

$\text{Mo}_4(\eta^3\text{-allyl})_4\text{Cl}_2(\text{OH})_2(\text{CO})_8$: the first cubane-type Mo^{2+} organometallic complex with $\mu_3\text{-OH}$ and $\mu_3\text{-Cl}$ bridges

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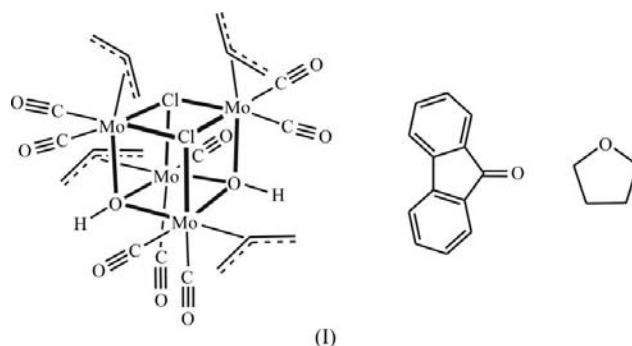
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The reaction between fluorenyllithium and $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{NCMe})_2(\text{CO})_2$ led to the isolation of di- μ_3 -chlorido-di- μ_3 -hydroxido-tetrakis[$(\eta^3\text{-allyl})\text{dicarbonylmolybdenum(II)}$]-9-fluorenone-tetrahydrofuran (1/1/1), $[\text{Mo}_4(\text{C}_3\text{H}_5)_4\text{Cl}_2(\text{OH})_2(\text{CO})_8]\cdot\text{C}_4\text{H}_8\text{O}\cdot\text{C}_{13}\text{H}_8\text{O}$. The tetrametallic Mo_4 unit constitutes the first example of a complex containing simultaneously two $\mu_3\text{-OH}$ groups and two $\mu_3\text{-Cl}$ anions capping the metallic trigonal prism. The four crystallographically independent Mo^{2+} centres exhibit distorted octahedral geometry with the $\eta^3\text{-allyl}$ groups being *trans*-coordinated to a $\mu_3\text{-OH}$ group and the carbonyl groups occupying the equatorial plane. Space-filling tetrahydrofuran and 9-fluorenone molecules are engaged in strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions with $\text{Mo}_4(\eta^3\text{-allyl})_4\text{Cl}_2(\text{OH})_2(\text{CO})_8$ complexes.

Comment

The family of $\eta^3\text{-allyl}$ dicarbonyl complexes of Mo^{2+} plays an important role in coordination chemistry and catalytic organic transformations. The reactivity of these complexes depends on the nature of the ligands which compose the first coordination sphere (Saraiva *et al.*, 2008, and references therein). Since the discovery of the complex $\text{Mo}(\eta^3\text{-allyl})\text{Cl}(\text{CH}_3\text{CN})_2(\text{CO})_2$ in the late 1960s (Hayter, 1968), a series of derivatives containing the $[\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2]^+$ moiety have been prepared by substitution of the labile nitrile ligands and/or Cl. Our research group has been particularly interested in the preparation of $\text{Cp}'\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2$ (Cp' is cyclopentadienyl, indenyl or fluorenyl) using $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{NCMe})_2(\text{CO})_2$ as a starting material (Ascenso *et al.*, 1995). As part of our ongoing research, in this paper we report a compound containing the first cubane-type complex of a transition metal (T) exhibiting two pairs of distinct μ_3 -capping bridges, *viz.* di- μ_3 -chlorido-di- μ_3 -hydroxido-tetrakis[$(\eta^3\text{-allyl})\text{dicarbonylmolybdenum(II)}$]-9-fluorenone-tetrahydrofuran (1/1/1), $\text{Mo}_4(\eta^3\text{-allyl})_4\text{Cl}_2(\text{OH})_2(\text{CO})_8\cdot\text{C}_{13}\text{H}_8\text{O}\cdot\text{THF}$, (I). A search in the literature and in the Cambridge Structural Database (Allen,

2002) consolidates the uniqueness of this compound. Despite cubane-type structures with four capping oxygen or halogen atoms (X) being common, *i.e.* T_4O_4 or T_4X_4 , only a handful of compounds contain two types of capping ligands; moreover, none of the known structures is an organometallic complex, they are all either Mn or Cu complexes with carboxylates or β -diketonates (Aronica *et al.*, 2007; Hendrickson *et al.*, 1992; Wang *et al.*, 1996; Wemple *et al.*, 1993, 1995).



The neutral $\text{Mo}_4(\eta^3\text{-allyl})_4\text{Cl}_2(\text{OH})_2(\text{CO})_8$ complex depicted in Fig. 1 contains a central cationic $[\text{Mo}_4(\mu_3\text{-Cl})_2(\mu_3\text{-OH})_2]^{4+}$ core best described as a trigonal prism of Mo atoms having two of the faces capped by $\mu_3\text{-OH}$ groups and the other two by $\mu_3\text{-Cl}$ anions. This arrangement is reminiscent of a distorted $\text{Mo}_4\text{O}_2\text{Cl}_2$ cubane. The four crystallographically distinct Mo^{2+} centres are each coordinated to two carbonyl groups [$\text{Mo}-\text{C} = 1.919(5)\text{--}1.953(5)\text{ \AA}$] and one $\eta^3\text{-allyl}$ moiety [$\text{Mo}-\text{C} = 2.188(5)\text{--}2.337(5)\text{ \AA}$] (Table 1). For simplification, in Fig. 1, all the $\text{Mo}-\text{C}$ bonds to the allyl groups have been replaced by a dashed bond to the respective centre of gravity (C_g), with the four crystallographically

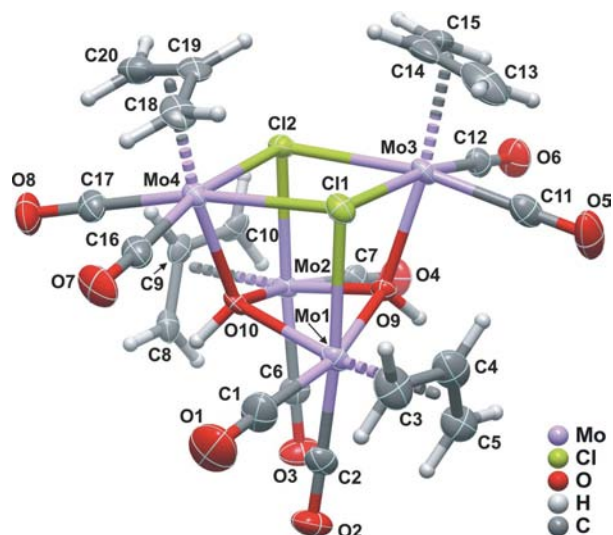


Figure 1
Schematic representation of the tetrametallic $\text{Mo}_4(\eta^3\text{-allyl})_4\text{Cl}_2(\text{OH})_2(\text{CO})_8$ molecular unit, showing the labelling scheme for all non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres. $\text{Mo}-\text{C}$ bonds to the $\eta^3\text{-allyl}$ groups have been replaced by a dashed bond to the corresponding centre of gravity of the coordinated moiety. See Table 1 for the coordination bond lengths.

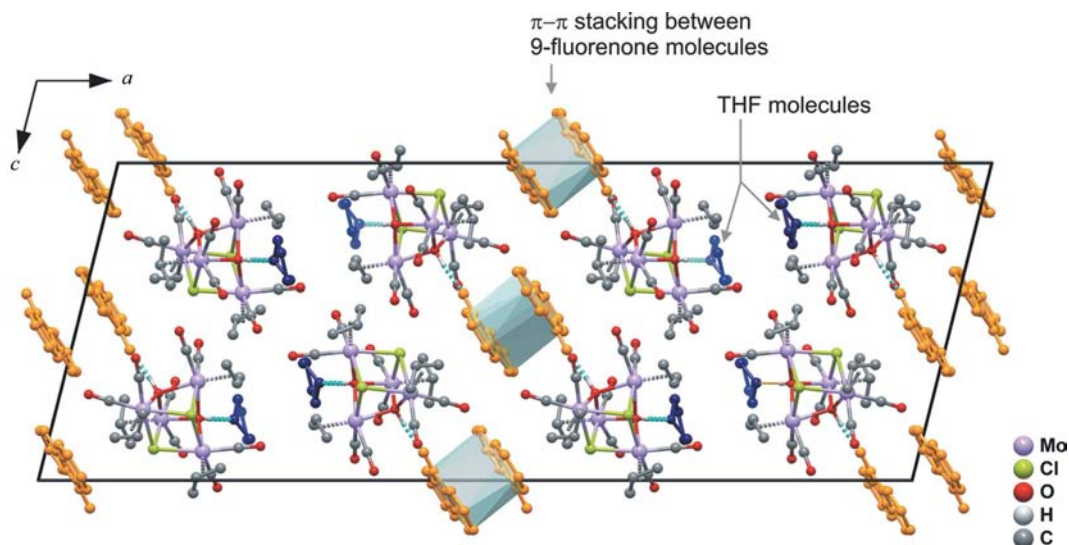


Figure 2

A parallel view along the [010] direction of the unit cell of the crystal packing of the title compound, with hydrogen bonds represented as dashed lines. See Table 2 for details of the hydrogen-bonding geometry. H atoms not involved in hydrogen bonds and all Mo—C bonds to the η^3 -allyl groups have been omitted for clarity. (THF and 9-fluorenone molecules are shown in dark blue and orange, respectively, in the electronic version of the paper.)

distinct Mo—Cg distances ranging from 2.03 to 2.04 Å. The presence of two distinct capping ligands leads to two types of coordination environment: while Mo1 and Mo2 contain two OH[−] and one Cl[−] anion completing their coordination spheres, Mo3 and Mo4 have instead one OH[−] and two Cl[−] anions. The overall coordination spheres can thus be envisaged as highly distorted octahedra with internal (Cg,Cl,O)—Mo—(Cg,Cl,O) *cis* and *trans* angles of 72.41 (10)—104.56 (13)^o and 162.30 (17)—172.78 (13)^o, respectively. All η^3 -allyl groups are *trans*-coordinated to a μ_3 -OH group and all the carbonyl groups occupy the equatorial plane of the Mo²⁺ octahedra. The presence of two pairs of capping ligands leads to a symmetrization of the cubane core, with the Mo—Cl and Mo—O distances falling into relatively narrow ranges, *viz.* 2.6068 (12)—2.6538 (11) and 2.181 (3)—2.255 (3) Å, respectively (Table 1). The internal Mo···Mo distances were between 3.459 (1) and 4.077 (1) Å; while the former concerns the Mo₄ tetrahedron edge formed by the two adjacent μ_3 -OH groups, the latter is that of the edge having the two μ_3 -Cl anions, thus reflecting the steric impediment associated with these large anions (which promotes a larger separation between metallic centres). We note the presence of a number of weak intramolecular C—H···O interactions involving the allyl groups and the neighbouring carbonyl moieties (Fig. 1), with *D*···*A* distances ranging from *ca* 3.09 to 3.28 Å and *D*—H···*A* angles from *ca* 126 to 139^o.

The crystal structure contains two extra organic molecules, one tetrahydrofuran (THF) solvent molecule and 9-fluorenone, a by-product of the reaction. These two molecular species seem to stabilize the crystal structure of (I) by acting as space-filling entities. Individual Mo₄(η^3 -allyl)₄Cl₂(OH)₂(CO)₈ complexes close-pack in the *bc* plane of the unit cell forming layers (Fig. 2) and available space between layers is alternately occupied by either THF or 9-fluorenone molecules. The latter are further engaged pairwise in strong π — π interactions about centres of inversion, as depicted in Fig. 2, with the distance

between centres of gravity being *ca* 3.61 Å. These two organic species are strongly hydrogen bonded to the Mo complex, acting as acceptors in O—H···O interactions with the two μ_3 -OH groups (see Table 2 for hydrogen-bonding geometry).

Experimental

Fluorenyllithium (Üffing *et al.*, 1998) and Mo(η^3 -C₃H₅)Cl(NCMe)₂(CO)₂ (Ascenso *et al.*, 1995) were synthesized according to reported methods. Solid fluorenyllithium (0.13 g, 0.74 mmol) and Mo(η^3 -C₃H₅)Cl(NCMe)₂(CO)₂ (0.23 g, 0.74 mmol) were cooled to 193 K in a Schlenk tube. Precooled dry THF (40 ml) was added and the temperature raised slowly to room temperature. After 24 h, the mixture was filtered and the solution dried. Recrystallization of the crude product from a mixture of hexane and diethyl ether (2:1) at 277 K yielded orange crystals of the title compound after two months.

Crystal data

[Mo ₄ (C ₃ H ₅) ₄ Cl ₂ (OH) ₂ (CO) ₈] _n ·C ₄ H ₈ O·C ₁₃ H ₈ O	$\beta = 104.133 (4)^\circ$
$M_r = 1129.33$	$V = 8115.6 (9) \text{ \AA}^3$
Monoclinic, C2/c	$Z = 8$
$a = 46.383 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.3975 (6) \text{ \AA}$	$\mu = 1.40 \text{ mm}^{-1}$
$c = 17.3531 (12) \text{ \AA}$	$T = 150 (2) \text{ K}$
	$0.06 \times 0.03 \times 0.01 \text{ mm}$

Data collection

Bruker X8 KappaCCD APEXII diffractometer	45728 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1998)	9024 independent reflections
$T_{\min} = 0.918$, $T_{\max} = 0.977$	6026 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.081$	
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$
9024 reflections	$\Delta\rho_{\text{min}} = -0.69 \text{ e \AA}^{-3}$
502 parameters	
2 restraints	

Table 1
Selected bond lengths (Å).

Mo1—C1	1.947 (5)	Mo3—C11	1.926 (6)
Mo1—C2	1.930 (5)	Mo3—C12	1.937 (5)
Mo1—C3	2.327 (5)	Mo3—C13	2.319 (5)
Mo1—C4	2.197 (5)	Mo3—C14	2.188 (5)
Mo1—C5	2.337 (5)	Mo3—C15	2.334 (4)
Mo1—O9	2.255 (3)	Mo3—O9	2.181 (3)
Mo1—O10	2.196 (3)	Mo3—Cl2	2.6142 (12)
Mo1—Cl1	2.6302 (11)	Mo3—Cl1	2.6361 (11)
Mo2—C6	1.919 (5)	Mo4—C16	1.937 (5)
Mo2—C7	1.953 (5)	Mo4—C17	1.922 (5)
Mo2—C8	2.327 (4)	Mo4—C18	2.329 (4)
Mo2—C9	2.199 (4)	Mo4—C19	2.200 (4)
Mo2—C10	2.328 (4)	Mo4—C20	2.319 (5)
Mo2—O9	2.187 (3)	Mo4—O10	2.181 (3)
Mo2—O10	2.252 (3)	Mo4—Cl1	2.6068 (12)
Mo2—Cl2	2.6399 (11)	Mo4—Cl2	2.6538 (11)

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O9—H9...O11	0.94 (3)	1.84 (3)	2.770 (4)	168 (4)
O10—H10...O12	0.93 (3)	1.851 (16)	2.761 (4)	164 (4)

H atoms bound to C atoms were placed in idealized positions and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H})$ values fixed at $1.2U_{\text{eq}}(\text{C})$. The C—H distances used ranged from 0.95 (for the aromatic and allyl H atoms) to 0.99 Å (for the methylene H atoms associated with the THF molecule). Those H atoms associated with the two μ_3 -OH groups were markedly visible in difference Fourier maps and were included in subsequent least-squares refinement cycles with the O—H distances restrained to 0.95 (1) Å in order to ensure a chemically reasonable geometry for these bridging groups. These H atoms had $U_{\text{iso}}(\text{H})$ values fixed at $1.5U_{\text{eq}}(\text{O})$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Branden-

burg, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3094). Services for accessing these data are described at the back of the journal.

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