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(η^6-Arene)ruthenium oxomolybdenum and oxotungsten clusters. Stereochemical non-rigidity of [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$Mo$_4$O$_{16}$] and crystal structure of [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$W$_2$O$_{10}$]

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According to a multinuclear NMR study, the cluster [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$Mo$_4$O$_{16}$] exists as two isomers, the windmill-like form and the triple-cubane form, which are in equilibrium in solution, while the tungsten analogue, which has been obtained together with the double-cubane type cluster [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$W$_2$O$_{10}$] by reaction of [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)Cl$_2$}$_2$] with (NBu$^n_4$)$_2$[WO$_4$] in acetonitrile, only displays the windmill-like structure.

Organometallic derivatives of polyoxometalates now form a full class of compounds.[1] We have recently reported a series of integrated organometallic oxo(alkoxo)molybdenum clusters containing *fac*-{M(CO)$_3$}$^+$ (M = Mn or Re) units.[2] The apparent structural relationships between these clusters and those of previously reported polyoxo(alkoxo)molybdates underscore the electronic connection between d^6-*fac*-{ML$_3$} (M = Mn or Re) and d^0-*fac*-{MoO$_3$} or d^0-*fac*-{MoO$_2$(OR)}$^+$ units. Then we turned towards the reactivity of [{(η^6-arene)RuCl$_2$}$_2$] with oxometalates in order to extend the concept of topological equivalent units.

The cluster [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$W$_4$O$_{16}$] **2**, whose molybdenum analogue [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$Mo$_4$O$_{16}$] **1** was recently reported by Süss-Fink *et al.*,[3,4] has been obtained by reacting [{(η^6-*p*-MeC$_6$H$_4$Pr^i)RuCl$_2$}$_2$] with (NBu$^n_4$)$_2$[WO$_4$] in acetonitrile.† In the solid state, **2** is isostructural with **1** and displays the so-called windmill-like structure,[3,4] *i.e.* it consists of a [W$_4$O$_{16}$]$^{8-}$ cubic core capped by four {Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$^{2+}$ groups each bound to a triply bridging and two terminal oxo ligands.‡ The only previous example of a polyoxoanion-supported organometallic complex based on [W$_4$O$_{16}$]$^{8-}$ is [{Ir(cod)}$_6$W$_4$O$_{16}$].[5] The ^{1}H, ^{183}W and ^{17}O NMR spectra indicate that **2** exists in a single form in chloroform. Moreover, the ^{17}O NMR spectrum of **2** is fully consistent with the windmill-like structure. Indeed, it displays four signals in approximate relative intensities 1 : 1 : 1 : 1 assigned to terminal (O$_t$), doubly bridging (there are two sets of four μ_2-O ligands) and quadruply bridging (μ_4-O) oxo ligands, in the order of increasing shielding (Fig. 1). On the other hand, a different pattern has been reported for the ^{17}O NMR spectrum of **1** in CD$_2$Cl$_2$,[4] and this prompted us to reinvestigate the behaviour of **1**.

During the course of this study, **1** and **1**·C$_6$H$_5$Me have been characterized by X-ray diffraction in addition to **1**·2C$_6$H$_5$Me that was described by Süss-Fink *et al.*[3,4] In the three compounds **1** displays the windmill-like geometry. The ^{1}H NMR spectra of the three compounds in solution are similar apart from the signals due to toluene. However the ^{1}H, ^{17}O and ^{95}Mo NMR spectra are dependent on the solvent and indicate the presence of two distinct species. Indeed two signals (^{95}Mo) or two sets of signals (^{1}H and ^{17}O) are observed with nearly equal intensities in chloroform but quite different intensities in dichloromethane. The change in solution was shown to be reversible. The major set of ^{17}O resonances in CH$_2$Cl$_2$ is consistent with the triple-cubane structure **1b** (Fig. 1). Indeed, it is composed of three signals in relative intensities 2 : 1 : 1, assigned to O$_t$, μ_3-O and μ_4-O, respectively, in the order of increasing shielding. This assignment, which is at variance with that of Süss-Fink *et al.*,[4] is further supported by the comparison with the ^{17}O NMR spectrum of the triple-cubane cluster [(Cp*Rh)$_4$Mo$_4$O$_{16}$].[6] The minor set of signals in CH$_2$Cl$_2$ is consistent with the windmill-like structure **1a**. It follows from this multinuclear NMR study that **1** predominantly exists in the triple-cubane form **1b** in dichloromethane. Considering the significant change in the equilibrium constant on going from dichloromethane to chloroform, the energy difference between the two forms of **1** should be low. This stereochemical change, which is slow on the NMR time scales, does not depend on the residual water content and could involve a concerted motion of two {Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$^{2+}$ groups (Fig. 1). There are only a few precedents for the mobility of organometallic cations on polyoxometalates.[7] In addition to the equilibrium between **1a** and **1b**, there is a faster dynamic process which exchanges the μ_2-O oxo ligands in **1a**.

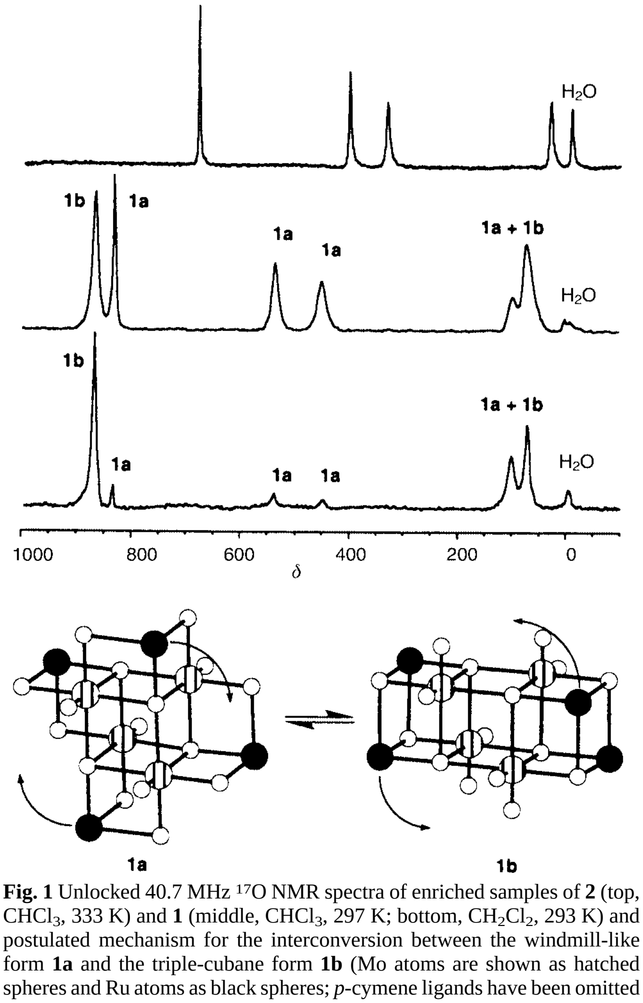

Fig. 1 Unlocked 40.7 MHz ^{17}O NMR spectra of enriched samples of **2** (top, CHCl$_3$, 333 K) and **1** (middle, CHCl$_3$, 297 K; bottom, CH$_2$Cl$_2$, 293 K) and postulated mechanism for the interconversion between the windmill-like form **1a** and the triple-cubane form **1b** (Mo atoms are shown as hatched spheres and Ru atoms as black spheres; *p*-cymene ligands have been omitted for clarity).

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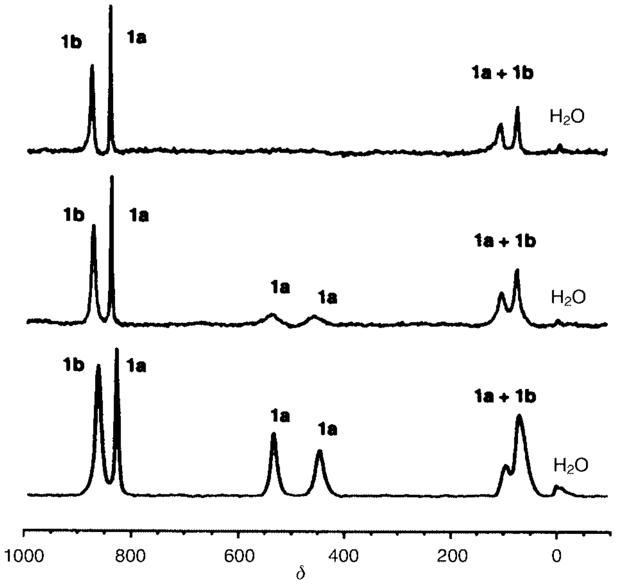

Fig. 2 Unlocked 40.7 MHz ^{17}O NMR spectra of enriched samples of **1** in CHCl$_3$ at 333 K (top), 313 K (middle) and 297 K (bottom).

Indeed the signals for the two types of μ_2-O ligands broaden as the temperature is raised and are hardly observed above 313 K (Fig. 2). The most likely mechanism to explain this phenomenon is a concerted motion of the four organometallic units along the diagonals of the faces of the central cubic core.

Another cluster, [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$W$_2$O$_{10}$]·3H$_2$O (**3**·3H$_2$O), was obtained as a by-product in the preparation of **2**. An X-ray structure analysis‡ revealed that **3** displays a double-cubane framework consisting of two fused [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_2$W$_2$O$_8$] cubes (Fig. 3). Discrete mono-cubane,[2,8] triple-cubane[6,9] and quadruple-cubane[9] clusters have been reported. To the best of our knowledge, **3** provides the first example of a discrete double-cubane cluster. The mono-cubane clusters [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_2$W$_2$O$_{10}$] (M = Mo or W) are not expected to be stable because the environments of the two M atoms would violate the Lipscomb rule.[10] Thus such units, once formed, should undergo condensation processes.

We are currently investigating the influence of the arene on the equilibium between the two forms of **1** and we are exploring the potential of these and related species in catalytic reactions.

Notes and references

† *Synthesis* of **2** and **3**. A solution of [{(η^6-*p*-MeC$_6$H$_4$Pr^i)RuCl$_2$}$_2$] (306 mg, 0.5 mmol) and (NBu$^n{}_4$)$_2$[WO$_4$] (733 mg, 1 mmol) in MeCN (15 mL) was stirred at room temperature for 5 h upon which a yellow precipitate of **2** formed. It was filtered and washed with 3 mL MeCN (215 mg, 51%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 1.34$_5$ (d, *J* 6.9 Hz, 3H), 1.35 (d, *J* 6.9 Hz, 3H), 2.41 (s, 3 H), 3.05 (heptet, *J* 6.9 Hz, 1H), 5.34 (d, *J* 5.7 Hz, 1H), 5.56 (d, *J* 5.8 Hz, 1H), 5.64 (d, *J* 5.7 Hz, 1H), 5.75 (d, *J* 5.8 Hz, 1H); ^{17}O NMR (40.7 MHz, CHCl$_3$, 333 K): δ 27 (4O), 329 (4O), 399 (4O), 676 (4O); ^{183}W NMR (20.8 MHz, CDCl$_3$): δ 351; IR (KBr pellet, $\bar{\nu}$/cm^{-1}): 935s(W=O), 878w, 803s, 750s, 644w(W–O), 608m, 492m; Anal.: C, 24.29; H, 2.91; Ru, 19.23; W. 37.35. C$_{40}$H$_{56}$O$_{16}$Ru$_4$W$_4$ requires C, 24.86; H, 2.92; Ru, 20.92; W, 38.05%.

Slow evaporation of the filtrate at 25–30 °C afforded red sticky crystals of **3**·3H$_2$O (40 mg, 10%); ^{1}H NMR (300.13 MHz, CDCl$_3$): δ 1.39 (d, *J* 6.8 Hz, 6H), 2.29 (s, 3 H), 3.07 (heptet, *J* 6.8 Hz, 1H), 5.29 (d, *J* 5.9 Hz, 2H), 5.34 (d, *J* 5.9 Hz, 2H); IR (KBr pellet, $\bar{\nu}$/cm^{-1}): 916s, 897s (W=O), 652m, 624(sh), 607s, 574m, 512m (W–O); Anal.: C, 31.59; H, 4.19; Ru, 25.13; W, 23.79. C$_{40}$H$_{62}$O$_{13}$Ru$_4$W$_2$ requires C, 31.55; H, 4.07; Ru, 26.55; W 24.14%.

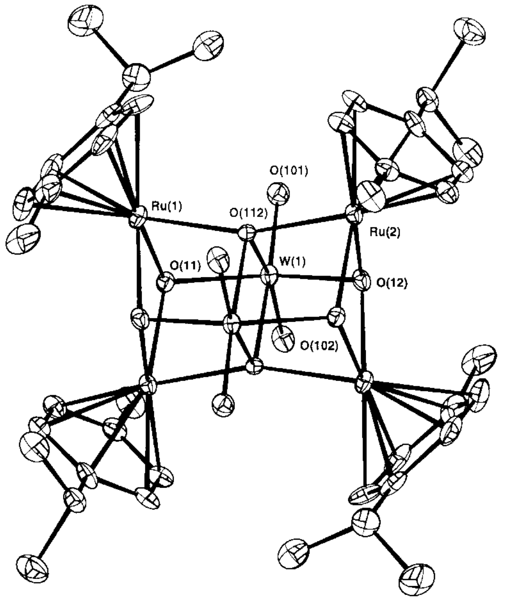

Fig. 3 Molecular structure of [{Ru(η^6-*p*-MeC$_6$H$_4$Pr^i)}$_4$W$_2$O$_{10}$] in **3**·3H$_2$O. Selected bond lengths (Å): W(1)–O(11) 1.947(7), W(1)–O(12) 1.932(8), W(1)–O(101) 1.731(9), W(1)–O(102) 1.748(9), W(1)–O(112) 2.180(7), W(1)–O(112)′ 2.268(7), Ru(1)–O(11) 2.104(8), Ru(1)–O(12)′ 2.089(9), Ru(1)–O(112) 2,084(7), Ru(2)–O(11)′ 2.114(8), Ru(2)–O(12) 2.085(8), Ru(2)–O(112) 2.095(7). Primed atoms are generated by the crystallographic inversion centre. Carbon atom labels have been omitted for clarity.

‡ *Crystal data*: for **2**·C$_6$H$_5$Me: *M* = 2116.83, *a* = 15.031(5), *b* = 15.303(5), *c* = 15.334(6) Å, α = 72.85(3), β = 73.09(3), γ = 64.30(3)°, *U* = 2982(2) Å^3, *T* = 298 K, space group $P\bar{1}$, *Z* = 2. Single crystals of **2**·C$_6$H$_5$Me were obtained from a CH$_2$Cl$_2$ solution of **2** layered by toluene; they decayed during data collection so that accurate structural parameters could not be obtained owing to an insufficient number of observed data.

For **3**·3H$_2$O: *M* = 1522.90, *a* = 13.857(7), *b* = 13.898(8), *c* = 14.232(6) Å, α = 114.01(4), β = 91.01(4), γ = 112.79(4)°, *U* = 2257(3) Å^3, *T* = 298 K, space group $P\bar{1}$, *Z* = 2, μ(Mo–Kα) = 2.24 cm^{-1}, 8300 reflections measured, 7942 unique (R_{int} = 8.3%). Structure solution (direct methods) and refinement (full matrix least squares on F^2) based on 5326 refgictions with I > 3σ(I) converged at a conventional *R* of 0.056.

CCDC 182/1597. See http://www.rsc.org/suppdata/cc/b0/b000782j/ for crystallographic files in .cif format.

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