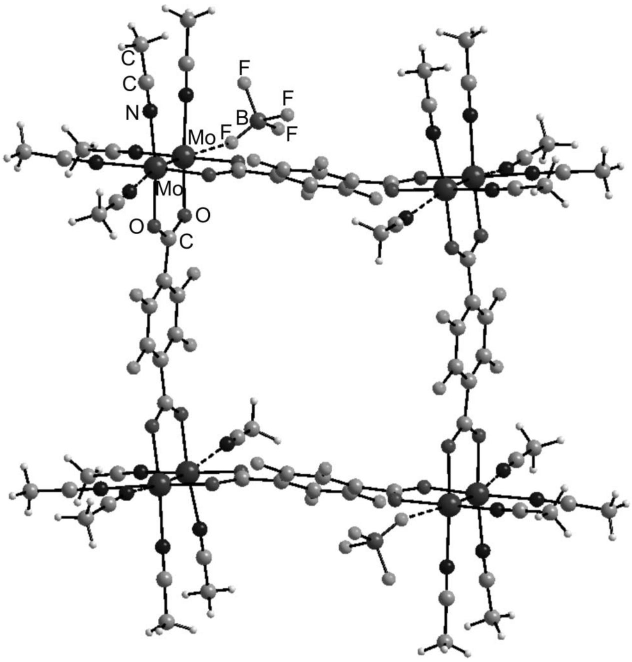
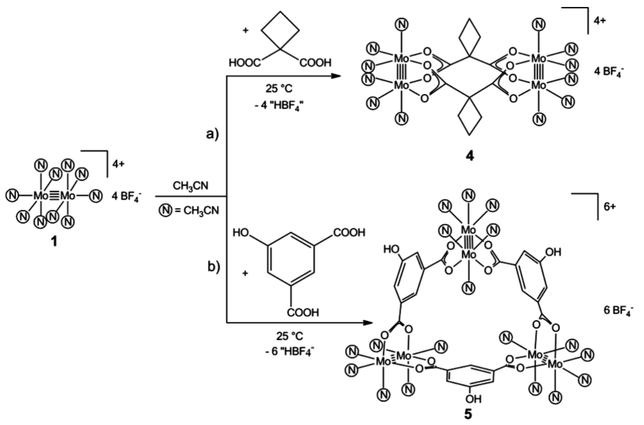


Fig. 2 Molecular structure of **3** in the solid state with a pore aperture width of around 9.5 Å which is partially coordinated by BF_4^- anions in axial positions. The remaining six BF_4^- anions are omitted for clarity.

The reaction of 1 equiv. $[Mo_2(NCCH_3)_{10}][BF_4]_4$ with 1 equiv. 1,1-cyclobutanedicarboxylic acid leads to the formation of the molecular loop $[(CH_3CN)_6Mo_2(OOC–C_4H_6–COO)]_2[BF_4]_4$ **4** in yields of 75% (Scheme 2a). Compound **4** is characterised by ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopy. As expected, the ^{11}B NMR shows one singlet at 7.25 ppm (related to BF_4^-) and the ^{19}F NMR exhibits two adjacent singlets at −146.4 and −146.5 ppm (originating from BF_4^-). The ^1H NMR shows three signals at 3.35 ppm (t, $–C_{quat}CH_2–$, 8H), at 2.37 ppm (m, $–CH_2CH_2CH_2–$, 4 H) and at 1.96 ppm (s, free CH_3CN, *ca.* 30 H) with an integral ratio of 2 : 1 : 7.5, indicating the removal of two axially coordinating acetonitrile ligands upon drying under vacuum. In the case of removing five acetonitrile ligands, calculated values for elemental analysis concur with [**4** – 5 MeCN]. In comparison to the free

Table 2 Selected NMR shifts in compounds **3**, **4**, **5** and in corresponding free linkers in CD_3CN. In comparison to free acids, a general trend to low field shifted peaks can be observed

δ (ppm)	**3**	Free acid **3**	**4**	Free acid **4**	**5**	Free acid **5**
^{1}H	—	—	**3.35** CH_2 **2.37** CH_2	**2.48** CH_2 **1.94** CH_2	**8.66** OH **7.99** $C_{ar}H$	**7.45** OH **7.61** $C_{ar}H$
^{19}F	**−132.9** F_{ar}	**−135.1** F_{ar}	—	—	—	—



Scheme 2 Synthesis of (a) $[(CH_3CN)_6Mo_2(OOC–C_4H_6–COO)]_2[BF_4]_4$ **4** and (b) $[(CH_3CN)_6Mo_2(m\text{-bdc–OH})]_3[BF_4]_6$ **5**.

dicarboxylic acid (see Table 2), the methylene signals are shifted to low field. Four signals in the ^{13}C NMR spectrum can be assigned to compound **4**, *i.e.* the carboxyl group (187.9 ppm), the quaternary carbon atom (147.6 ppm) and the methylene groups (60.0 and 32.7 ppm). Complex **4** is pink in colour and exhibits a maximum absorbance at 533 nm in the UV-Vis spectrum.

The molecular structure of **4** is shown in Fig. 3. The compound crystallises in the triclinic space group $P\bar{1}$ with one formula unit per unit cell and an inversion centre located at the centre of the molecule. Two dimolybdenum units are linked by two bent 1,1-cyclobutanedicarboxylate linkers forming a molecular loop **4**. The midpoints of the Mo_2 bonds and the quaternary C atoms C2 and C2′ of the linker molecules define a rhombus having four almost equidistant sides (d = 4.35 Å). The rhombic triangle exhibits two angles 99.04(4)° for Mo2–C2–Mo2′ and 80.81(4)° for C2–Mo2–C2′ whose opposite angles are equal. The area of the rhombus defined by the midpoints of the Mo_2 bonds and the quaternary C atoms is 17.7 Å^2. The Mo_2 units are oriented parallel to each other and form a rectangle with four right angles. Since the average Mo–O bond length in **4** (2.09 Å) is shorter and stronger than in Cotton's malonate loop $[cis\text{-}Mo_2(DAniF)_2]_2(O_2CCH_2CO_2)_2$ (2.14 Å), the Mo_2 entities in **4** (d = 6.3 Å) are about 0.2 Å closer to each other than in Cotton's loop (d = 6.5 Å).[10] Due to the bent nature of the linker (angle C6–C2–C1′ of 103.3° in **4**), the geometry of **4** is predetermined. Labels are given in the ESI.† Similar to compounds **1–3**, the four Mo atoms exhibit an octahedral coordination environment. The parallel oriented Mo_2 units are surrounded by two *cis*-oriented carboxylate groups and six acetonitrile ligands. The molecular rhombus **4** is the first example of a molecular loop containing a 1,1-cyclobutanedicarboxylate linker. Cotton *et al.* synthesised a similar loop by using malonate as the linker.[10]

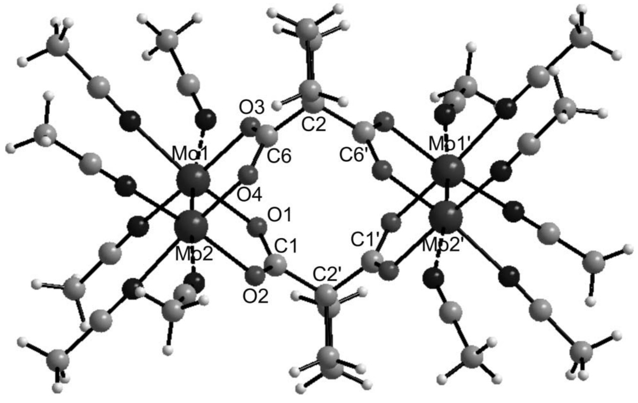


Fig. 3 Molecular structure of **4** in the solid state. The BF_4^- anions are omitted for clarity.

So far, the passivation of **4** with stoichiometric amounts of glacial acetic acid was not successful. When an excess of glacial acetic acid is used, **4** reacts to $[Mo_2(OAc)_4]$ as confirmed by a single resonance at 2.59 ppm related to the methyl groups of the coordinating acetates in the ^{1}H NMR spectrum (in THF-d_8). Similarly to **3**, it is possible to substitute all acetonitrile with benzonitrile ligands.

The reaction of equimolar amounts of **1** and 5-hydroxyisophthalic acid (m-bdc–OH) yields the bowl-shaped molecular triangle $[(CH_3CN)_6Mo_2(m\text{-bdc–OH})]_3[BF_4]_6$ **5** in yields of 50% (see Scheme 2b). The purity of compound **5** is confirmed by NMR spectroscopy. The ^{11}B and ^{19}F NMR spectra show typical shifts related to the BF_4^- anion. Low field shifted singlets (compared to free 5-hydroxyisophthalic acid, see Table 2) in the ^{1}H NMR can be assigned to the hydroxyl group (8.66 ppm) and to aromatic hydrogen atoms (7.99 and 7.82 ppm) of the 5-hydroxyisophthalate linker. Since the hydroxyl group is interacting with Mo in solution, a sharp and low field shifted singlet is observed. As usual, a singlet at 1.96 ppm can be observed, originating from free acetonitrile molecules. The ^{13}C NMR spectrum shows signals at 181.4, 159.0, 147.5 and 132.6 ppm which are assigned to COO^-, COH, C_{quat} and $C_{ar}H$. Again, the coordination of the ligand to the Mo_2 units causes low field shifts. UV-Vis experiments of the red complex reveal a maximum absorbance at 416 nm. According to elemental analysis, the drying of **5** *in vacuo* leads to the removal of eight acetonitrile ligands.

The molecular structure of compound **5** is shown in Fig. 4. It crystallises in the monoclinic space group $P2_1/c$ with four formula units per unit cell. Each dimolybdenum unit represents a corner of the triangular bowl-shaped array with two *cis*-oriented bridging 5-hydroxyisophthalate linkers and either five or six coordinating acetonitrile molecules.

The Mo_2 units define an equilateral triangle exhibiting Mo_2–Mo_2–Mo_2 angles of ~60° and average distances d between centroids of Mo_2 bonds of ~9.5 Å. Thus, the distances between the midpoints of the Mo_2 bonds in Cotton's triangle

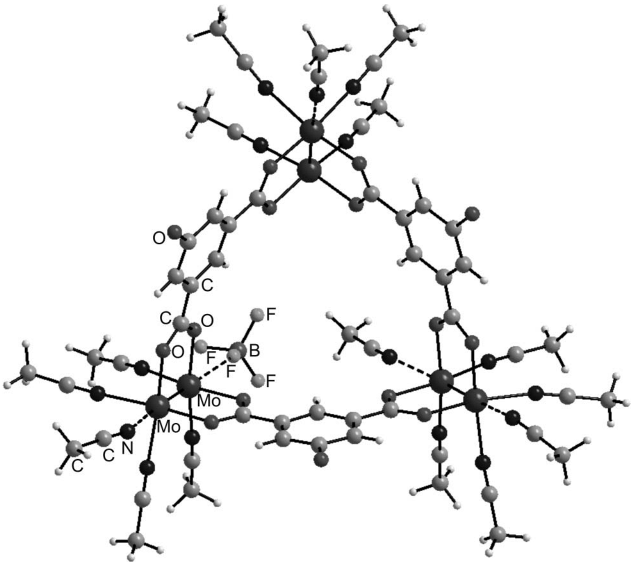


Fig. 4 Molecular structure of **5** in the solid state with a pore width of 6.3 Å. One BF_4^- anion coordinates to the axial position of one Mo_2 corner. The remaining five BF_4^- anions are omitted for clarity.

[*cis*-Mo_2(DAniF)$_2$]$_3$(*trans*-1,4-$O_2CC_6H_{10}CO_2$)$_3$[11] are about 1.7 Å longer than in **5**. The Mo–Mo bond lengths are 2.145, 2.150 and 2.152 Å and therefore similar to those in **4** and about 0.04 Å smaller than in **1** (see Table 1). Again, the coordination of carboxylic groups to the Mo_2 centre causes a shortening of the Mo_2 bond. The Mo–O bonds in **5** (average bond length of 2.08 Å) are shorter than in Cotton's triangle (average bond length of 2.15 Å). In two of the three Mo_2 units one axial position is not occupied by acetonitrile. In one case, a BF_4^- anion coordinates to the Mo atom (Mo5–F7 bond length of 2.624 Å) as in **3**. The unoccupied axial position of the second Mo_2 unit allows a weak intermolecular HO···Mo interaction (Mo3–O15 bond length of 2.902 Å) between the triangles leading to the formation of molecular chains in the solid state and in solution (Fig. 5). Since the Mo_2 corners are surrounded by different ligands, the Mo–N_{ax} bond lengths vary from 2.507 for Mo4–N11, 2.585 for Mo6–N16, 2.630 for Mo2–N6 to 2.701 Å for Mo1–N5. This variation is due to electronic effects arising from the different nature of coordinating ligands. In general, molecular triangles based on linear linkers such as oxalate or terephthalate exhibit bridging angles of 180°. The bent nature of *m*-bdc–OH in **5** leads to the connection of the Mo_2 units with an angle of 120° and an unusual bowl-shaped structure. Labels are given in the ESI.†

Conclusions

The compound [$Mo_2(NCCH_3)_{10}$][BF_4]$_4$ serves as a building unit for defined oligomeric structures **2–5**. The molecular loop **4** and the triangle **5** are novel compounds with regard to the linker and the shape. Compounds **2–5** formally represent the first steps toward the synthesis of more complex architectures such as polygons or 1D-, 2D- and 3D-network structures. In comparison to Cotton's 'passivated' compounds (due to bulky and strongly coordinating ligands), the substitution of labile acetonitrile ligands in complexes **2–5** by dicarboxylic acids should be much easier in order to create highly ordered frameworks. The role of the anion, especially the influence of larger, less coordinating anions such as $B(C_6F_5)_4^-$ on the reactivity of **3** is currently being investigated. In general, the possibility of substituting weakly bound acetonitrile ligands leads to numerous connection possibilities. Compounds **2–5**, especially **2** and **3**, are potential building blocks for MOFs. So far, in nearly all cases, MOFs are prepared under solvothermal conditions and in the case of PW MOFs the M_2 unit is formed *in situ*. Hence, the controlled assembly of the 'lego bricks' **2** and **3** to larger architectures would represent a novel access to MOFs.

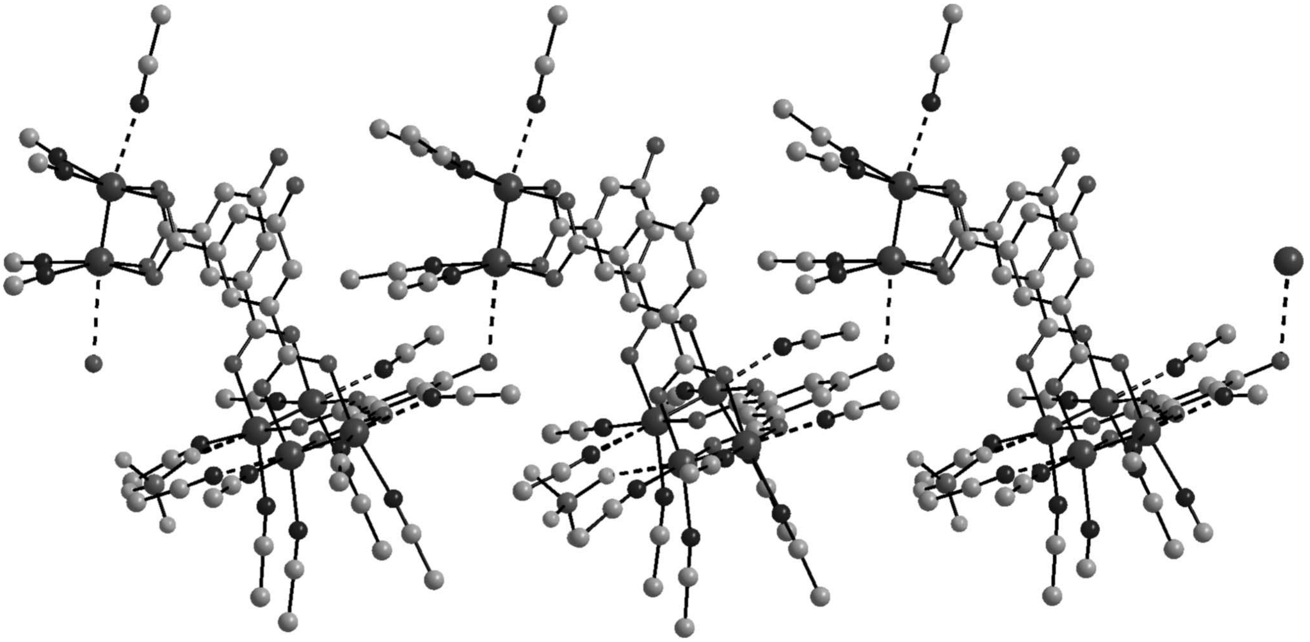


Fig. 5 Bowl-shaped triangles **5** are interacting by weak HO···Mo-bonding to form molecular chains bearing O···Mo bonds which are also present in solution.

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