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# Synthesis and structure of the incomplete cuboidal clusters $[W_3Se_4H_3(dmpe)_3]^+$, $[W_3Se_4H_{3-x}(OH)_x(dmpe)_3]^+$ and $[W_3Se_4(OH)_3(dmpe)_3]^+$, and the mechanism of the acid-assisted substitution of the coordinated hydrides

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The novel incomplete cuboidal cluster $[W_3Se_4H_3(dmpe)_3](PF_6)$, [**1**]$(PF_6)$, has been prepared by reduction of $[W_3Se_4Br_3(dmpe)_3](PF_6)$ with $LiBH_4$ in THF solution. The trihydroxo complex $[W_3Se_4(OH)_3(dmpe)_3](PF_6)$, [**2**]$(PF_6)$, was obtained by reacting $[W_3Se_4Br_3(dmpe)_3](PF_6)$ with NaOH in MeCN–$H_2O$ solution. The complexes [**1**]$(PF_6)$ and [**2**]$(PF_6)$ were converted to their $BPh_4^-$ salts by treatment with $NaBPh_4$. Recrystallisation of [**1**]$(BPh_4)$ in the presence of traces of water affords the mixed dihydride hydroxo complex $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$. The crystal structures of [**1**]$(BPh_4)$, [**2**]$(BPh_4)$ and $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$ have been resolved. Although the [**1**]$^+$ trihydride does not react with an excess of halide salts, reaction with HX leads to $[W_3Se_4X_3(dmpe)_3]^+$ (X = Cl, Br). The kinetics of this reaction has been studied at 25 °C in MeCN–$H_2O$ solution (1 : 1, v/v) and found to occur with two consecutive kinetic steps. The first step is independent of the nature and concentration of the $X^-$ anion but shows a first order dependence on the concentration of acid ($k_1 = 12.0\ mol^{-1}\ dm^3\ s^{-1}$), whereas the second one is independent of the nature and concentration of both the acid and added salts ($k_2 = 0.024\ s^{-1}$). In contrast, the reaction of [**2**]$^+$ with acids occurs in a single step with $k_{obs} = 0.63\ s^{-1}$ (HCl) and $0.17\ s^{-1}$ (HBr). These kinetic results are discussed on the basis of the mechanism previously proposed for the reactions of the analogous $[W_3S_4H_3(dmpe)_3]^+$ cluster, with special emphasis on the effects caused by the change of S by Se on the rate constants for the different processes involved.

## Introduction

Transition metal cluster sulfides are often used as industrial catalysts and as models for the active sites of biological molecules,[1–4] the soft character of the sulfur atom playing an important role in the stabilization of these polynuclear complexes. Although selenido ligands have a great potential for this purpose, the chemistry of metal selenide complexes is less studied. Trinuclear clusters with cuboidal $[M_3(\mu_3\text{-}Q)(\mu\text{-}Q)_3]^{4+}$ (Q = S, Se) units are a dominant feature of the chemistry of molybdenum and tungsten in their four oxidation state.[5] Although most of these compounds have been prepared in water by reaction of the $[M_3Q_4(H_2O)_9]^{4+}$ aqua complexes with a variety of inorganic and organic ligands, other synthetic strategies such as the cluster excision from polymeric solids have also proven to be very useful.[6] Kinetic studies on the substitution of coordinated water in these aqua complexes revealed the existence of two types of kinetically different water molecules, the one *trans* to the capping chalcogen being less labile than the other two.[7] Replacement of the capping sulfur by selenium in the molybdenum trimer results in a retardation of the substitution of the more labile water molecule, the opposite effect being observed upon substitution of the bridging sufide by selenide.[8,9] In all cases, there is an acceleration of the substitution reaction when the acid concentration is decreased, which is interpreted as a consecuence of the formation of more labile hydroxo complexes.[10]

In the course of our investigation on the reactivity of the $[W_3S_4H_3(dmpe)_3]^+$ cluster complex with HX acids, we found that the formal substitution of the coordinated hydrides for $X^-$ ions occurs with a rate that increases with the acid concentration, which constitutes the first evidence for the existence of acid-assisted substitutions in this kind of W–S clusters.[11] It appears reasonable to consider that subtle changes in the coordination sphere may allow an appropriate adjustment of the reactivity, which may be of particular interest with respect to the potential applications of these compounds in homogeneous catalysis.[3] For this reason, we investigate in this work the influence of the substitution of sulfur by selenium on the reactivity of trinuclear transition metal cluster hydrides. Procedures have been developed for the synthesis of the $[W_3Se_4H_3(dmpe)_3]^+$ cuboidal trimer and its hydroxo analog, and the kinetics of reaction of $[W_3Se_4H_3(dmpe)_3]^+$ with acids has been studied, which provides additional information on the mechanism of protonation of these clusters.

## Experimental

### Materials and physical measurements

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. The molecular triangular cluster $[W_3Se_4Br_3(dmpe)_3](PF_6)$ was prepared according to literature methods.[12] The remaining reactants were obtained

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from commercial sources and used as received. Solvents for synthesis were dried by standard methods before use.

Elemental analyses were carried out with a C. E. analyzer, model EA 1108. The $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded with Varian 300 and 500 MHz spectrometers, using $CD_2Cl_2$ as a solvent. $^1$H and $^{13}$C are referenced to TMS and $^{31}$P to external 85% $H_3PO_4$. For the low temperature NMR monitoring of the reaction of the complexes with acids and the determination of the $T_1$ values, a Varian Unity 400 spectrometer was used. IR spectra were recorded on a Perkin-Elmer System 2000 FTIR using KBr pellets. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 19 spectrophotometer. Electrospray mass spectra were recorded on a Micromass Quattro LC instrument using nitrogen as drying and nebulising gas.

## Synthesis

**$[W_3Se_4H_3(dmpe)_3](PF_6)$, [1]($PF_6$).** To a green solution of $[W_3Se_4Br_3(dmpe)_3](PF_6)$ (0.08 g, 0.05 mmol) in dry THF (20 mL), an excess of $LiBH_4$ (2 M in THF) (250 µL, 0.5 mmol) was added at room temperature. The mixture was stirred and the colour of the solution changed from green to violet after 20 min, although stirring was continued for 24 h. The resulting mixture was dried under vacuum and redissolved in 20 mL of $CH_2Cl_2$. Four water extractions (×20 mL) were done to remove the inorganic salts formed in the reaction. The violet organic solution was dried with anhydrous $MgSO_4$ and filtered. Finally, diethylether was added to precipitate the desired air stable violet product (57 mg, 74%) (Found: C, 14.64; H, 3.18. $C_{18}H_{51}F_6W_3P_7Se_4$ requires C, 14.75; H 3.51%). $^{31}P\{^1H\}$ NMR: $\delta$ ($CD_2Cl_2$): 16.30 (d, 3P, $^2J_{PP'}$ = 4.3 Hz, $^1J_{PW}$ = 169.8 Hz), −10.50 (d, 3P, $^2J_{PP'}$ = 4.3 Hz, $^1J_{PW}$ = 107.2 Hz), −143.93 (septet, 1P, $^1J_{P-F}$ = 705.8). $^1$H NMR: $\delta$ −2.45 (dd, 3H, $^2J_{HP}$ = 47.0 and 30.0 Hz, $^1J_{HW}$ = 57.0 Hz), 0.60 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.0 Hz), 1.70 (m, 3H, $CH_2$), 1.90 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.0 Hz), 2.05 (m, 3H, $CH_2$), 2.30 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.0 Hz), 2.25 (m, 3H, $CH_2$), 2.55 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.0 Hz), 2.70 (m, 3H, $CH_2$), $^{13}C\{^1H\}$ NMR: $\delta$ 17.30 (d, $CH_3$, $^1J_{CP}$ = 23.3 Hz), 24.80 (d, $CH_3$, $^1J_{CP}$ = 37.4 Hz), 25.60 (d, $CH_3$, $^1J_{CP}$ = 34.7 Hz), 27.60 (d, $CH_3$, $^1J_{CP}$ = 32.0 Hz), 30.05 (dd, $CH_2$, $^1J_{CP}$ = 31.3 Hz, $^2J_{CP}$ = 11.5 Hz), 31.10 (dd, $CH_2$, $^1J_{CP}$ = 30.1 Hz, $^2J_{CP}$ = 12.2 Hz); IR (KBr)/cm$^{-1}$: 1416 (s, P–$CH_2$), 1280 (m, P–$CH_3$), 1096 (s), 934 (s), 897 (s), 839 (s, P–F), 739 (m), 712 (m), 653 (m), 557 (s, P–F), 445 (w), 342 (w); UV-vis ($CH_3CN$)/nm: 255 (br), 323 (br), 389 (br), 548 (br); *m*/*z* ($CH_3CN$) 1321 ($M^+$), 1171 (M − dmpe)$^+$ (positive-ion electrospray-MS 65 V).

**$[W_3Se_4(OH)_3(dmpe)_3](PF_6)$, [2]($PF_6$).** To a green solution of $[W_3Se_4Br_3(dmpe)_3](PF_6)$ (168 mg, 0.098 mmol) in 200 mL of $CH_3CN$–$H_2O$ (1:1, v/v), 4 mL of an aqueous solution of 0.1 M NaOH (0.4 mmol) were added dropwise, and the mixture was stirred at room temperature for 4 h. After removing part of the solvent (*ca.* 100 mL) under reduced pressure, the desired product was extracted with 60 mL. (×2) of $CH_2Cl_2$ and the resulting dark green organic solution was dried with $MgSO_4$, filtered and concentrated. Addition of ether to the above solution precipitates the desired product that was separated and filtered to yield an air stable dark green product (59 mg. 37%) (Found: C, 14.28; H, 3.40. $C_{18}H_{51}O_3F_6W_3P_7Se_4$ requires C, 14.34; H 3.21%).

$^{31}P\{^1H\}$ NMR: $\delta$ ($CD_2Cl_2$): 13.75 (s, 3P, $^1J_{PW}$ = 195.8 Hz), −7.25 (s, 3P, $^1J_{PW}$ = 170.2 Hz), −143.93 (septet, 1P, $^1J_{P-F}$ = 705.8). $^1$H NMR: $\delta$ 0.62 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.2 Hz), 1.65 (d, 9H, $CH_3$, $^2J_{HP}$ = 8.4 Hz), 1.80 (m, 3H, $CH_2$), 1.87 (m, 3H, $CH_2$) 1.92 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.6 Hz), 2.10 (m, 3H, $CH_2$) 2.39 (d, 9H, $CH_3$, $^2J_{HP}$ = 9.2 Hz), 2.69 (m, 3H, $CH_2$), 3.75 (br s, 3H, OH) $^{13}C\{^1H\}$ NMR: $\delta$ 8.10 (d, $CH_3$, $^1J_{CP}$ = 22.3 Hz), 11.12 (d, $CH_3$, $^1J_{CP}$ = 33.4 Hz), 15.82 (d, $CH_3$, $^1J_{CP}$ = 30.7 Hz), 24.30 (d, $CH_3$, $^1J_{CP}$ = 39.0 Hz), 27.58 (dd, $CH_2$, $^1J_{CP}$ = 30.3 Hz, $^2J_{CP}$ = 9.5 Hz), 29.10 (dd, $CH_2$, $^1J_{CP}$ = 33.1 Hz, $^2J_{CP}$ = 11.2 Hz); IR (KBr)/cm$^{-1}$: 1417 (s, P–$CH_2$), 1300 (m), 1286 (m, P–$CH_3$), 1135 (m, $CH_3$), 995 (w), 948 (s, $CH_3$), 924 (s), 897 (s, $CH_3$), 839 (s, P–F), 803 (m), 749 (m, $CH_2$), 713 (m, $CH_2$), 651 (m), 557 (s, P–F), 489 (s), 449 (m), 337 (m); UV-vis ($CH_3CN$)/nm: 276 (sh), 326 (sh), 350 (br), 577 (br); *m*/*z* ($CH_3CN$) 1369 ($M^+$), 1219 (M − dmpe)$^+$ (positive-ion electrospray-MS 65 V).

## X-Ray data collection and structure refinement

Suitable crystals for X-ray studies of compounds [**1**]($BPh_4$) and [**2**]($BPh_4$) were grown by slow diffusion of ether into sample solutions in $CH_2Cl_2$. Replacement of the $PF_6^-$ anion in clusters [**1**]($PF_6$) and [**2**]($PF_6$) was done by addition of an excess of $NaBPh_4$ to methanol solutions of [**1**]$^+$ and [**2**]$^+$ that precipitate the desired tetraphenylborate salts. Crystals of [**1**]($BPh_4$) could only be grown from rigorously dried solvents under nitrogen. During crystallisation of this compound, it was observed that the presence of traces of water in the solvent favours the formation of single crystals that contain a mixture of complexes of formula $[W_3Se_4H_x(OH)_{3-x}(dmpe)_3]^+$ with different hydride and hydroxo ligands ratios based on the mass spectrometry analysis. The composition of these crystals is not representative of that of the mother-liquor, which mainly contains the [**1**]($BPh_4$) hydride. One of them was chosen for X-ray diffraction and the final refinement agreed with the formulation $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$ although its mass spectra show signals due to the $[W_3Se_4H_3(dmpe)_3]^+$, $[W_3Se_4H_2(OH)(dmpe)_3]^+$ and $[W_3Se_4H(OH)_2(dmpe)_3]^+$cluster cations.

All the crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxi cement. X-Ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo-Kα radiation ($\lambda$ = 0.71073 Å) at room temperature. The data were collected with a frame width of 0.3° in $\omega$ and a counting time of 30, 25 and 15 s per frame for compounds [**1**]($BPh_4$), $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$ and [**2**]($BPh_4$), respectively, at a crystal to detector distance of 4 cm. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[13,14] The structures were solved by direct methods and refined by the full-matrix method based on $F^2$ using the SHELXTL software package.[15] The crystal parameters and basic information relating data collection and structure refinement for the three compounds are summarized in Table 1.

All the non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were generated geometrically, assigned isotropic thermal parameters and allowed to ride on their respective parent atoms. In particular, the hydrogen atoms on the hydroxyl ligand in [**2**]$^+$ were generated considering an idealized W–O–H tetrahedral geometry for the group. The final atomic positions give short contacts of *ca.* 1.7 Å between the hydroxyl and methyl hydrogens. In spite of these, there is free rotation around the W–O at room temperature as evidenced by the proton NMR broad signal associated to the hydroxyl ligands. The last Fourier map in the crystal $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$ showed three significant residual electron density peaks close to each metal site. These residual peaks were refined isotropically as partially occupied hydroxo groups yielding a final population of 0.33 oxygen atoms per metallic site. This assignment, which balances the overall charge in the cluster, is also supported by the mass spectra of the sample. In this structure the methyl, methylene and hydroxyl hydrogens were generated and refined as in [**2**]$^+$ to give even also shorter H · · · H contacts (*ca.* 1.6 Å) between the the hydroxyl and methyl hydrogens although the significance of these values diminish due to the disorder in the hydroxo positions.

CCDC reference numbers: 225461 for $[W_3Se_4H_2(OH)(dmpe)_3](BPh_4)$, 225462 for [**2**]($BPh_4$) and 225463 for [**1**]($BPh_4$).

See http://www.rsc.org/suppdata/dt/b3/b315841a/ for crystallographic data in CIF or other electronic format.

**Table 1** Crystallographic data for [**1**]($BPh_4$), [**2**]($BPh_4$) and [$W_3Se_4H_2(OH)(dmpe)_3$]($BPh_4$)

| Compound | [**1**]($BPh_4$) | [**2**]($BPh_4$) | [$W_3Se_4H_2(OH)(dmpe)_3$] ($BPh_4$) |
|---|---|---|---|
| Empirical formula | $C_{42}H_{71}BP_6Se_4W_3$ | $C_{42}H_{71}BO_3P_6Se_4W_3$ | $C_{42}H_{71}BOP_6Se_4W_3$ |
| Formula weight | 1640.01 | 1688.01 | 1656.01 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| $a$/Å | 15.081(6) | 11.1941(14) | 15.097(2) |
| $b$/Å | 11.364(5) | 15.1541(18) | 11.3593(15) |
| $c$/Å | 33.098(16) | 17.022(2) | 33.118(4) |
| $\alpha$/° |  | 82.358(2) |  |
| $\beta$/° | 98.730(12) | 82.591(3) | 98.760(3) |
| $\gamma$/° |  | 88.462(2) |  |
| $V$/Å$^3$ | 5607(4) | 2837.8(6) | 5613.1(13) |
| $Z$ | 4 | 2 | 4 |
| $T$/K | 293(2) | 293(2) | 293(2) |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 8.934 | 8.833 | 8.927 |
| Reflections collected | 31351 | 15950 | 31377 |
| $\phi$ Range for data collection/° | 1.24–25.00 | 1.22–25.00 | 1.24–25.00 |
| Unique reflections ($R_{int}$) | 9883 (0.1280) | 9996 (0.0364) | 9897 (0.1038) |
| Goodness-of-fit on $F^2$ | 0.991 | 0.915 | 0.973 |
| $R1^a$, $wR2^b$ | 0.0572, 0.1159 | 0.0396, 0.0834 | 0.0527, 0.1073 |
| $R1^a$/$wR2^b$ (all data) | 0.1291, 0.1553 | 0.0686, 0.0969 | 0.1082, 0.1223 |
| Residual $\rho$/e Å$^{-3}$ | 1.749 (1.1 Å from W(2)) and −1.495 | 2.270 (0.9 from Å W(1)) and −1.554 | 1.079 and −1.208 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]]^{½}$.

### Kinetic experiments

The kinetics of reaction of the [**1**]$^+$ and [**2**]$^+$ clusters with HCl and HBr was studied at 25.0 °C in MeCN–$H_2O$ (1 : 1, v/v) solution using an Applied Photophysics SX17MV stopped-flow instrument provided with a diode-array detector. Because preliminary experiments showed that solutions of the [**1**]$^+$ complex in acetonitrile–water solutions are not stable, the kinetic experiments were carried out by mixing in the stopped-flow instrument an acetonitrile solution of the complex with an aqueous solution of the acid that also contained the amount of $KNO_3$ required to keep a constant ionic strength of 0.5 M. The same conditions were also used for the reactions of the [**2**]$^+$ cluster. Although the mixing of solutions in different solvents causes a significant increase in the mixing time of the stopped-flow instrument, the rate constants of the reactions studied are not very large and no problems were found to analyze the kinetic data. The analysis of the data collected with the diode-array detector was carried out using program GLINT.[16] The concentrations of the acid solutions were determined by titration with a previously standardized KOH solution.

## Results and discussion

### Synthesis and structure of the trinuclear selenide clusters

The development of transition metal cluster chemistry is closely related to the availability of rational synthetic routes. The excision of polymeric $\{M_3Q_7X_4\}_x$ (M = Mo, W; Q = S, Se) phases has proven to be the most efficient synthetic entry to molecular trinuclear clusters with [$M_3Q_7$] and [$M_3Q_4$] units.[17,18] We have recently shown that the excision of these polymeric phases with diphosphines is an excellent route for the preparation of trimetallic complexes with formula [$M_3Q_4X_3$(diphosphine)$_3$]$^+$ (M = Mo, W; Q = S, Se and X = Cl, Br).[12,19,20] Reactivity studies on the tungsten sulfide excision product with dmpe, namely the [$W_3S_4Br_3(dmpe)_3$]$^+$ cuboidal trimer, show that the halide atom can be replaced by hydride and hydroxyl groups to yield stable cluster derivatives.[11,21] In this work we have extended this chemistry to the homologous seleno derivatives of the tungsten trimers. The reaction of [$W_3Se_4Br_3(dmpe)_3$]($PF_6$) with $LiBH_4$ affords the hydride cluster [**1**]($PF_6$) in 74% yield. Substitution of the bromide ligands in [$W_3Se_4Br_3(dmpe)_3$]$^+$ by hydroxyl groups is achieved by reaction with an aqueous solution of NaOH in acetonitrile at room temperature, which leads to the hydroxo cluster [**2**]($PF_6$) in 37% yield. The products obtained are air stable both in the solid state and in solution. However, crystallization of [**1**]$^+$ in the presence of traces of water gives solids with stoichiometry [$W_3Se_4H_{3-x}(OH)_x(dmpe)_3$]$^+$ ($x$ = 0, 1, 2). The quantitative conversion of the [**1**]$^+$ cation into the [**2**]$^+$ hydroxo cluster can be achieved by refluxing the hydride complex in water–acetonitrile mixtures for 24 h. Although complex [**1**]$^+$ does not react with an excess of halide salts, the substitution of hydrogen by halogens occurs readily in the presence of HX acids, as observed for the analogous sulfide complex. The kinetic study of this reaction is presented in the next section.

The structures of the compounds [**1**]($BPh_4$) and [**2**]($BPh_4$) together with the mixed hydride–hydroxo derivative [$W_3Se_4H_2(OH)(dmpe)_3$]($BPh_4$) have been determined by single crystal X-ray diffraction. These complexes share the structural features reported for other [$M_3Q_4$] compounds with an incomplete cubane type unit, as illustrated for the [**2**]$^+$ cation in Fig. 1, where the carbon atoms of the phosphine ligands have been omitted for clarity. The three metal atoms in all these clusters define an equilateral triangle with one capping and three bridging selenium ligands. If the metal–metal bonds are not considered, the coordination environment around each tungsten atom is pseudo-octaedral. Table 2 contains a list of the most relevant averaged bond distances for the cations [**1**]$^+$, [**2**]$^+$ and

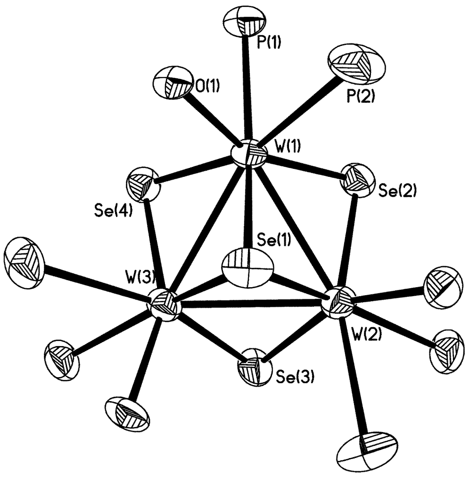

**Fig. 1** ORTEP representation of [**2**]$^+$ (50% probability ellipsoids) with atom numbering scheme. Carbon atoms of the phosphine ligands have been omitted for clarity.

**Table 2** Selected averaged bond distances (Å) for compounds [**1**]($BPh_4$), [**2**]($BPh_4$), [$W_3Se_4H_2(OH)(dmpe)_3$]($BPh_4$) and [$W_3Se_4Br_3(dmpe)_3$]($PF_6$)

| | [$W_3Se_4H_3(dmpe)_3$] ($BPh_4$) | [$W_3Se_4(OH)_3(dmpe)_3$] ($BPh_4$) | [$W_3Se_4H_2(OH)(dmpe)_3$] ($BPh_4$) | [$W_3Se_4Br_3(dmpe)_3$] ($PF_6$) ref. 12 |
|---|---|---|---|---|
| W–W | 2.819(5) | 2.820(13) | 2.819(6) | 2.8365(8) |
| W–$\mu_3$-Se(1) | 2.495(3) | 2.502(2) | 2.4923(6) | 2.4871(17) |
| W–$\mu_2$-Se(2)[a] | 2.467(6) | 2.464(4) | 2.462(3) | 2.4539(14) |
| W–$\mu_2$-Se(2)[b] | 2.462(2) | 2.444(6) | 2.458(4) | 2.4157(14) |
| W–P(1) | 2.484(9) | 2.509(11) | 2.483(9) | 2.523(4) |
| W–P(2) | 2.525(12) | 2.562(4) | 2.522(16) | 2.597(4) |
| W–O | | 2.030(13) | 2.07(8) | |

[a] W–$\mu_2$-Se distance *trans* to Mo–Y bond. [b] W–$\mu_2$-Se distance *trans* to Mo–P(2) bond.

[$W_3Se_4H_2(OH)(dmpe)_3$]$^+$ together with those of the trinuclear precursor [$W_3Se_4Br_3(dmpe)_3$]$^+$.

The W–W distances in all these cluster cations are consistent with a metal oxidation state of IV.[6] Substitution of bromine in [$W_3Se_4Br_3(dmpe)_3$]$^+$ by either hydrogen or an hydroxyl group shortens the tungsten–tungsten bond length by *ca.* 0.01 Å. Although neither the hydride ligands or the hydrogen atoms of the hydroxo ligand are detectable in the crystal structure, their presence is fully supported by the $^1$H and $^{31}$P NMR spectra. The $^{31}$P spectrum registered for [**1**]$^+$ when selective decoupling of all but the hydridic hydrogen nuclei, shows a splitting of the signals with $^2J_{PH}$ coupling constants of 47 and 30 Hz, which agrees within the experimental error with the values calculated from the $^1$H spectrum. In addition, the positions of the hydrogen atoms in [**1**]$^+$ can be also inferred by inspection of the structure, which reveals the existence of three vacant sites, one on each tungsten atom, at the positions occupied by the bromine atoms in the [$W_3Se_4Br_3(dmpe)_3$]$^+$ precursor. The metal–oxygen bond lengths of 2.07(8) and 2.030(13) Å for [$W_3Se_4H_2(OH)(dmpe)_3$]$^+$ and [**2**]$^+$, respectively, agree with the formulation of hydroxo ligands coordinated to tungsten. Thus, similar W–OH distances (2.100[6] Å) have been observed for the analogous sulfide complex [$W_3S_4(OH)_3$-$(dmpe)_3$]$^+$ while the M–$H_2O$ bond lengths in [$W_3S_4(PPh_3)_3$-$Cl_4(H_2O)_2$] are considerably longer (2.249(5) Å).[22] The replacement of an halide by either an hydroxo or a hydride group is also reflected in the tungsten-bridging selenide bond lengths. The W–$\mu_2$-Se bond distance *trans* to the phosphine in [$W_3Se_4Br_3(dmpe)_3$]$^+$ and [$W_3Se_4(OH)_3(dmpe)_3$]$^+$ are 0.04 and 0.02 Å longer, respectively, than the W–$\mu_2$-Se bond length *trans* to the bromine or the hydroxyl group. This asymmetry in the bridging selenide coordination is not observed in the hydride cluster [**1**]$^+$ due to the similar *trans* influences of the hydride and phosphine ligands. The remaining metal–ligand distances follow the same tendencies observed for the analogous sulfur trinuclear complexes.[11,21]

## The kinetics and mechanism of reaction of [$W_3Se_4H_3(dmpe)_3$]$^+$ with acids

In a previous paper,[11] we have shown that the [$W_3S_4H_3(dmpe)_3$]$^+$ cluster reacts with HX acids (X = Cl, Br) to form the corresponding [$W_3S_4X_3(dmpe)_3$]$^+$ complexes, the reaction being easily monitored by NMR spectroscopy. We have now monitored this reaction using the Se analogue [**1**]$^+$ and found that it also reacts with these acids in $CD_3CN$ and acetonitrile–water solutions according to eqn. (1).

$$[W_3Se_4H_3(dmpe)_3]^+ + 3\,HX \longrightarrow [W_3Se_4X_3(dmpe)_3]^+ + 3\,H_2;\ X = Cl, Br \quad (1)$$

Stopped-flow experiments in MeCN : $H_2O$ solution (1 : 1, v/v; 0.5 mol dm$^{-3}$ ionic strength adjusted with $KNO_3$; 25 °C) using a diode-array detector showed that the reaction of [**1**]$^+$ with both HCl and HBr according to eqn. (1) occurs with two kinetically resolvable steps. The experimental data were fitted with program GLINT to a model with two consecutive processes, which yielded the values of the rate constants for both steps ($k_{1obsSe}$ and $k_{2obsSe}$) and the spectra of the starting complex, the reaction intermediate **I** and the final reaction product (Fig. 2).

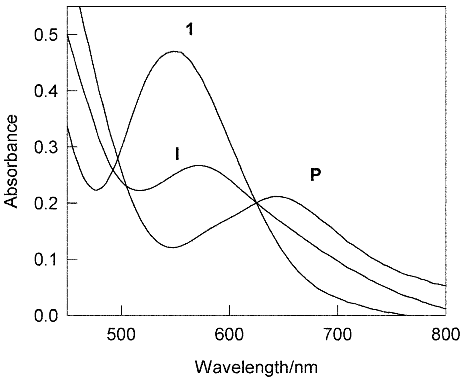

**Fig. 2** Spectra calculated for the starting complex (**1**), the reaction intermediate (**I**) and the final reaction product (**P**) from the spectral changes with time during the reaction of [**1**]$^+$ with HCl in MeCN–$H_2O$ (1 : 1, v/v).

The values of $k_{1obsSe}$ change linearly with the concentration of acid (eqn. (2)), although they are independent of the nature of the acid and remain unaffected upon addition of an excess of halide salt (see Fig. 3). The value derived for the second order rate constant $k_{1Se}$ is 12.0 ± 0.2 dm$^3$ mol$^{-1}$ s$^{-1}$. In contrast, $k_{2obsSe}$ does not change with the concentration of acid, although it is

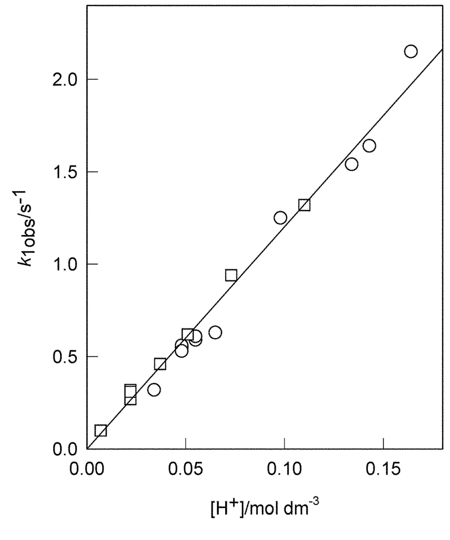

**Fig. 3** Plot of the observed rate constants for the first step in the reaction of the [$W_3Se_4H_3(dmpe)_3$]$^+$ cluster with acids in MeCN–water (1 : 1 v/v) at 25.0 °C. The plot includes data for the reaction with HCl (circles) and HBr (squares). For both acids, the plot includes the results obtained for the acid (HX) alone and the acid in the presence of an excess (0.25 M) of KX salt. The ionic strength was adjusted in all cases to 0.50 mol dm$^{-3}$ by adding the amount of $KNO_3$ required in each case.

also independent of the nature of the acid and of the concentration of added halide salt, a value of 0.024 ± 0.003 $s^{-1}$ being derived from the whole set of kinetic experiments.

$$k_{1obsSe} = k_{1Se}[HX] \qquad (2)$$

In the previous kinetic study using the analogous $[W_3S_4H_3(dmpe)_3]^+$ cluster,[11] three consecutive steps could be resolved and the mechanism in eqns. (3)–(6) was proposed. According to this mechanism, there is an initial attack by the proton to the W–H bond to yield a labile dihydrogen intermediate (eqn. (3)) that rapidly releases $H_2$ to form a coordinatively unsaturated complex (eqn. (4)). This complex adds water in the next step to form an aqua complex (eqn. (5)) that completes the reaction by substituting coordinated water by the $X^-$ anion (eqn. (6)). Depending on the acid concentration, the aqua complex is in equilibrium with variable amounts of its corresponding hydroxo complex $[W_3S_4H_2(OH)(dmpe)_3]^+$. In order to obtain a complete description of the reaction mechanism all the steps in eqns. (3)–(6) must be repeated for each W–H bond, which leads to the formation of the final reaction product $[W_3S_4X_3(dmpe)_3]^+$. The factor of 3 included in the rate constants appears as a consequence of the statistical kinetics at the three metal centers that makes reactions at the first W–H bond to occur with a rate constant three times higher than the experimentally determined values.

$$W_3S_4H_3(dmpe)_3{}^+ + H^+ \longrightarrow W_3S_4H_2(H_2)(dmpe)_3{}^{2+};\ 3k_{1S} \qquad (3)$$

$$W_3S_4H_2(H_2)(dmpe)_3{}^{2+} \longrightarrow W_3S_4H_2(dmpe)_3{}^{2+} + H_2;\ \text{fast} \qquad (4)$$

$$W_3S_4H_2(dmpe)_3{}^{2+} + H_2O \longrightarrow W_3S_4H_2(H_2O)(dmpe)_3{}^{2+};\ 3k_{2S} \qquad (5)$$

$$W_3S_4H_2(H_2O)(dmpe)_3{}^{2+} + X^- \longrightarrow W_3S_4H_2X(dmpe)_3{}^+ + H_2O;\ 3k_{3S} \qquad (6)$$

The most outstanding feature of this mechanism consists in the initial attack by the acid to the coordinated hydride, which is finally the causer of the acid-promoted substitution of $H^-$ by $X^-$. In the previous work with the W–S cluster, the proposal of attack at the hydride positions was based on theoretical calculations and on the lack of changes in the spectrum of the first reaction intermediate with the nature of the solvent.[11] Although a large difference in the energies corresponding to the protonation products resulting from attacks at the hydride and the $\mu_2$-$S^{2-}$ or $\mu_3$-$S^{2-}$ ligands was obtained for the W–S cluster, there is the possibility that substitution of S by Se lead to a change in the protonation site and that the initial acid attack occurs at a bridging $Se^{2-}$. However, additional evidence favouring attack at the hydride also for the W–Se cluster has been obtained in this work by measuring the $T_1$ relaxation time of the hydrides in the $[\mathbf{1}]^+$ cluster both in the absence and in the presence of an excess of HCl. The experiments were carried out in $CD_2Cl_2$ solution using HCl generated from $ClSiMe_3$ and MeOH, and the measurements with acid excess had to be limited at low temperatures, where the reaction is slow enough to allow the detection of the hydride signal for unreacted $[\mathbf{1}]^+$. The results are presented in Fig. 4 and indicate a significant decrease of the hydride relaxation time in the presence of acid, the minimum value ($T_{1min}$) decreasing from 0.68 to 0.52 s, which can be interpreted in terms of formation of a dihydrogen bond between the coordinated hydride and the acid.[23] If the excess of relaxation rate is assigned to formation of an adduct with an interaction of the type W–H ··· HCl and all the complex is considered to be converted to the adduct, a H ··· H distance of *ca.* 2.44 Å is obtained by application of eqn. (7),[24] where $r_{H\text{–}H}$ is the H ··· H distance in Å, $T_{1min}$ is the relaxation time corresponding to the dihydrogen interaction and $v$ is the working frequency of the NMR spectrometer. Although this distance is probably too large to be considered a real dihydrogen bond, it clearly reflects an interaction of the starting hydride with the acid and supports the initial attack at this position in the reactions of the $[\mathbf{1}]^+$ cluster with acids.

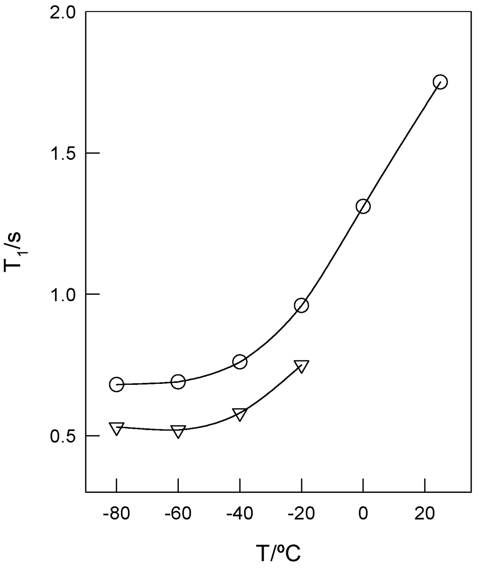

**Fig. 4** Plot of the temperature dependence of the $T_1$ values of coordinated hydrides in the $[\mathbf{1}]^+$ cluster in $CD_2Cl_2$ solution. The circles correspond to experiments with the complex alone and the triangles to experiments in the presence of an excess of HCl.

$$r_{H\text{–}H} = 5.815\sqrt[6]{\frac{T_{1min}}{v}} \qquad (7)$$

Although the structural similitude of the $W_3S_4$ and $W_3Se_4$ clusters and the analogies observed in the kinetics of reaction of both compounds with acids makes reasonable to assume that a common mechanism operates for both compounds, the reaction of the $W_3S_4$ cluster occurs with three kinetic steps and only two steps can be resolved for the Se analogue. Nevertheless, under certain experimental conditions the observed rate constants for the first step in the reaction of the S cluster were found to be smaller than $k_{2S}$ and only two kinetic steps ($k_{1S}$ and $k_{3S}$) could be resolved.[11] This occurs, for example, when the solvent is a 1 : 1 mixture of water and acetonitrile and so, it is tempting to consider that the same circumstances also apply to the reactions of $[\mathbf{1}]^+$ and that the value of $k_{2obsSe}$ should be compared with $k_{3S}$ and not with $k_{2S}$. Actually, the value of $k_{1Se}$ is only 3.6 times smaller than $k_{1S}$, whereas $k_{2obsSe}$ is only 1.5 times higher than $k_{3S}$; if $k_{2Se}$ and $k_{2S}$ were also close to each other, the value of $k_{2Se}$ should be around 0.3 $s^{-1}$, certainly too close to the values of $k_{1obsSe}$ in Fig. 3 to allow the measurement of the $k_{2Se}$ step. As a consequence, biphasic kinetics with rate constants $k_{1Se}$ and $k_{3Se}$ would be observed for the Se cluster, in agreement with the experimental findings.

However, for these considerations to be valid, the spectrum for the intermediate **I** in Fig. 2 should coincide with that of the $[W_3Se_4(H_2O)_3(dmpe)_3]^{4+}$ complex. Although this species has not been isolated, its spectrum can be obtained by treatment of the $[\mathbf{2}]^+$ hydroxo complex with $HNO_3$ in the same solvent of the kinetic experiments. The spectrum obtained in this experiment shows a band centred at 620 nm, clearly different from the spectrum of **I** in Fig. 1. This difference led us to study the kinetics of the substitution reaction in eqn. (8) to obtain a direct measurement of the rate of substitution of coordinated water.

$$W_3Se_4(OH)_3(dmpe)_3{}^+ + 3H^+ + 3X^- \longrightarrow W_3Se_4X_3(dmpe)_3{}^+ + 3H_2O \qquad (8)$$

For this purpose, a solution of [**2**]$^+$ in neat MeCN (band centred at 590 nm) was mixed in the stopped-flow instrument with aqueous solutions of HCl and HBr containing the amount of $KNO_3$ required to adjust the ionic strength in the mixed solution to 0.5 mol dm$^{-3}$. In all cases the spectrum obtained immediately after mixing displays the band at 620 nm corresponding to the aqua complex, although there are slower spectral changes associated to the formation of the halogen complexes. These changes can be fitted by a single exponential and the resulting values of the observed rate constant are independent of the concentration of added acid within the range 0.1–0.5 mol dm$^{-3}$: $k_{Cl} = 0.63 \pm 0.02$ s$^{-1}$ and $k_{Br} = 0.17 \pm 0.01$ s$^{-1}$. Both values are significantly larger than $k_{2obsSe}$ and indicate that the aqua complex is not formed at a detectable extent during the reaction of the hydride complex with acids. For the reaction in eqn. (1), intermediate **I** should then correspond to a coordinatively unsaturated species analogous to that proposed for the S analogue. After formation of this intermediate, it reacts with water with a rate constant of 0.024 s$^{-1}$, although the aqua complex does not accumulate during the process because it reacts more rapidly with the anions to form the halogen complexes. Direct attack of the $X^-$ anions to **I** appears unlikely because the rate of disappearance of this intermediate is independent of the nature of $X^-$.

## Conclusion

The kinetic results in the present paper confirm the existence of acid-promoted substitution in the $[W_3Q_4H_3(dmpe)_3]^+$ clusters (Q = S, Se) and provide additional support to the mechanism previously proposed.[11] According to this mechanism, the formal substitution of the coordinated hydrides is a consequence of the acid attack to the hydride ligands with generation of a labile dihydrogen complex. This mechanism clearly contrasts with the well-established acid-promoted substitutions in related Fe–S clusters,[25–27] for which the acceleration of the substitution process in the presence of acid is caused by acid attack to a bridging sulfide. The close values of the kinetic parameters for the reaction with acids of the $[W_3Q_4H_3(dmpe)_3]^+$ clusters of S and Se also rule out the possibility of initial acid attack to a bridging $Q^{2-}$ ligand followed by migration of the proton to the hydride ligand; in that case significantly different rate constants for the first step in the reactions of both complexes should be found.

Once confirmed that the reaction with acids of the $[W_3Q_4H_3(dmpe)_3]^+$ clusters (Q = S, Se) occurs through a similar mechanism, it is possible to compare the values of the rate constants found for the reactions of both compounds. Comparison of the values measured in the present work (25 °C, 1 : 1 MeCN–$H_2O$ solvent) with those reported[11] for the S analogue under the same conditions indicate that the rate constants for both the initial attack by the acid (eqn. (3)) and water attack to the coordinatively unsaturated intermediate (eqn. (5)) are faster in the S complex ($k_{1S} = 3.6k_{1Se}$; $k_{2S} = 11.7k_{2Se}$), whereas the substitution of coordinated water is faster in the Se cluster ($k_{3Se} = 31k_{3S}$ for reaction with $Cl^-$ and $k_{3Se} = 10k_{3S}$ for reaction with $Br^-$).

It has been pointed out above that the presence of traces of water during the crystallization of [**1**]$^+$ leads to the substitution of hydride ligands by hydroxyl groups, with formation of the mixed hydride–hydroxo complexes $[W_3Se_4H_2(OH)(dmpe)_3]^+$ and $[W_3Se_4H(OH)_2(dmpe)_3]^+$. Kinetic experiments carried out by mixing in the stopped-flow instrument an acetonitrile solution of [**1**]$^+$ with water reveal spectral changes that can be fitted by a single exponential with $k_{H_2O} = (3.0 \pm 0.1) \times 10^{-3}$ s$^{-1}$. Although the final spectrum still shows the band typical of the starting hydride, the spectral changes clearly indicate a decrease in the intensity of this band and an absorbance increase at wavelengths close to 580–620 nm, consistent with partial conversion to aqua or hydroxo complexes. Thus, it is not surprising that a solid with average composition $[W_3Se_4H_2(OH)(dmpe)_3]^+$ could be isolated by crystallization of [**1**]$^+$ in the presence of water. These observations indicate that the [**1**]$^+$ hydride is basic enough to react with water according to eqn. (1), which contrasts with the behavior of the analogous $[W_3S_4H_3(dmpe)_3]^+$ cluster that is stable in MeCN–$H_2O$ solutions (1 : 1, v/v) for days. Despite the higher basicity of [**1**]$^+$ with respect to the related S cluster, the rate constant for acid attack is somewhat smaller ($k_{1S} = 3.6k_{1Se}$), which is somewhat surprising when the general tendency of the rate of proton transfer processes to increase with the acidity difference between the acid and the base is considered.[28] However, similar anomalous dependences of the rate of protonation with the acidity difference between the reagents has been previously found for the reaction of other hydride complexes with acids.[29–31]

For the $[W_3S_4H_3(dmpe)_3]^+$ cluster, it was proposed[11] on the basis of theoretical calculations that the slow addition of water to the coordinatively unsaturated intermediate (eqn. (5)) is a consequence of the stabilization of this intermediate by an increased donation of electron density from the μ-$S^{2-}$ ligand *trans* to the vacant site. Substitution of S by the better electron donor Se appears to favor this stabilization, thus resulting in an increased activation barrier for water addition and making the value of $k_{2Se}$ an order of magnitude slower than $k_{2S}$. On the other hand, the higher lability of the aqua Se cluster towards substitution with halide ions with respect to the S analogue (eqn. (6)) is in agreement with previous findings for the $[M_3Q_4(H_2O)_9]^{4+}$ complexes,[8,9] for which a higher *trans* labilising effect of the μ-$Se^{2-}$ ligands has been reported. The different values of $k_{Cl}$ and $k_{Br}$ for substitution of coordinated water also deserve some comment. For the $[M_3Q_4(H_2O)_9]^{4+}$ complexes, substitutions of water by $X^-$ in aqueous solution occur with second order kinetics and have been proposed to occur through a dissociative interchange mechanism, although water exchange occurs through an associative interchange.[7] Our results for substitution of coordinated water by $Cl^-$ and $Br^-$ are consistent with the operation of the latter mechanism, although only the limiting rate constant for the interchange, *i.e.* the exchange of water by $X^-$ in the outer-sphere complex, would be measured under the experimental conditions used. This is probably caused by the combined effect of the higher concentrations of entering anion used and the higher stability of the outer sphere complex in the mixed solvent used, which has a dielectric constant significantly lower than water. According to this mechanism, the ordering $k_{Cl} > k_{Br}$ would be a consequence of the faster associative interchange with the smaller entering ligand. For the related S compound, the values obtained[11] for $k_{Cl}$ (0.020 s$^{-1}$) and $k_{Br}$ (0.017 s$^{-1}$) show smaller differences but they still support the present explanation. However, these conclusions about the mechanism of the substitution process must be taken with care because the reaction in eqn. (8) (and the similar one with the S cluster) occurs under conditions of reversible equilibrium and the observed rate constants include contributions from both the forward and backward processes. Further work must be done in the future to determine the relative contribution of both processes and to gain insight into the details of the mechanism of substitution in these compounds

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