Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

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

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Single Crystal X-Ray Structure Determination of Compound 2

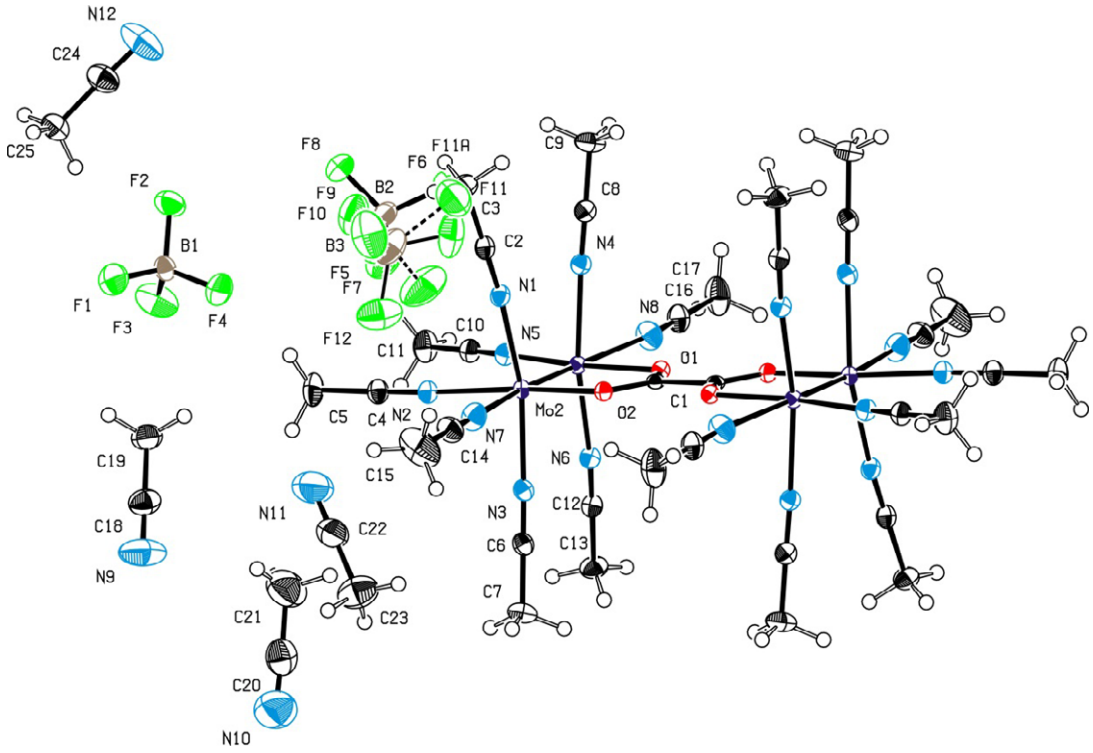

Figure F1 – Ortep drawing with 50% ellipsoids. [6]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{50}\ H_{72}\ B_6\ F_{24}\ Mo_4\ N_{24}\ O_4$
	$[(C_{34}\ H_{48}\ Mo_4\ N_{16}\ O_4)^{6+}]$, $6[(B\ F_4)^-]$, $8(C_2\ H_3\ N)$
Crystal Color / Shape	Red prism
Crystal Size	Approximate size of crystal fragment used for data collection: $0.30 \times 0.41 \times 0.56$ mm

Molecular Weight:	1977.94 a.m.u.
F_{000}:	1972
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\,2_1/n$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9252 reflections with the programs "APEX suite" and "SAINT" [1,2]; theta range 1.72° < θ < 25.46°; Mo($K\overline{\alpha}$); λ = 71.073 pm a = 1498.96(4) pm b = 1836.86(5) pm β = 92.7229(14)° c = 1550.71(4) pm V = 4264.9(2)· 10^6 pm^3; Z = 2; D_{calc} = 1.540 g cm^{-3}; Mos. = 0.68
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo($K\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.72° < θ < 25.46°; h: -18/18, k: -22/22, l: -18/18
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 8 runs; 3202 films / scaled: 8 runs; 3202 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 45.0 mm
LP - Correction:	Yes [2]
Intensity Correction	No/Yes; during scaling [2]
Absorption Correction:	Multi-scan; during scaling; μ = 0.680 mm^{-1} [2] Correction Factors: T_{min} = 0.6608 T_{max} = 0.7452
Reflection Data:	84136 reflections were integrated and scaled 1464 reflections systematic absent and rejected 82672 reflections to be merged 7880 independent reflections 0.021 R_{int}: (basis F_o^2) 7880 independent reflections (all) were used in refinements 7572 independent reflections with $I_o > 2\sigma(I_o)$ 99.7 % completeness of the data set 536 parameter full-matrix refinement 14.7 reflections per parameter
Solution:	Direct Methods [3]; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit: 58 Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 98 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.
Atomic Form Factors:	For neutral atoms and anomalous dispersion [4]
Extinction Correction:	no
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0175; b: 5.3086; P: [Maximum(0 or F_o^2)+2∗F_c^2]/3
Shift/Err:	Less than 0.001 in the last cycle of refinement:
Resid. Electron Density:	+0.76 e_0/Å^3; -0.56 e_0/Å^3
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$
[$F_o > 4\sigma(F_o)$; N=7572]:	= 0.0220
[all reflctns; N=7880]:	= 0.0232
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$
[$F_o > 4\sigma(F_o)$; N=7572]:	= 0.0524
[all reflctns; N=7880]:	= 0.0537
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$ = 1.079
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$

[1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).

[3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, Moliterni A. G. G.; A.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. "**SIR97**", A New Tool for Crystal Structure Determination and Refinement; *J. Appl. Crystallogr.* **1999**, *32*, 115-119.

[3a] Sheldrick, G. M. "**SHELXS-97**", Program for Crystal Structure Solution, Göttingen, (1997).
[4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.
[5] Sheldrick, G. M. "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).
[6] Spek, A. L. "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).
[7] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, *32*, 837-838.

Single Crystal X-Ray Structure Determinations of Compound 3-5

Operator: *** Bettina Bechlars ***

General:

Crystallographic details for compounds **3-5** are summarised in Table S1. The data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ–CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation (λ = 0.71073 Å), and a graphite monochromator by using the SMART software package. [1] The measurements were performed on single crystals coated with Paratone oil and mounted on Kaptan loops. Each crystal was frozen under a stream of nitrogen. A matrix scan using at least 20 centred reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarisation effects, scan speed, and background using SAINT 4.15. [2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [2] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [7] based on SHELXS-97. [3a] Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2\text{-}F_c^2)^2$ with SHELXL-97 [5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [4] Images of the crystal structures were generated by PLATON [6].

***Remarks on the refinement of compounds 3, 4 and 5*:**

3: Since the disorder of non-coordinated acetonitrile molecules could not be resolved, SQUEEZE was applied to remove 297 electrons corresponding to 13.5 acetonitrile molecules per unit cell. Furthermore, a disorder of the tetrafluorophenyl ring of one of the bridging ligands was resolved. The refinement, however did not lead to reasonable values. The non-hydrogen atoms C2a, C2b, C5a, C5b, C6b, and C36 were refined isotropically, since anisotropic refinement led to negative anisotropic displacement

parameters. These problems did not allow a full structure refinement. Hence, bond distances and angles are not discussed in any detail.

4: Full refinement was possible without running into problems.

5: Only for two of the four disordered tetrafluoroborate molecules a reasonable model was found to describe the disorder. This gives rise to additional electron density that could not be assigned.

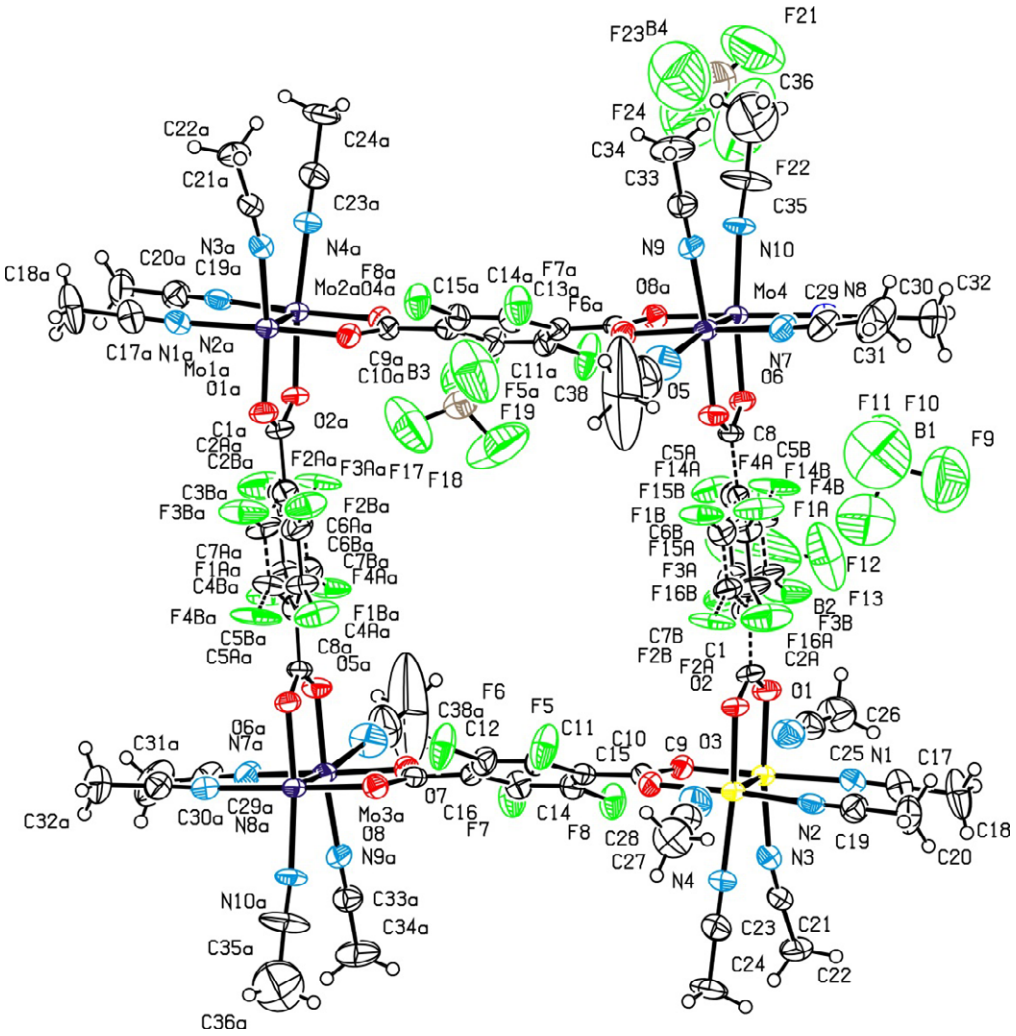

Figure F2 – Ortep drawing of compound **3** with 50% ellipsoids. [6]

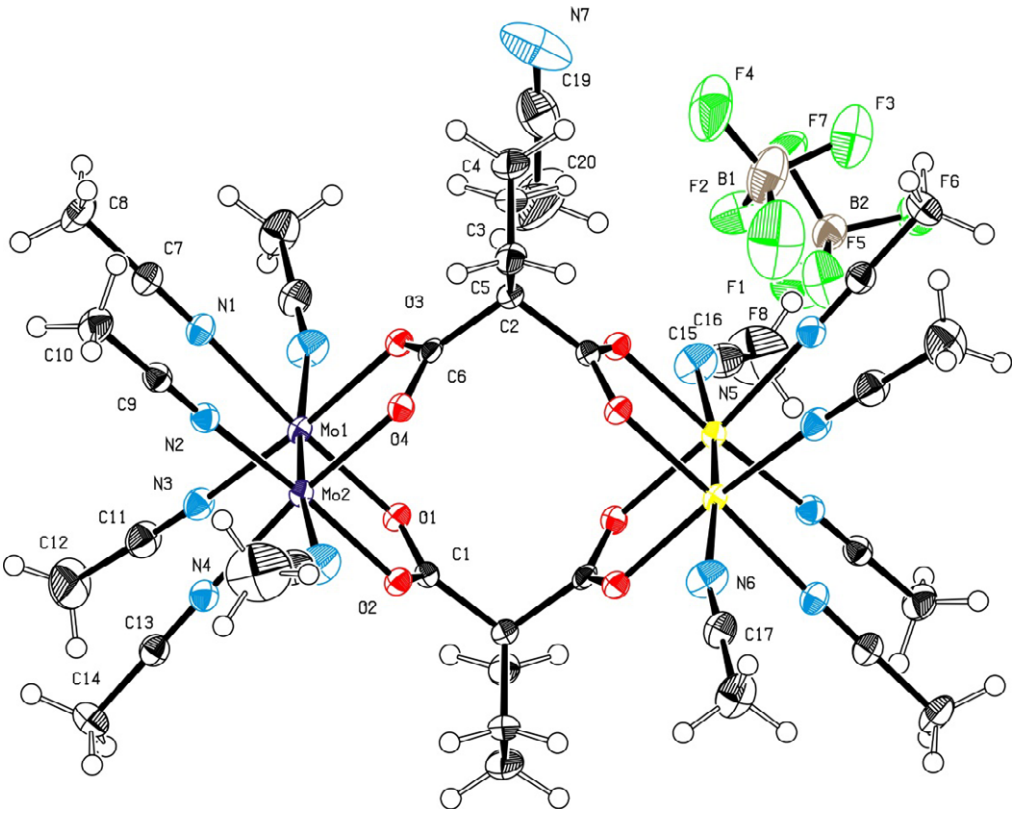

Figure F3 – Ortep drawing of compound **4** with 50% ellipsoids. [6]

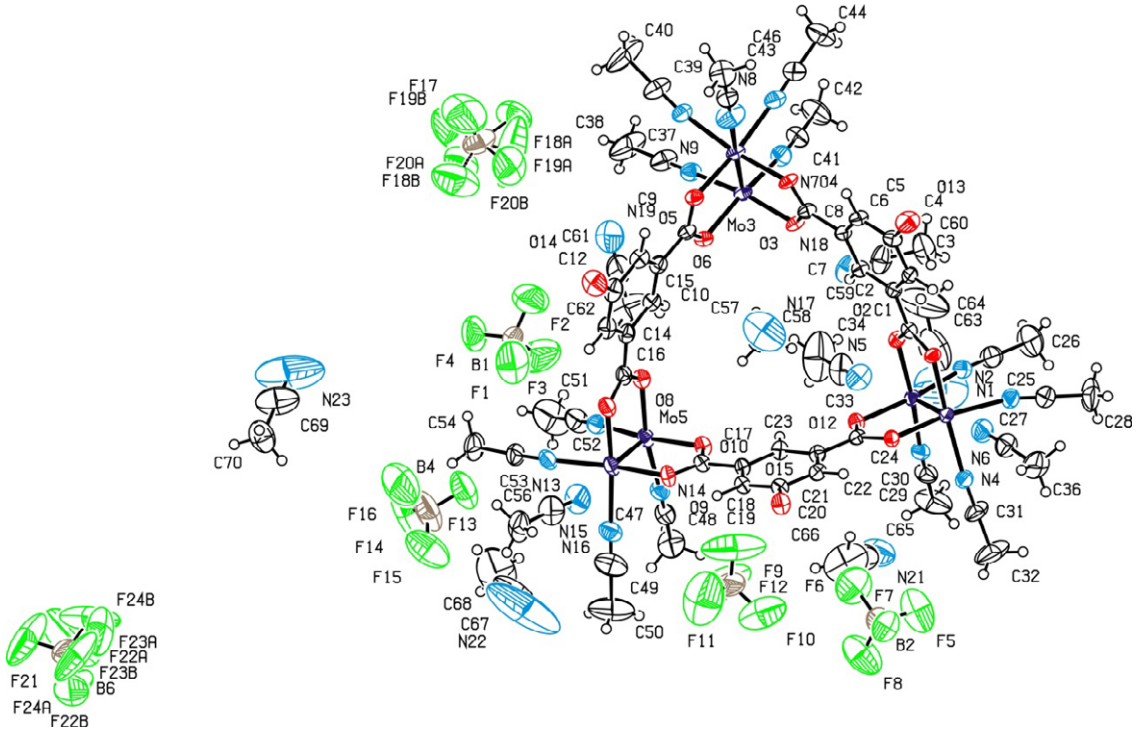

Figure F4 – Ortep drawing of compound **5** with 50% ellipsoids. [6]

Table S1. Crystallographic details of compounds **3**, **4** and **5**.

Compound Name	**3**	**4**	**5**
Sum formula	$C_{76}H_{66}Mo_8N_{22}O_{16}F_{16}$, $8(BF_4)$	$C_{36}H_{48}Mo_4N_{14}O_8$, $4(BF_4)$, $2(C_2H_3N)$	$C_{56}H_{57}Mo_6N_{16}O_{15}$, $6(BF_4)$, $7(C_2H_3N)$
M_r (g/mol)	1654.75	1589.97	2578.05
Crystal description	Red fragment	Red fragment	Red fragment
Crystal dimensions (mm^3)	0.22 x 0.22 x 0.33	0.18 x 0.51 x 0.51	0.10 x 0.13 x 0.25
T (K)	173(1)	123(1)	173(1)
crystal system, space group	Triclinic, $P\bar{1}$ (I.T.-No.: 2)	Triclinic, $P\bar{1}$ (I.T.-No.: 2)	Monoclinic, $P2_1/c$ (I.T.-No.: 14)
a (Å)	14.2639(6)	10.6698(4)	14.7364(6)
b (Å)	16.9759(8)	10.7944(5)	32.6112(13)
c (Å)	17.5316(7)	15.1873(6)	22.5349(9)
α(°)	96.067(2)	89.095(2)	90
β (°)	98.424(2)	86.007(2)	104.233(2)
γ(°)	99.904(2)	64.711(2)	90
V ($Å^3$)	4099.3(3)	1577.53(1)	10497.2(7)
Z	1	1	4
D_{calc} (g/cm^3)	1.341	1.674	1.631
F_{000}	1612	788	5108
μ (mm^{-1})	0.693	0.880	0.803
Index ranges($\pm$h, $\pm$k, $\pm$l)	15/-15, 17/-17, 18/-18	13/-13, 13/-13, 18/-18	17/-17, 39/-39, 27/-27
Θ-ranges (°)	1.18-22.02	1.34-26.00	1.12-25.43
Collected reflections	83623	27873	171685
Unique reflections [all data]	9338	6159	19264
R_{int}/R_σ	0.0294/0.0155	0.0300/0.0223	0.0416/0.0248
Unique reflections [I_0>2 $\sigma(I_0)$]	8299	5979	16530
Data/Restraints/Parameter	9338/81/878	6159/0/395	19264/0/1377
GoF (on F^2)	1.111	1.058	1.178
R_1/wR_2 [I_0>2 $\sigma(I_0)$]	0.0571/0.1721	0.0231/0.0622	0.0658/0.1442
R_1/wR_2 [all data]	0.0611/0.1679	0.0238/0.0628	0.0787/0.1523
Max./Min. residual electron density	1.46/-0.69	0.90/-0.68	1.74/-1.02
Remarks	Refinements aborted		Refinements aborted