Synthesis and X-ray structure of a complex containing two (η^3-allyl)Mo^{II} units bridged by $Mo^{VI}O_4^{2-}$ and exhibiting an unusual type of aggregation

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Received (in Basel, Switzerland) 3rd July 1998, Accepted 26th October 1998

Treatment of the [Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$(Me$_2$CO)]$^+$ cation with an aqueous MoO_4^{2-} solution enabled the first structural characterisation of an (η^3-allyl)MoO complex, which aggregates to a dimer showing Mo=O···H–C contacts in the solid state.

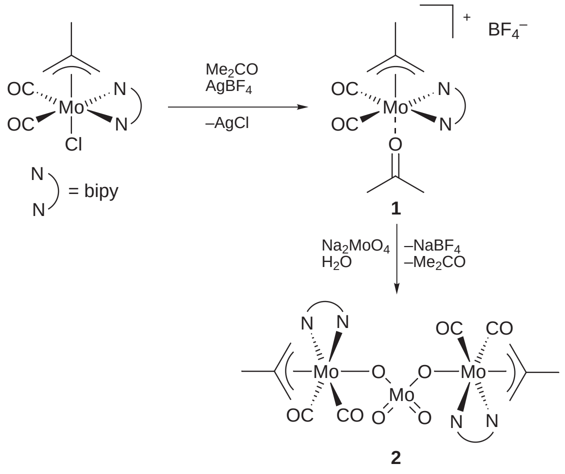
Organotransition-metal chalcogenide complexes are noteworthy in representing a link between solid, more or less ionic, metal chalcogenides and low-valent molecular organometallic systems.[1] Despite the potential importance of organomolybdenum oxo systems containing molybdenum in the highest oxidation states +5 and +6 as catalytic intermediates in industrial processes,[2] there are known as yet few model complexes of this sort.

One example of heterogeneous catalysis where such species might play a significant role entails the oxidation of propene to acrolein using MoO_3/Bi_2O_3 as the catalyst and this has gained considerable technical importance. Nontheless, the reaction mechanism has remained for the most part speculative. The results of their experiments on isotopic enrichment lead Grasselli and Burrington to suggest the intermediate formation of symmetric π-allyl complexes (or the chemisorption of delocalised allyl radicals) to Mo centres of the catalyst's surface.[3] Furthermore recent investigations suggest that in heterogeneous oxidation catalyses where Mo-oxides are employed the oxygen atoms found in the organic oxidation products have their origin in previously *bridging* positions.[4]

So far there are no compounds existent in the literature which could be regarded as functional models for the oxo molybdenum π-allyl surface intermediates under discussion. Only few allyl molybdenum compounds containing ligands with oxygen donor functions of any kind have been synthesised and characterised structurally,[5] and none of those bear the terminal or bridging O^{2-} ligands characteristic to the catalyst.

We have shown that complexes with (η^3-allyl)Mo units in oxygen-rich coordination spheres containing RO^- ligands (R = Me, H) can be obtained if cationic complexes with labile ligands are employed as starting materials.[6] Making use of the same principles we have now achieved for the first time the synthesis and structural characterisation of an allyl–Mo complex containing an O^{2-} link to another Mo centre.

The interface reaction of a [Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$(Me$_2$CO)]BF$_4$ **1** solution in acetone—prepared by treatment of [Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$Cl] with AgBF$_4$ as established for the corresponding η^3-C_3H_5 complex[7]—with a solution of Na_2MoO_4 in water leads to the precipitation of a crystalline maroon solid insoluble in all common organic solvents. However, its elemental analysis suggested the composition [{Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$}$_2$(μ-MoO$_4$)] **2**† which had been aimed at (Scheme 1).



Scheme 1

An X-ray diffraction analysis‡ of a single crystal yielded the structure shown in Fig. 1, which clearly proves the presence of an O–MoO$_2$–O moiety bridging two Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$ units. One of the latter [Mo(3/4)] was disordered through a rotation by 0.5° around the Mo(1)–O(2) axis and in Fig. 1 for clarity only the Mo(4) fragment is shown. The Mo(3/4)–O(2) and Mo(2)–O(1) distances [2.092(3) and 2.107(3) Å] lie within a range characteristic for bonds of the molybdate unit to other Mo centres (2.02–2.15 Å)[8] indicating a real bonding situation rather than a weak coordination of the MoO_4^{2-} unit. The Mo(1)–O(1/2) bridging distances [1.795(3) and 1.797(2) Å] are also typical (1.75–1.85 Å) and the angles found within the central unit of **2** are all very close to the perfect tetrahedral angle. However, if just the solid state structure of the *individual* molecule is considered it does seem surprising that the two organometallic fragments coordinated to the MoO_4^{2-} unit are not oriented symmetrically with respect to the latter: Mo(1/2/4) and O(1/2) are almost in a plane intersecting the C(13)–Mo(2)–C(15) angle while the corresponding C(55)–Mo(4)–C(53) angle of the other subunit escapes intersection by a rotation of this fragment by *ca.* 90° around the Mo(4)–O(2) bond.

An explanation can be found if the structure as a whole is considered: As obvious from Fig. 2 the molecules can pack very efficiently through an internal rotation as described and this

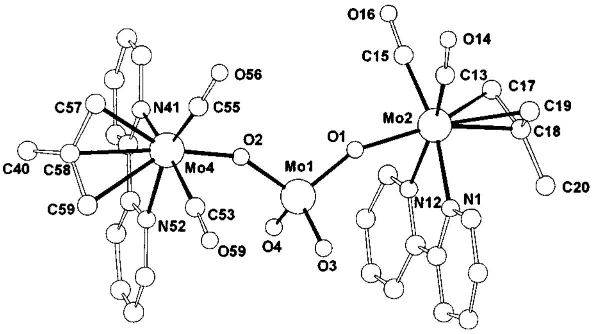


Fig. 1 Structural representation of [{Mo(η^3-C_3H_4Me)(bipy)(CO)$_2$}$_2$(μ-MoO$_4$)] **2**. Selected bond lengths (Å) and angles (°): Mo(1)–O(3) 1.731(3), Mo(1)–O(4) 1.739(3), Mo(1)–O(1) 1.795(3), Mo(1)–O(2) 1.797(3), Mo(2)–O(1) 2.107(3), Mo(3/4)–O(2) 2.092(4); Mo(1)–O(1)–Mo(2) 156.8(2), Mo(1)–O(2)–Mo(3/4) 150.8(2), O(3)–Mo(1)–Mo(4) 107.6(2), OC–Mo(2)–CO 78.7(2), OC–Mo(3/4)–CO 76.2(5); averaged distances and angles: Mo(2)–C_{meso} 2.243(4), Mo(2)–C_{term} 2.323(5), Mo–N 2.254(9), Mo–CO 1.97(1), OC–Mo–N_{trans} 168.9(5), OC–Mo–N_{cis} 104.1(5).

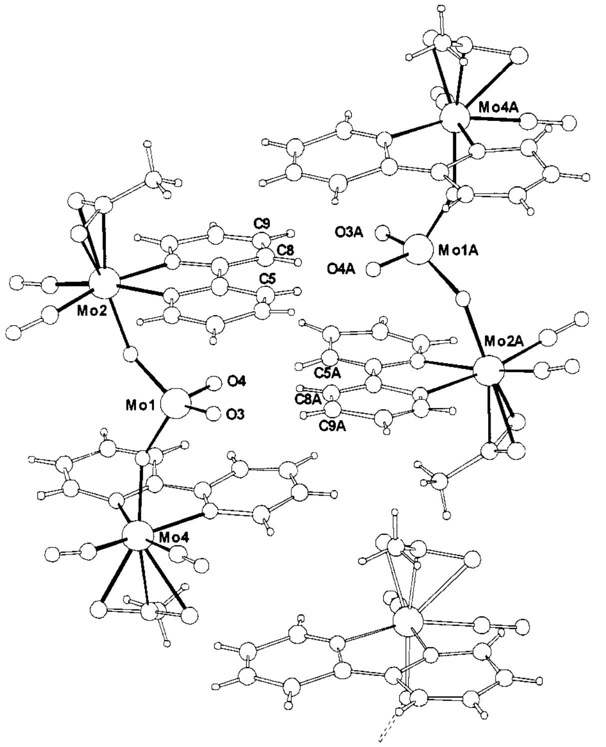


Fig. 2 Structural arrangement of the molecules of **2** in the unit cell. Selected bond lengths (Å): O(3)–C(9A) 3.180, O(3)–C(8A) 3.279, O(4)–C(5A) 3.213, O(4)–C(8A) 3.421.

leads to symmetric dimeric aggregates. These show very short Mo=O$\cdots$C distances suggesting that there are intermolecular contacts between the protons of the bipy ligands and the Mo=O groups (compare Fig. 2 where the calculated H positions are shown; the Mo=O$\cdots$H distances were calculated to lie between 2.39 and 2.77 Å). Of course the short C–H$\cdots$O=Mo distances neither have to be indicative of attractive interactions,[9] nor is the presence of the corresponding contacts necessary to explain the structural features observed, so that attention now focused on the Mo=O bonds. The Mo=O bond lengths in d^0 molybdenum dioxo complexes usually fall in a narrow range and are not strongly effected by the nature of the other ligands at the metal.[10] It has been shown, though, that *classical* H-bridging to a $HNEt_4^+$ cation[8c] can selectively lengthen one of two Mo=O bonds in a MoO_2 unit by *ca.* 0.03 Å. The Mo=O distances observed in **2** [1.731(3) and 1.739(3) Å] are certainly located at the 'tail' of the d(Mo=O) distribution and have to be described as long, which may support the idea of attractive interactions.

Complex **2** is EPR silent and magnetic measurements showed it to be diamagnetic at room temperature, which suggests the presence of a hitherto unknown Mo^{II}–O–Mo^{VI}–O–Mo^{II} unit. Few compounds possessing two oxo bridged Mo centres differing in their oxidation states by *two* are known. An organometallic representative involving a bridging MoO_4^{2-} unit, too, is the complex $[(Cp^{Me}{}_2Mo^{IV})_2(\mu\text{-}Mo^{VI}O_4)_2]$.[8a] In **2** the difference in oxidation states amounts to *four*, which is unusual and had to find an explanation in the redox potentials of the two subunits. Indeed—probably due to the strongly π-accepting ligands—the $[Mo^{II}(\eta^3\text{-}C_3H_4Me)(bipy)(CO)_2(Me_2CO)]^+$ cation showed a reversible oxidation wave at a potential as high as 0.88 V (*vs.* SCE), which cannot be reached by molybdate[11] and this fact allowed the isolation of **2**.

The molybdate complex reported here contains π-allyl–Mo fragments which are bonded *via* 'pure' oxygen bridges to Mo^{VI} centres also providing Mo^{VI}=O groups in close proximity. It therefore already meets some of the requirements to serve as a structural model complex for surface intermediates during molybdenum oxide catalysed propene oxidation. However, other important features like the high oxidation states of all metal centres are still missing so that **2** is not suitable to simulate the properties of these intermediates. Methallyl radicals are released at 193 °C but no oxidation or allyl shift occurs, probably due to the large intramolecular separation of the coordinated allyl ligands from the oxo groups.

C. L. is grateful to the Deutsche Forschungsgemeinschaft for a scholarship and C. B. acknowledges financial support through the Landesgraduiertenförderung Baden-Württemberg. We also wish to thank Professor Dr G. Huttner for his generous support.

Notes and references

† 0.389 g (2 mmol) of $AgBF_4$ in 15 ml acetone were added to a suspension of 0.798 g (2 mmol) of $[Mo(\eta^3\text{-}C_3H_4Me)(bipy)(CO)_2Cl]$ in 30 ml of acetone *via* cannula. After 20 min of stirring the AgCl precipitated was removed by filtering and the filtrate overlayered by a solution of 0.492 g (2 mmol) $Na_2MoO_4\cdot H_2O$ in a mixture of 10 ml of deoxygenated water and 15 ml of acetone. At the interface crystals suitable for X-ray diffraction grew within 24 h. If the solution is stirred **2** precipitates immediately and almost quantitatively. The precipitate is washed with water and thf and dried *in vacuo*. Yield: 0.84 g (0.9 mmol, 95%). Anal. Calc. for $C_{32}H_{30}Mo_3N_4O_8$: C, 43.35; H, 3.41; N, 6.35. Found: C, 43.50; H, 3.56; N 6.14%. Characteristic bands in the IR spectrum (KBr/cm^{-1}): 1934s [ν(CO)], 1851s [ν(CO)], 914w, 876s, 838vs (br), 805s (sh), 734m [all ν(Mo–O) and ν(Mo=O)].

‡ *Crystal structure* data for **2**·0.5 Me_2CO: $C_{33.5}H_{33}N_4Mo_3O_{8.5}$, M_r = 915.46, triclinic, space group $P\bar{1}$, Z = 2, a = 10.700(2), b = 13.361(3), c = 13.654(3) Å, α = 71.98(3), β = 83.48(3), γ = 69.02(3)°, V = 1733.20 Å^3, 3.4 < 2θ < 54°, Mo-Kα radiation, λ = 0.71073 Å, ω-scan, T = 200 K, μ = 1.126 mm^{-1}, D_c = 1.754 g cm^{-3}, measured 15768, independent 6904, and observed reflections 4892, criterion: $I > 2\sigma(I)$, structure solved by direct methods (program: SHELXS-97), refined *versus* F^2 (program: SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms, 519 refined parameters with R = 0.039, residual electron density (max./min.): 0.698/−0.837 e Å^{-3}. CCDC 182/1069. See http://www.rsc.org/suppdata/cc/1998/2729/ for crystallographic data in .cif format.

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Communication 8/05154B