# Oxygen transfer from peroxometalates as a new and general route to the synthesis of oxopolymetalates: rational synthesis of $Mo_2O_7{}^{2-}$, $Mo_6O_{19}{}^{2-}$ and $Mo_7O_{24}{}^{6-}$. Evidence of a $M_2O_7{}^{2-}$ with linear M–O–M axis

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## Abstract

The oxopolymolybdates, $[Mo_2O_7]^{2-}$, $[Mo_6O_{19}]^{2-}$ and $[Mo_7O_{24}]^{6-}$ have been obtained via oxygen transfer reaction from a peroxomolybdate $[Mo_2O_2(\mu_2\text{-}O)(O_2)_4(H_2O)_2]^{2-}$, obtained by the treatment of HOOH on $MoO_3$. In the case of dimolybdate, the oxygen acceptor is $Ph_3P$, while $Ph_3GeCl$ functions as an oxygen receptor for the generation of higher polymolybdates. Three dimensional X-ray structure analysis indicates that $(PPN)_2[Mo_2O_7]$ contains a linear Mo–O–Mo axis and $MoO_3$ oxygens in each fragment are staggered with respect to those of the other. The structural identity of the $PPh_4$ and PPN salts of hexamolybdate and the $PPh_4$ salt of heptamolybdate has been established by their superimposable X-ray powder diffractogram with those of the respective authentic samples prepared. This work presents further evidences in favour of our recent contention that peroxometalates serve as a useful precursor intermediate for the synthesis of oxopolymetalates.

## Introduction

In the inaugural report [1] demonstrating the use of $H_2O_2$ as an interesting reagent in the preparation of an uncommon (not obtainable by conventional $H^+$ treatment on $MO_4{}^{n-}$) oxopolymetalate, $W_6O_{19}{}^{2-}$, from a tetraoxometalate, viz. $WO_4{}^{2-}$, it was not possible to confirm the reaction route, nor was it apparent that such a route was a general one, though both the aspects were suggested [1] from an intuitive approach. The elicit philosophy was that a polynuclear peroxometalate might serve as an intermediate in the production of a desired oxopolymetalate, via an apparently obvious and implied pathway: oxygen transfer from the said peroxometalate intermediate. In the case of tungsten, the formation of $W_6O_{19}{}^{2-}$ was very fast and the peroxometalate intermediate was not isolable [1].

Acidification of aqueous $M_2[MoO_4]$ (M = Na, K or $NH_4$) does not afford the $Mo_2O_7{}^{2-}$ or $Mo_6O_{19}{}^{2-}$ species [2]. $M'_2[Mo_2O_7]$ (M' = M and Ag) was prepared by a time-consuming molten salt reaction and the products are network solid [3]. The compound $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ containing discrete $[Mo_2O_7]^{2-}$ ion was prepared [4] by the reaction of $(n\text{-}C_4H_9)_4NOH$ with $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ in $CH_3CN$. The dimolybdate was subsequently obtained quite unexpectedly by air oxidation of the anion $[(\eta\text{-}C_5H_4R)Mo(CO)_3]^-$ [5].

We herein report that the PPN ($Ph_3P{=}\overset{+}{N}{=}PPh_3$) (**1**) and $PPh_4$ (**2**) salts of $Mo_2O_7{}^{2-}$ can be prepared via a very easily obtainable (by the treatment of $H_2O_2$ on $MoO_3$) peroxomolybdate intermediate $A_2[Mo_2O_2(\mu_2\text{-}O)(O_2)_4(H_2O)_2]$ [6] (A = PPN (**3**) or $PPh_4$ (**4**)), involving an oxygen transfer process which is facilitated by the presence of $Ph_3P$ as an oxygen acceptor. We also report that the oxygen transfer process can be continued further using another powerful oxygen receptor, $Ph_3GeCl$, to yield $A_2[Mo_6O_{19}]$ (A = PPN (**5**) or $PPh_4$ (**6**)), which is ultimately converted to $A_6[Mo_7O_{24}]\cdot 4H_2O$ (A = $PPh_4$ (**7**); PPN salt not yet isolable). Interestingly enough, the structural characterization of **1** shows a linear Mo–O–Mo axis with staggered $MoO_3$ oxygen atoms in striking contrast with the previously known [4, 5] structure of the n-$Bu_4N$ and $[(n\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-}dppm)Pt(dppm)]^+$ (dppm = $Ph_2PCH_2PPh_2$) salts where the said oxygen atoms are in eclipsed conformation and the Mo–O–Mo axis (also compare with the Cr–O–Cr axis in $Cr_2O_7{}^{2-}$ [7]) is bent.

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## Experimental

### *Preparation of $A_2[Mo_2O_{11}(H_2O)_2]$ (A = PPN (3) or $PPh_4$ (4))*

The pale yellow solution obtained by dissolving $MoO_3$ (0.2 g; 1.4 mmol) in 30% $H_2O_2$ was treated with an aqueous ethanol (1:1) solution (15 ml) of PPNCl (1.5 g; 2.78 mmol) or $PPh_4Cl$ (1.05 g; 2.80 mmol) when a white precipitate was obtained. The solid in each case was collected by filtration, washed successively with water, 95% ethanol and finally with diethyl ether and dried over $CaCl_2$ at reduced pressure. The yield was 0.78 g (~81%) for **3** and 0.57 g (~76%) for **4**.

*Anal.* Calc. for $(PPN)_2[Mo_2O_{11}(H_2O)_2]$: C, 58.4; H, 4.08; N, 1.89; P, 8.36; Mo, 12.9; $H_2O$, 2.43. Found: C, 58.1; H, 4.10; N, 1.85 (Perkin-Elmer 240C elemental analyser); P, 8.31; Mo, 12.8; $H_2O$, 2.39% (DT 30 Shimadzu thermoanalyzer). IR (KBr disc, 4000–200 cm$^{-1}$, Perkin-Elmer 597 IR spectrophotometer): $\nu(Mo{=}O)$ 965(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 730(m), $\nu(Mo{-}O{-}Mo)_{sym}$ 445(w), $\nu(O{-}O)$ 865 cm$^{-1}$. Molar conductance (in $CH_3CN$); 280 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

*Anal.* Calc. for $(PPh_4)_2[Mo_2O_{11}(H_2O)_2]$: C, 53.2; H, 4.09; P, 5.72; Mo. 17.7. Found: C, 53.0; H, 4.12; P, 5.69; Mo, 17.4%. IR: $\nu(Mo{=}O)$ 965(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 730(m), $\nu(Mo{-}O{-}Mo)_{sym}$ 455(w), $\nu(O{-}O)$ 865 cm$^{-1}$. Molar conductance (in $CH_3CN$): 290 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

### *Preparation of $(PPN)_2[Mo_2O_7]$ (1)*

To an acetonitrile solution (15 ml) of compound **3** (0.25 g; 0.17 mmol), an acetonitrile solution (60 ml) of $PPh_3$ (0.178 g; 0.68 mmol) was added and the resulting colorless solution was allowed to stand for 24 h. The solid mass obtained by evaporation of the solution was extracted with diethyl ether. The residue left (the extract gave $Ph_3PO$) contained $(PPN)_2[Mo_2O_7]$, which was crystallized from acetonitrile–diethyl ether. Colorless crystals thus obtained were dried over fused $CaCl_2$ at reduced pressure. The yield was 0.21 g (~90%).

*Anal.* Calc. for $(PPN)_2[Mo_2O_7]$: C, 62.6; H, 4.38; N, 2.03; P, 8.97; Mo, 13.9. Found: C, 62.3; H, 4.41; N, 2.00; P, 8.89; Mo, 13.7%. IR: $\nu(Mo{=}O)$ 885(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 795(m), $\nu(Mo{-}O{-}Mo)_{sym}$ 450(w) cm$^{-1}$. Molar conductance (in $CH_3CN$): 285$\Omega^{-1}$ cm$^2$ mol$^{-1}$.

The compound $(PPN)_2[Mo_2O_7]$ can also be prepared by repeated crystallization (3–4 times) of the compound **3** from dichloromethane, acetonitrile or dimethyl formamide using diethyl ether as the precipitating agent.

### *Preparation of $(PPh_4)_2[Mo_2O_7]$ (2)*

The same method as described for **1** was followed using the compound **4**, when a 90% yield of the product **2** was obtained.

*Anal.* Calc. for $(PPh_4)_2[Mo_2O_7]$: C, 58.7; H, 4.10; P, 6.30; Mo, 19.5. Found: C, 58.5; H, 4.13; P, 6.26; Mo, 19.4%. IR: $\nu(Mo{=}O)$ 885(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 790(m), $\nu(Mo{-}O{-}Mo)_{sym}$ 460(w) cm$^{-1}$. Molar conductance (in $CH_3CN$): 295 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

### *Preparation of $(PPN)_2[Mo_6O_{19}]$ (5)*

To a solution (15 ml) of the compound **3** (0.25 g; 0.17 mmol) in acetonitrile, an acetonitrile solution (50 ml) of $Ph_3GeCl$ (0.29 g; 0.85 mmol) was added when a pale yellow solution was obtained. Diethyl ether (15 ml) was added to the solution and it was allowed to stand for *c.* 2–3 days when pale yellow crystals of $(PPN)_2[Mo_6O_{19}]$ separated out. The yield was 0.09 g (~82%).

*Anal.* Calc. for $(PPN)_2[Mo_6O_{19}]$: C, 44.2; H, 3.09; N, 1.43; P, 6.33; Mo, 29.4. Found: C, 43.9; H, 3.12; N, 1.40; P, 6.29; Mo, 29.1%. IR: $\nu(Mo{=}O)$ 965(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 805(s); $\nu(Mo{-}O{-}Mo)_{sym}$ 445(w) cm$^{-1}$. Molar conductance (in $CH_3CN$): 270 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV–Vis (in $CH_3CN$; Hitachi model U-3400 spectrophotometer): 323 ($\epsilon = 6830$) nm.

After the separation of **5**, the filtrate became colorless and was allowed to stand for a couple of days more when colorless crystals of $(Ph_3Ge)_2O$ were obtained. The yield was 0.245 g (~92%).

*Anal.* Calc. for $(Ph_3Ge)_2O$: C, 69.3; H, 4.85. Found: C, 69.1; H, 4.79%. IR: 3080(w), 1490(m), 1440(s), 1100(s), 1000(w), 865(s), 740(s), 700(s), 680(w), 480(w), 460(m), 340(m), 325(w) cm$^{-1}$. UV–Vis (in $CH_3CN$): 264 ($\epsilon = 1480$), 259 ($\epsilon = 1600$), 253 ($\epsilon = 1190$) nm. The data are in agreement with those of the authentic compound [8].

### *Preparation of $(PPh_4)_2[Mo_6O_{19}]$ (6)*

The same method as described in the case of the PPN salt was followed and the pale yellow solution obtained as above was evaporated. The solid product obtained by evaporation was extracted with chloroform. The insoluble portion left after chloroform extraction (which gave $Ph_3GeOGePh_3$) contained pure $(PPh_4)_2[Mo_6O_{19}]$ which was recrystallized from acetonitrile–diethyl ether at 0 °C when pale yellow crystals were obtained. The yield was ~92%.

*Anal.* Calc. for $(PPh_4)_2[Mo_6O_{19}]$: C, 37.0; H, 2.59; P, 3.97; Mo, 36.9. Found: C, 36.8; H, 2.62; P, 3.94; Mo, 36.6%. IR: $\nu(Mo{=}O)$ 960(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 800(s), $\nu(Mo{-}O{-}Mo)_{sym}$ 440(w) cm$^{-1}$. Molar conductance (in $CH_3CN$): 280 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. UV–Vis (in $CH_3CN$): 325 ($\epsilon = 6795$) nm. *d* Spacings (Phillips model PW 1730/PW 1710 XRD system using Cu K$\alpha$

radiation (1.5418 Å): 10.63(s), 9.21(s), 8.67(s), 6.91(s), 6.46(w), 4.27(w), 3.25(w) Å.

*Preparation of* $(PPh_4)_6[Mo_7O_{24}]\cdot 4H_2O$ *(7)*

The pale yellow solution obtained after adding an acetonitrile solution (40 ml) of $Ph_3GeCl$ (0.42 g; 1.2 mmol) to the acetonitrile solution (15 ml) of $(PPh_4)_2[Mo_2O_{11}(H_2O)_2]$ (**4**) (0.25 g; 0.23 mmol) as described in the case of **6**, above, was allowed to stand at room temperature (28 °C) for 3–4 days when the solution became colorless. To the colorless solution 15 ml of diethyl ether was added and the solution mixtures was allowed to stand for 24 h at 0 °C when colorless crystals of $(PPh_4)_6[Mo_7O_{24}]\cdot 4H_2O$ separated out. The yield was 0.155 g (~75%).

*Anal.* Calc. for $(PPh_4)_6[Mo_7O_{24}]\cdot 4H_2O$: C, 54.7; H, 4.08; P, 5.87; Mo, 21.2; $H_2O$, 2.28. Found: C, 54.1; H, 4.04; P, 5.82; Mo, 20.7; $H_2O$, 2.30%. IR: $\nu(Mo{=}O)$ 945(s); 915(s), $\nu(Mo{-}O{-}Mo)_{asym}$ 850(m); 810(m), $\nu(Mo{-}O{-}Mo)_{sym}$ 410(w); 370(w) $cm^{-1}$. Molar conductance (in $CH_3CN$): 770 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV–Vis (in $CH_3CN$): 317 ($\epsilon = 1855$) nm. *d* Spacings: 12.99(s), 10.91(s), 10.16(m), 7.50(w), 6.91(w), 3.14(m), 2.87(w) Å. The compounds **6** and **7** were also prepared by the literature methods [9, 2] and their X-ray powder diffractograms were found to be superimposable with those of the products obtained by the present method.

## Results and discussion

Conventional proton induced polyanionic aggregation from discrete monoanions also operates via oxygen atom transfer whereby water elimination is an invariable step. Our contention is that besides proton, other oxygen acceptors, like $Ph_3E$ (E = P, As, Sb) or $R'_3GeCl$ (R' = alkyl or aryl) also serve the purpose specially when the substrate is oxygen rich. The peroxo product, i.e. the anion of **3** or **4** reacts with $Ph_3P$ in acetonitrile medium to produce $Mo_2O_7^{2-}$ according to eqn. (1). It is noteworthy that the oxygen rich anion (i.e. **3** or **4**) when repeatedly crystallized from $CH_3CN$, $CH_2Cl_2$ or DMF also gives $[Mo_2O_7]^{2-}$ presumably evolving dioxygen (eqn. (2)).

$$[Mo_2O_2(\mu_2\text{-}O)(O_2)_4(H_2O)_2]^{2-} + 4Ph_3P \xrightarrow{CH_3CN} [Mo_2O_7]^{2-} + 4Ph_3PO + 2H_2O \qquad (1)$$

$$[Mo_2O_2(\mu_2\text{-}O)(O_2)_4(H_2O)_2]^{2-} \xrightarrow[\text{crystallizations}]{\text{repeated}} [Mo_2O_7]^{2-} + 2O_2 + 2H_2O \qquad (2)$$

Reactions (1) and (2) are quantitative irrespective of whether **3** or **4** is used as the starting material. $Ph_3P$ treatment or the repeated crystallization process, however, can only affect the oxygen transfer commensurate to the polyanion formation up to the extent of dimolybdate. On the other hand if $Ph_3GeCl$ is used as an oxygen acceptor, the reaction proceeds almost quantitatively up to the hexamolybdate stage as shown in eqn. (3). Hexamolybdate is also obtained, though very slowly, when $[Mo_2O_7]^{2-}$ reacts with $Ph_3GeCl$ and this can also be described as an oxygen transfer reaction as shown in eqn. (4).

$$3[Mo_2O_2(\mu_2\text{-}O)(O_2)_4(H_2O)_2]^{2-} + 28Ph_3GeCl \xrightarrow[\text{very fast}]{CH_3CN} [Mo_6O_{19}]^{2-} + 14[Ph_3GeOGePh_3] + 6H_2O \qquad (3)$$

$$3[Mo_2O_7]^{2-} + 4Ph_3GeCl \xrightarrow[\text{slow}]{CH_3CN} [Mo_6O_{19}]^{2-} + 2[Ph_3GeOGePh_3] \qquad (4)$$

Since, the heptamolybdate is obtainable if the hexamolybdate solution is allowed to stand in air, it may be implied that $[Mo_6O_{19}]^{2-}$ abstracts oxygen from air ($Ph_3GeOGePh_3$ remains intact in quantities) to pass on to the more stable $[Mo_7O_{24}]^{6-}$. The high stability of $[Mo_7O_{24}]^{6-}$ in the solid state is also reflected by the fact that solid $(PPh_4)_2[Mo_2O_7]$ on being left for 60–70 days becomes completely converted to **7** (infrared probing).

Compounds **1–6**, as expected, are 2:1 electrolytes in acetonitrile [10], while **7** shows a 6:1 electrolytic character in the same solvent [10], as required by its molecular formula. The compounds **3** and **4**, like their pyridinium salts [6], should also have an anti-$Mo_2O_3^{6+}$ configuration since, here also [11] only one $\nu(Mo{=}O)$ vibration is found to be infrared active. **1** and **2** each also contains a single $\nu(Mo{=}O)$ vibration [4] which is compatible with the tetrahedral $MoO_4$ environment of each Mo atom in $Mo_2O_7^{2-}$. The structures of **5** and **6** [12] dictate that only one $\nu(Mo{=}O)$ vibration [13] should be obtained in the infrared spectrum which in fact occurs. However, the $Mo_7O_{24}^{6-}$ group is arranged in such a fashion [14, 15] that the molecule possesses $C_{2v}$ symmetry and quite naturally more than one $\nu(Mo{=}O)_t$ and $\nu(Mo{-}O{-}Mo)_b$ are predictable, as is also observed here. The $\nu(Mo{-}O{-}Mo)_{asym}$ vibrations in the peroxo compounds appear at lower wave numbers compared to those of the oxopolymetalates. The $\nu(O{-}O)$ vibrations for the coordinated peroxo group in **3** and **4** are shown in 'Experimental'. The $O_{p\pi} \rightarrow Mo_{d\pi}$ LMCT in $[Mo_6O_{19}]^{2-}$ as observed here at 325 nm compared to 295 nm for the corresponding tungsten compound [1] is quite realistic insofar as the optical electronegativity of W(VI) is lower than that of its Mo analogue. This band, however, occurs at a slightly lower wave number region in $[Mo_7O_{24}]^{6-}$.

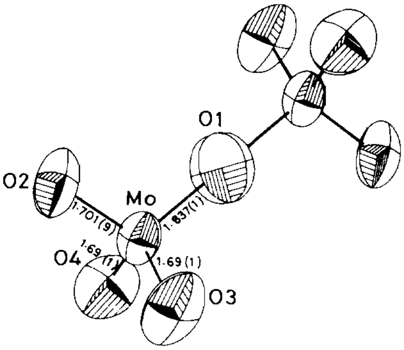

Fig. 1. Molecular structure of $[Mo_2O_7]^{2-}$. Bond angles (°): Mol–O1–Mol′ 180.0(9); O1–Mol–O2 109.2(3); O1–Mol–O3 109.5(4); O1–Mol–O4 110.4(4); O2–Mol–O3 108.8(5); O2–Mol–O4 109.0(5); O3–Mol–O4 109.9(5). Space group *Pcab*, $a = 15.712(7)$, $b = 20.739(13)$, $c = 19.521(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6361.0(56)$ Å$^3$ $\mu$(Mo K$\alpha$) = 5.375 cm$^{-1}$, $\lambda$(Mo K$\alpha$) = 0.71069 Å, $D_{calc}/D_{obs} = 1.442/1.432$ g cm$^{-3}$, $Z = 4$, $R/R_w = 5.5/6.7\%$.

The molecular structure of the anion $Mo_2O_7^{2-}$ existing in the PPN salt, **1**, is shown in Fig. 1, where some important crystal data as well as bond lengths (Å) and bond angles (°) are given (Details will be discussed elsewhere [16]). It is noteworthy, that **1** shows a perfectly straight Mo—O—Mo axis. It will be very interesting to examine whether or not the Cr—O—Cr fragment in $(PPN)_2[Cr_2O_7]$ is also linear.

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