Preliminary communication / Communication

2D sheet frameworks constructed from a diruthenium paddlewheel complex and hexamolybdenum halide clusters

Tomonori Sugiura, Koji Ota, Masahiro Ebihara *, Takashi Kawamura

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

Abstract

The reaction of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ with $(^nBu_4N)_2[(Mo_6X^i_8)X^a_6]$ (X^i, X^a = Cl, Cl; Cl, Br; Br, Cl) in CH_2Cl_2 afforded 2D sheet structure of $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6X^i_8)X^a_6\}]_n \cdot 2n$ CH_2Cl_2 (X^i, X^a = Cl, Cl (**1**·2 CH_2Cl_2); Cl, Br (**2**·2 CH_2Cl_2); Br, Cl (**3**·2 CH_2Cl_2)). **1**·2 CH_2Cl_2 and **2**·2 CH_2Cl_2 are crystallized in isostructural triclinic unit cells and **3**·2 CH_2Cl_2 in a monoclinic unit cell. All structures have 2D sheet of square lattices with molybdenum clusters as corners and ruthenium complexes as edges. In **1**·2 CH_2Cl_2 and **2**·2 CH_2Cl_2, all the Mo_6 and Ru_2 units in a sheet lie in a plane. Diruthenium units in **3**·2 CH_2Cl_2 are repeatedly sited above and below the plane of Mo_6 units along the *b* axis. Then the sheet structure of **1**·2 CH_2Cl_2 and **2**·2 CH_2Cl_2 is flat, while that of **3**·2 CH_2Cl_2 is waved. ***To cite this article: T. Sugiura et al., C. R.Chimie 8 (2005)***.
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Résumé

La réaction de $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ avec $(^nBu_4N)_2[(Mo_6X_8)X'_6]$ (X, X'= Cl, Cl; Cl, Br; Br, Cl) dans CH_2Cl_2 a conduit à la structure en feuillet 2D de $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6X_8)X'_6\}]_n \cdot 2n$ CH_2Cl_2 (X, X'= Cl, Cl (**1**·2 CH_2Cl_2); Cl, Br (**2**·2 CH_2Cl_2); Br, Cl (**3**·2 CH_2Cl_2)). **1**·2 CH_2Cl_2 et **2**·2 CH_2Cl_2 cristallisent dans des mailles tricliniques isostructurales, tandis que **3**·2 CH_2Cl_2 cristallize dans une maille monoclinique. Toutes les structures présentent des feuillets 2D de réseaux carrés formés par les clusters de molybdène situés aux coins du réseau et les complexes de ruthenium formant les côtés. Dans **1**·2 CH_2Cl_2 et **2**·2 CH_2Cl_2, tous les motifs Mo_6 et Ru_2 d'un feuillet sont situés dans un plan. Dans **3**·2 CH_2Cl_2, les motifs diruthenium sont situés alternativement au-dessus et en dessous du plan formé par les motifs Mo_6 selon l'axe *b*. Il en résulte que, dans les structures de **1**·2 CH_2Cl_2 et **2**·2 CH_2Cl_2, les feuillets sont plans, tandis qu'ils sont ondulés dans **3**·2 CH_2Cl_2. ***Pour citer cet article : T. Sugiura et al., C. R. Chimie 8 (2005)***.
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Keywords: Diruthenium complexes; Molybdenum halide cluster; Metal–metal bonds; X-ray structures; 2-Dimensional structures

Mots clés : Complexes de diruthénium ; Halogénures à clusters de molybdène ; Liaisons métal–métal ; Structures par diffraction X ; Structures bidimensionnelles

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* Corresponding author.

E-mail address: ebihara@apchem.gifu-u.ac.jp (M. Ebihara).

1. Introduction

One-D to 3D polymerized structures of transition metal complexes have received much attention for the last decade. Not only mononuclear complexes but also various types of clusters, di-, tri-, tetra-, and hexa-nuclear ones, were used as building blocks. Preparation of a novel polymeric structure with paddlewheel complexes is one of our recent efforts. Paddlewheel complex is a useful building block, because it has rich redox chemistry with various electronic states depending on its bridging ligands, and strained bonding direction to its axial sites. We have synthesized 1 to 3D structures of halide-bridged rhodium or ruthenium paddlewheel complexes. The reaction of a dirhodium or diruthenium cation with halide anion gave only 1D chain structure [1–3]. The reaction of a mixture of cation and neutral complexes with halide linker afforded a 2D structure of $[\{Rh_2(acam)_4\}_3(\mu_3\text{-}Cl)_2]_n \cdot 4\,n\,H_2O$ [4] and a 3D structure of $[\{Rh_2(acam)_4\}_2(\mu_4\text{-}I)]_n \cdot 6\,n\,H_2O$ [5]. For the former structure, removal of the crystalline water molecules improved its electric conductivity. On the other hand, the latter has 10^5 higher conductivity in the hydrated form than in the partially dehydrated one. Other than halide bridges, only a few 2D and 3D polymer structures of paddlewheel dinuclear complexes with organic or anionic mononuclear complex linkers have been reported [6–9].

Hexametal cluster is also a good building block to make multi-dimensional frameworks, because they have a variety of cluster charges and electronic states with M_6Z_8 core (M = Mo, W, Re; Z = halide, chalocogenide). Some network structures with $Re_6Z_8^{n+}$ (Z = S, Se, Te) [10–12] or W_6S_8 [13] have been reported in the recent years. A novel framework constructed with paddlewheel complexes and hexametal clusters may lead to new physical properties and/or porosity. In this paper, we report synthesis and two types of crystal structures of $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6X^i_8)X^a_6\}]$ (X^i, X^a= Cl, Cl; Cl, Br; Br, Cl).

2. Experimental

2.1. Synthesis

2.1.1. General methods

$[Ru_2(O_2CCMe_3)_4Cl(H_2O)]$ was prepared according to a literature procedure [14] and $[Ru_2(O_2CCMe_3)_4$-

$(H_2O)_2]BF_4$ was synthesized from it by a modification of the method of Barral and coworkers for $[Ru_2(O_2CC_6H_4\text{-}p\text{-}CMe_3)_4(THF)_2]PF_6$ [15]. $(^nBu_4N)_2$-$[(Mo_6X_8)X'_6]$ (X = Cl, Br; X' = Cl, Br; I) was obtained by the reaction of Mo_6X_{12} with Bu^n_4NX' in HX'. Dichloromethane, n-hexane and acetonitrile were distilled from CaH_2 before use.

2.1.2. $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6Cl_8)Cl_6\}]$ (1)

A CH_2Cl_2 solution of $(^nBu_4N)_2[(Mo_6Cl_8)Cl_6]$ (0.026 g, 0.017 mmol) was added to a CH_2Cl_2 solution of $[Ru_2(O_2CCMe_3)_4(H_2O)]PF_6$ (0.024 g, 0.033 mmol). Reddish-brown powder was collected, washed with CH_2Cl_2 and dried in vacuo. Yield 0.026 g (69%). Anal. Calc. for $C_{40}H_{72}Cl_{14}Mo_6O_{16}Ru_4$; C, 21.02; H, 3.18%. Found: C, 21.02; H, 2.96%.

2.1.3. $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6Cl_8)Br_6\}]$ (2)

A CH_2Cl_2 solution of $(^nBu_4N)_2[(Mo_6Cl_8)Br_6]$ (0.031 g, 0.017 mmol) was added to a CH_2Cl_2 solution of $[Ru_2(O_2CCMe_3)_4(H_2O)]PF_6$ (0.022 g, 0.030 mmol). Reddish-brown powder was collected, washed with CH_2Cl_2 and dried in vacuo. Yield 0.024 g (62%). Anal. Calc. for $C_{40}H_{72}Br_6Cl_8Mo_6O_{16}Ru_4$; C, 18.83; H, 2.84%. Found: C, 18.89; H, 2.67%.

2.1.4. $[\{Ru_2(O_2CCMe_3)_4\}_2\{(Mo_6Br_8)Cl_6\}]$ (3)

A CH_2Cl_2 solution of $(^nBu_4N)_2[(Mo_6Br_8)Cl_6]$ (0.020 g, 0.011 mmol) was added to a CH_2Cl_2 solution of $[Ru_2(O_2CCMe_3)_4(H_2O)]PF_6$ (0.016 g, 0.022 mmol). Reddish-brown powder was collected, washed with CH_2Cl_2 and dried in vacuo. Yield 0.020 g (72%). Anal. Calc. for $C_{40}H_{72}Br_8Cl_6Mo_6O_{16}Ru_4$; C, 18.19; H, 2.75%. Found: C, 17.93; H, 2.74%.

2.2. X-ray structure determination

Crystals of $1 \cdot CH_2Cl_2$, $2 \cdot CH_2Cl_2$ and $3 \cdot CH_2Cl_2$ were obtained as follows: $(^nBu_4N)_2[(Mo_6X^i_8)X^a_6]$ was placed in a 6-mm-diameter glass tube and CH_2Cl_2 was gently added to it. Tightly rolled filter paper was put into the tube just above the solution and then a CH_2Cl_2 solution of $[Ru_2(O_2CCMe_3)_4(H_2O)]PF_6$ was layered. After standing at 15 °C for 3 days, brown crystals were obtained. Diffraction measurements were carried out on a Rigaku AFC7R Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Because crystals of $1 \cdot 2\,CH_2Cl_2$,

Table 1

Crystallographic data of **1**·2 CH$_2$Cl$_2$, **2**·2 CH$_2$Cl$_2$ and **3**·2 CH$_2$Cl$_2$

	1·2 CH$_2$Cl$_2$	**2**·2 CH$_2$Cl$_2$	**3**·2 CH$_2$Cl$_2$
Chemical formula	C$_{42}$H$_{76}$Cl$_{18}$Mo$_6$O$_{16}$Ru$_4$	C$_{42}$H$_{76}$Br$_6$Cl$_{12}$Mo$_6$O$_{16}$Ru$_4$	C$_{42}$H$_{76}$Br$_8$Cl$_{10}$Mo$_6$O$_{16}$Ru$_4$
Formula weight	2455.13	2721.83	2810.73
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	14.551 (3)	14.757 (3)	15.374 (6)
b (Å)	14.765 (3)	14.946 (3)	17.851 (7)
c (Å)	20.559 (5)	20.632 (5)	15.364 (6)
α (°)	108.656 (5)	109.179 (5)	
β (°)	104.429 (5)	104.016 (7)	91.247 (5)
γ (°)	91.671 (10)	91.26 (1)	
V (Å^3)	4024 (1)	4144 (1)	4215 (2)
Z	2	2	2
d (calcd) (g cm^{-3})	2.026	2.181	2.214
μ (mm^{-1})	2.275	4.917	5.721
T (°C)	–40	–100	–40
Reflections collected	33228	34466	34969
Reflections independent	18262	18869	9640
Reflections with $I > 2\,\sigma(I)$	14028	13194	6003
R_{int}	0.032	0.044	0.086
R, R_{w}[a]	0.047, 0.106	0.053, 0.107	0.108, 0.287
Residual (min, max) (e Å^{-3})	–1.29, 1.77	–1.93, 2.14	–4.48, 2.70
Goodness-of-fit	1.31	1.13	1.44

[a] $R = \Sigma \, ||Fo| - |Fc||/\Sigma \, |Fo|$ for data with $I > 2\,\sigma(I)$, $R_{\text{w}} = [\Sigma \, w \, (Fo^2 - Fc^2)^2/\Sigma \, w \, Fo^4]^{1/2}$ for all data.

2·2 CH$_2$Cl$_2$ and **3**·2 CH$_2$Cl$_2$ easily lost CH$_2$Cl$_2$ molecules in a crystal, reflection data were collected at low temperature using a Rigaku XR-TCS-2-050 temperature controller. All structures were solved and refined using the teXsan® crystallographic software package. Scattering factors for neutral atoms were from Cromer and Waber [16] and anomalous dispersion [17] was used. A numerical absorption correction [18] was applied. The structures were solved by direct methods SIR92 [19] and expanded by DIRDIF [20]. Full matrix least-squares refinement was employed. Final least square cycle included non-hydrogen atoms with anisotropic thermal parameters except disordered t-butyl groups were refined as rigid groups. Hydrogen atoms are not included in the refinement. Crystallographic data are summarized in Table 1.

3. Results and discussion

In a preliminary experiment, we have tried to make crystals of [{Ru$_2$(O$_2$CMe)$_4$}$_2${(Mo$_6$Cl$_8$)Cl$_6$}] in aceto-

nitrile. Mixing of solutions of [Ru$_2$(O$_2$CMe)$_4$]PF$_6$ and (^{n}Bu$_4$N)$_2$[(Mo$_6$Cl$_8$)Cl$_6$] did not precipitate crystals. Although evaporation of the solution afforded brown crystals, they include ruthenium complexes with axial acetonitrile ligands and discrete molybdenum clusters. In dichloromethane, reddish-brown powder was precipitated immediately after mixing of solutions of [Ru$_2$(O$_2$CCMe$_3$)$_4$(H$_2$O)$_2$]BF$_4$ and (^{n}Bu$_4$N)$_2$[(Mo$_6$Cl$_8$)Cl$_6$]. To make good crystals, very slow mixing of the solutions is needed.

A sheet structure of **1** in **1**·2 CH$_2$Cl$_2$ is shown in Fig. 1. Structure of **2**·2 CH$_2$Cl$_2$ is isostructural with **1**·2 CH$_2$Cl$_2$. There are four independent ruthenium complexes and two independent molybdenum clusters in a unit cell, all of which are at inversion centers (Mo$_6$: (0, 0, 0) and (0.5, 0, 0.5), Ru$_2$: (0.5, 0, 0), (0, 0.5, 0), (0, 0, 0.5) and (0.5, 0.5, 0.5)). In each of two independent 2D sheets at $c = 0$ and 0.5, the centers of Ru$_2$ complexes and those of Mo$_6$ clusters are located exactly in the plane. The sheet is made by squares of which corners are molybdenum clusters and edges are ruthenium complexes. Each hexamolybdenum cluster linked to
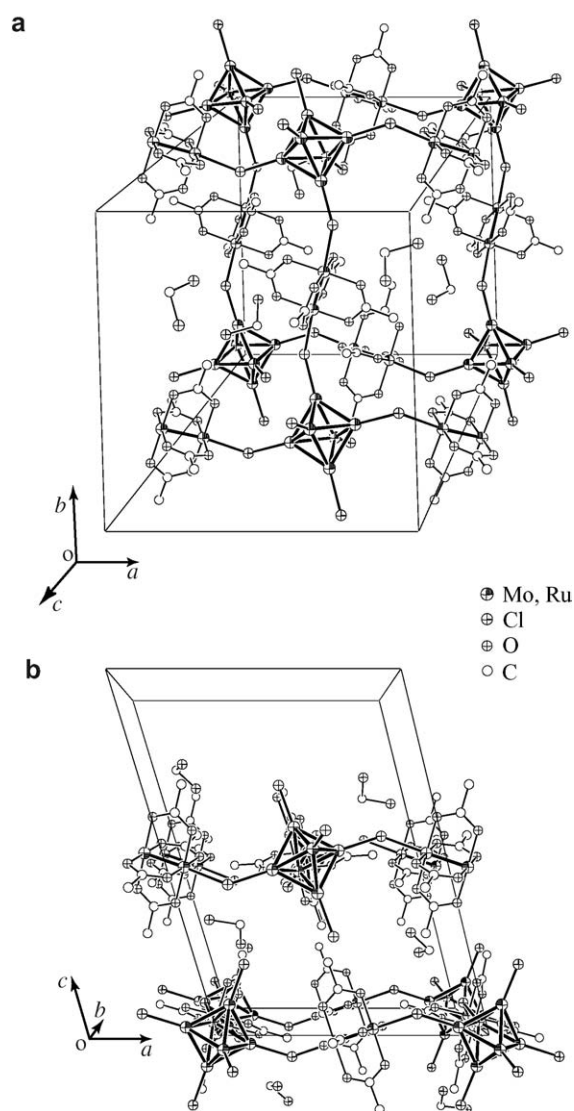
a

b

Fig. 1. Crystal structure of **1**·2 CH$_2$Cl$_2$. (**a**) Top view and (**b**) side view of the 2D sheet structure. Capping chloro ligands of the hexamolybdenum cluster and methyl carbon atoms are omitted for clarity.

⊕ Mo, Ru
⊕ Cl
⊕ O
○ C

Table 2
Selected bond distances (Å) and angles (°) of **1**·2 CH$_2$Cl$_2$[a]

Ru1–Ru1[I]	2.2734 (9)	Mo2–Mo3[V]	2.6077 (6)
Ru2–Ru2[II]	2.2715 (8)	Mo4–Mo5	2.6026 (6)
Ru3–Ru3[III]	2.2709 (9)	Mo4–Mo5[VI]	2.6116 (7)
Ru4–Ru4[IV]	2.2740 (9)	Mo4–Mo6	2.6085 (6)
Ru1–Cl5	2.616 (1)	Mo4–Mo6[VI]	2.6004 (7)
Ru2–Cl6	2.616 (1)	Mo5–Mo6	2.6143 (6)
Ru3–Cl12	2.619 (1)	Mo5–Mo6[VI]	2.6087 (6)
Ru4–Cl13	2.637 (1)	Mo1–Cl5	2.471 (1)
Mo1–Mo2	2.6135 (7)	Mo2–Cl6	2.482 (1)
Mo1–Mo2[V]	2.6007 (6)	Mo3–Cl7	2.396 (2)
Mo1–Mo3	2.6071 (6)	Mo4–Cl12	2.460 (1)
Mo1–Mo3[V]	2.6044 (7)	Mo5–Cl13	2.505 (1)
Mo2–Mo3	2.6095 (6)	Mo6–Cl14	2.394 (2)
Ru1[I]–Ru1–Cl5	176.25 (4)	Ru1–Cl5–Mo1	127.71 (5)
Ru2[II]–Ru2–Cl6	176.82 (5)	Ru2–Cl6–Mo2	131.34 (6)
Ru3[III]–Ru3–Cl12	173.32 (4)	Ru3–Cl12–Mo4	127.08 (6)
Ru4[IV]–Ru4–Cl13	174.52 (5)	Ru4–Cl13–Mo5	130.44 (6)

[a] I: 0.5 – x, –y, –z, II: –x, 0.5 – y, –z, III: –x, –y, 0.5 – z, IV: 0.5 – x, 0.5 – y, 0.5 – z, V: –x, –y, –z, VI: 0.5 – x, –y, 0.5 – z.

Table 3
Selected bond distances (Å) and angles (°) of **2**·2 CH$_2$Cl$_2$[a]

Ru1–Ru1[I]	2.274 (1)	Mo2–Mo3[V]	2.6117 (8)
Ru2–Ru2[II]	2.271 (1)	Mo4–Mo5	2.6021 (8)
Ru3–Ru3[III]	2.273 (1)	Mo4–Mo5[VI]	2.6105 (8)
Ru4–Ru4[IV]	2.278 (1)	Mo4–Mo6	2.6088 (7)
Ru1–Br1	2.7207 (9)	Mo4–Mo6[VI]	2.6012 (9)
Ru2–Br2	2.7309 (9)	Mo5–Mo6	2.6155 (8)
Ru3–Br4	2.7394 (9)	Mo5–Mo6[VI]	2.6108 (8)
Ru4–Br5	2.7562 (9)	Mo1–Br1	2.602 (1)
Mo1–Mo2	2.6113 (8)	Mo2–Br2	2.6119 (9)
Mo1–Mo2[V]	2.6002 (8)	Mo3–Br3	2.5505 (9)
Mo1–Mo3	2.6092 (8)	Mo4–Br4	2.594 (1)
Mo1–Mo3[V]	2.6050 (9)	Mo5–Br5	2.6422 (9)
Mo2–Mo3	2.6097 (8)	Mo6–Br6	2.5455 (9)
Ru1[I]–Ru1–Br1	174.56 (4)	Ru1–Br1–Mo1	123.60 (3)
Ru2[II]–Ru2–Br2	177.61 (4)	Ru2–Br2–Mo2	126.24 (3)
Ru3[III]–Ru3–Br	172.45 (4)	Ru3–Br–Mo4	122.73 (3)
Ru4[IV]–Ru4–Br5	176.24 (4)	Ru4–Br5–Mo5	125.39 (3)

[a] I: 0.5 – x, –y, –z, II: –x, 0.5 – y, –z, III: –x, –y, 0.5 – z, IV: 0.5 – x, 0.5 – y, 0.5 – z, V: –x, –y, –z, VI: 0.5 – x, –y, 0.5 – z.

four ruthenium complexes by axial halide ligands. A couple of axial ligands remain as terminal ones. The solvating dichloromethane molecules are sited between the sheets, which are easily lost even at room temperature. The selected distances and angles are summarized in Tables 2 and 3. The distances and angles in two independent sheets are almost identical. The average

Ru–Ru distances (**1**·2 CH$_2$Cl$_2$: 2.272 (1) Å, **2**·2 CH$_2$Cl$_2$: 2.274 (3) Å) are in the range of those observed in other Ru$_2$(O$_2$CCMe$_3$)$_4$$^+$ complexes [21–23]. The Mo–Mo distances in **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$ (2.607 (5) and 2.608 (5) Å, respectively) are similar to other hexamolybdenum clusters with capping chloride [24,25]. The ruthenium–halogen distances (2.622 (10) Å for

1·2 CH$_2$Cl$_2$ and 2.737 (15) Å for **2**·2 CH$_2$Cl$_2$) are similar to those observed in diruthenium halide-bridged chain structures [26,27]. The bond distances between molybdenum and bridging axial halides for **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$ are 2.480 (19) and 2.613 (21) Å, respectively, which are longer than those between molybdenum and terminal one, 2.395 (1) and 2.548 (4) Å, respectively. These elongated molybdenum–halide distances are also observed in MoCl$_2$ (= [(Mo$_6$Cl$_8$)Cl$_{4/2}$Cl$_2$]) in which each Mo$_6$Cl$_8$ unit connects to the four neighboring ones using four outer-chloride as bridges. The Ru–Br–Mo angles for **2** (122.73 (3)–126.24 (3)°) are slightly smaller than the Ru–Cl–Mo angles for **1**·2 CH$_2$Cl$_2$ (127.08 (6)–131.34 (6)°), which is due to the long Ru–X distance in **2**·2 CH$_2$Cl$_2$.

Crystals of **3**·2 CH$_2$Cl$_2$ includes another type of sheet structure that is shown in Fig. 2. The structure refinement is relatively poor due to the low quality of the crystals of **3**·2 CH$_2$Cl$_2$. However, it is sufficient to discuss the main feature of the structure. In this structure, the sheet extended on a dihedral plane between *a* and *c* axes is also built by squares which consist of four molybdenum clusters as corners and four ruthenium complexes as edges. In the structure of **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$, the sheet is flat, while in the structure of **3**·2 CH$_2$Cl$_2$, Ru$_2$ complexes are repeatedly sited above and below a plane made up of Mo$_6$ clusters, along *b*-axis. It means that the sheet is waved. Selected bond distances and angles are listed in Table 4. Mo–Mo distances are slightly elongated from those in **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$ and are similar to other bromide-capped clusters [28]. The Ru–Ru distance is very similar to those observed in **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$. A largely different structural parameter from **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$ is only the Mo–Cl–(Ru$_2$) Cl–Mo torsion angle which is 180° in **1**·2 CH$_2$Cl$_2$ and **2**·2 CH$_2$Cl$_2$ and 53.6 (3)° in **3**·2 CH$_2$Cl$_2$.
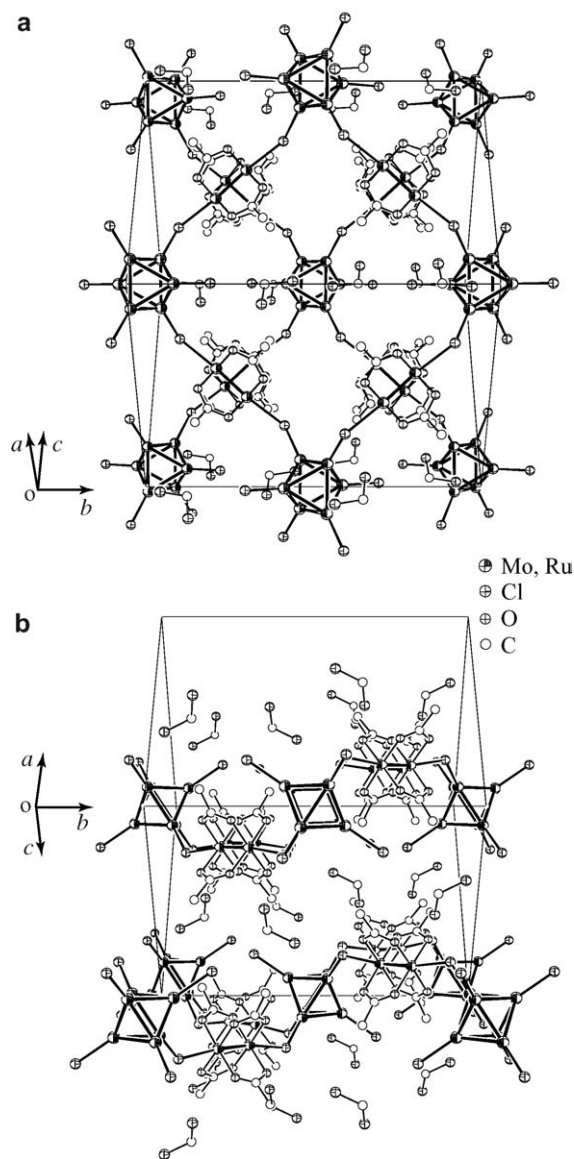

Fig. 2. Crystal structure of **3**·2 CH$_2$Cl$_2$. (**a**) Top view and (**b**) side view of the 2D sheet structure. Capping bromo ligand of the hexa-molybdenum cluster and methyl carbon atoms are omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) of **3**·CH$_2$Cl$_2$[a]

Ru1–Ru2	2.273 (2)	Mo1–Mo3′	2.631 (2)
Ru1–Cl1	2.598 (5)	Mo2–Mo3	2.629 (2)
Ru2–Cl2"	2.580 (5)	Mo2–Mo3′	2.626 (2)
Mo1–Mo2	2.623 (2)	Mo1–Cl1	2.450 (4)
Mo1–Mo2′	2.618 (2)	Mo2–Cl2	2.459 (5)
Mo1–Mo3	2.623 (2)	Mo3–Cl3	2.425 (4)
Ru2–Ru1–Cl1	170.7 (1)	Ru1–Cl1–Mo1	128.7 (2)
Ru1–Ru2–Cl2"	170.7 (1)	Ru2′–Cl2–Mo2	128.6 (2)

[a] ′: 1 – *x*, –*y*, 1–*z*, ": –*x*, 0.5 – *y*, –*z*.

Although the reaction of [Ru$_2$(O$_2$CCMe$_3$)$_4$-(H$_2$O)$_2$]BF$_4$ with other Mo$_6$ clusters (X^i, X^a = Cl, I; Br, Br; Br, I) gave only very small crystals, cell constants of the crystals suggest that these complexes may have a similar flat sheet structure to **1**·2 CH$_2$Cl$_2$ and

$2 \cdot 2$ CH$_2$Cl$_2$[1]. In the structure of Cs$_2$[{Fe(H$_2$O)$_2$}-{Re$_6$S$_8$(CN)$_6$}] [29], sheet structure of [{Fe(H$_2$O)$_2$}-{Re$_6$S$_8$(CN)$_6$}]$^{2-}$ in which square is made up of alternating Fe ion and Re clusters is waved as the Fe ions are up and down from a plane of the Re$_6$ clusters. An amplitude and a period of the wave in this complex are 1.65 and 18.55 Å, respectively, while those of **3**· CH$_2$Cl$_2$ are 2.27 and 17.85 Å, respectively. The difference of the amplitude is due to the bent Ru–Br–Mo angle compared with the Fe–N–C one.

In summary, two types of structures of [{Ru$_2$(O$_2$CCMe$_3$)$_4$}$_2${(Mo$_6$X$^i_8$)X$^a_6$}], flat and waved sheets are obtained by mixing of the solutions of [Ru$_2$(O$_2$CCMe$_3$)$_4$(H$_2$O)$_2$]$^+$ and [(Mo$_6$X$^i_8$)X$^a_6$]$^{2-}$. Unfortunately all crystals degrade by a loss of crystalline dichloromethane molecules. We are investigating to make stable crystals with other paddlewheel complexes and/or molybdenum clusters.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 247469–247471 for **1**·2 CH$_2$Cl$_2$, **2**·2 CH$_2$Cl$_2$ and **3**·2 CH$_2$Cl$_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44 1223 33 6033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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[1] Cell constant of the crystals obtained by the reaction of [Ru$_2$(O$_2$CCMe$_3$)$_4$(H$_2$O)$_2$]BF$_4$ with (^{n}Bu$_4$N)$_2$[(Mo$_6$X$^i_8$)X$^a_6$] are as follows: X^i, X^a = Cl, I; a = 15.217 (10), b = 15.288 (10), c = 21.14 (1) Å, α = 108.961 (7), β = 104.147 (8), γ = 90.594 (5)°, V = 4487 (4) Å^3. X^i, X^a = Br, Br; a = 14.844 (7), b = 14.969 (7), c = 20.65 (1) Å, α = 107.85 (1), β = 104.42 (2), γ = 91.25 (3)°, V = 4205 (3) Å^3. X^i, X^a = Br, I; a = 15.25 (1), b = 15.34 (1), c = 21.02 (2) Å, α = 109.45 (3), β = 103.72 (3), γ = 91.14 (6)°, V = 4477 (6) Å^3.