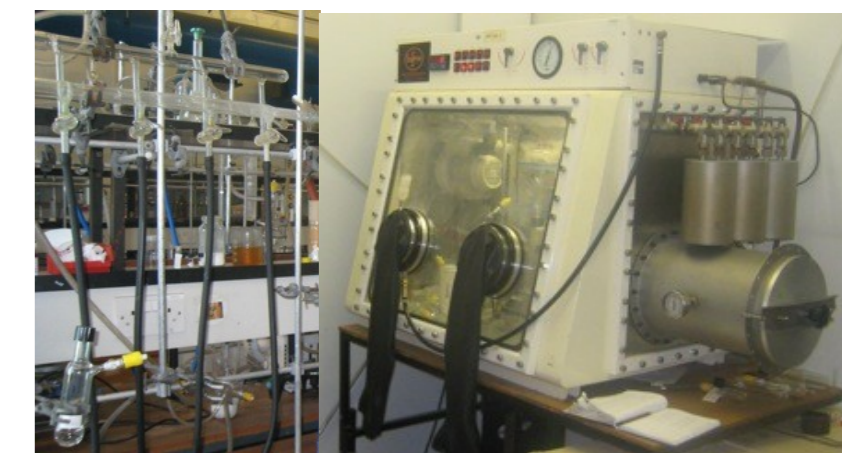


The Reactivity of Electron-Rich Molecular Metal Oxides



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Introduction and Aims

Polyoxometalates (POMs) are molecular anions made up of metal and oxygen atoms and are of great interest for catalysis and materials chemistry.

Theoretical studies suggest that the magnetic states of POMs capped by magnetic ions should be switchable by controlling the number of non-bonding electrons in the POM, i.e. by reduction / oxidation.

The aims were to:

- Synthesis a range of POMs by binding different elements to the surface of reduced $[\text{PMo}_{12}\text{O}_{40}]^{(3+n)-}$, where n electrons have been added.
- To add and remove electrons from the capped species in order to switch spin states.

Background Chemistry

The Keggin type POM $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ is readily reduced to the $[\text{PMo}_{12}\text{O}_{40}]^{(3+n)-}$ making it able to bind cations as capping groups.

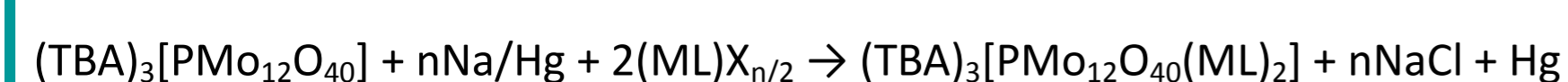
If the capping group has a spin and couples to another capping group with a spin they can be tuned by modifying the electron density in the core.

The POM being used has the advantage of having a central phosphorus atom which gives us an easy way of following these reactions by ^{31}P NMR spectroscopy.

These reactions are self indicating as there is a change in colour from yellow to dark blue which indicates that the POM has been reduced. This change is due to the delocalised electrons in the POM core.

Reactions of Reduced POM with Metal Halides

General equation for these reactions is



The first reactions required the reduction of the POM followed by the addition of the metal halide (VOCl_3 , SbCl_3 , TeCl_4 and FeCl_2)

Key to Atom Colours

- Red—Oxygen
- Blue—Molybdenum
- Purple—Phosphorus
- Yellow—Vanadium
- Brown—Antimony

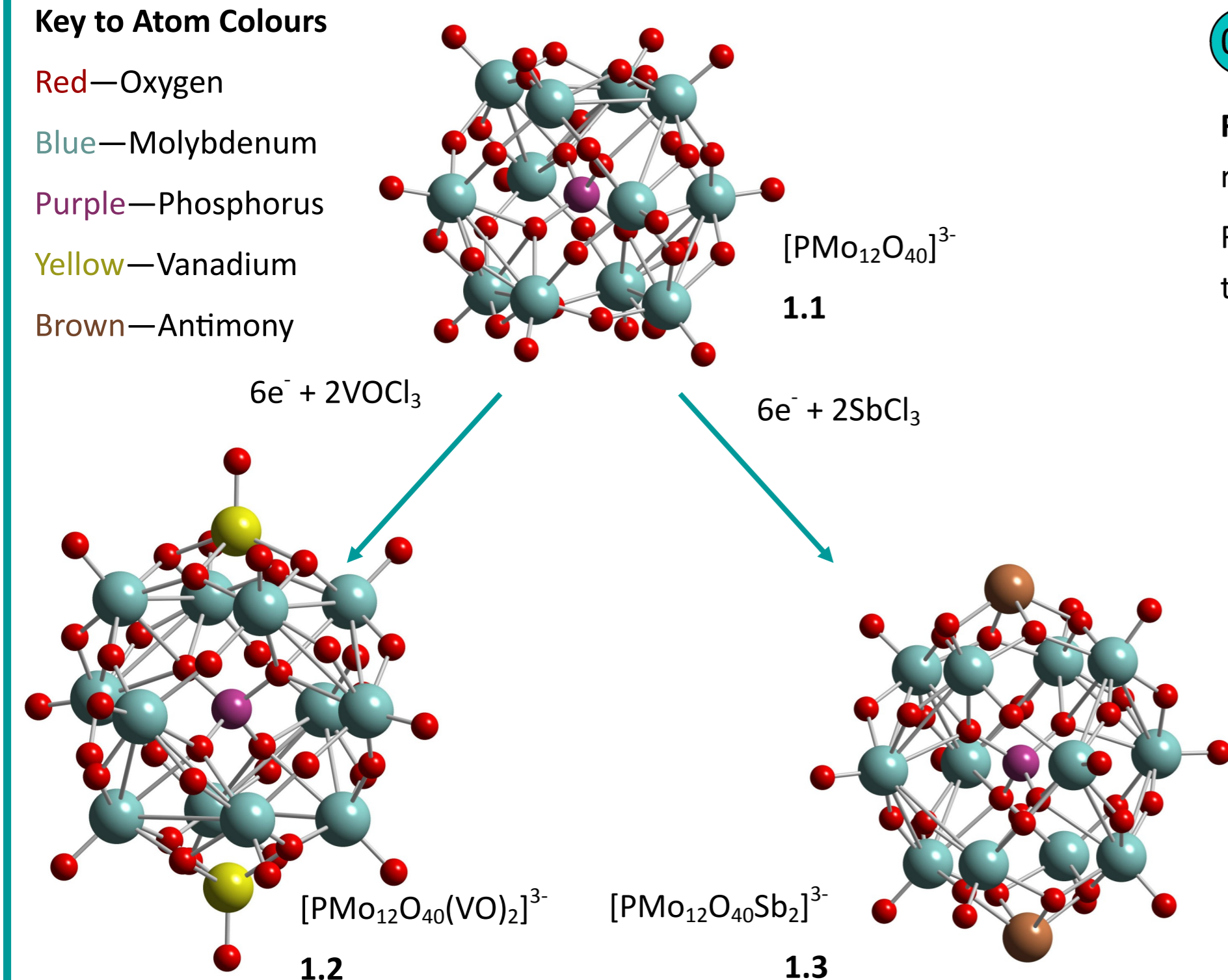


Figure 1. Structures of capped and uncapped POMs

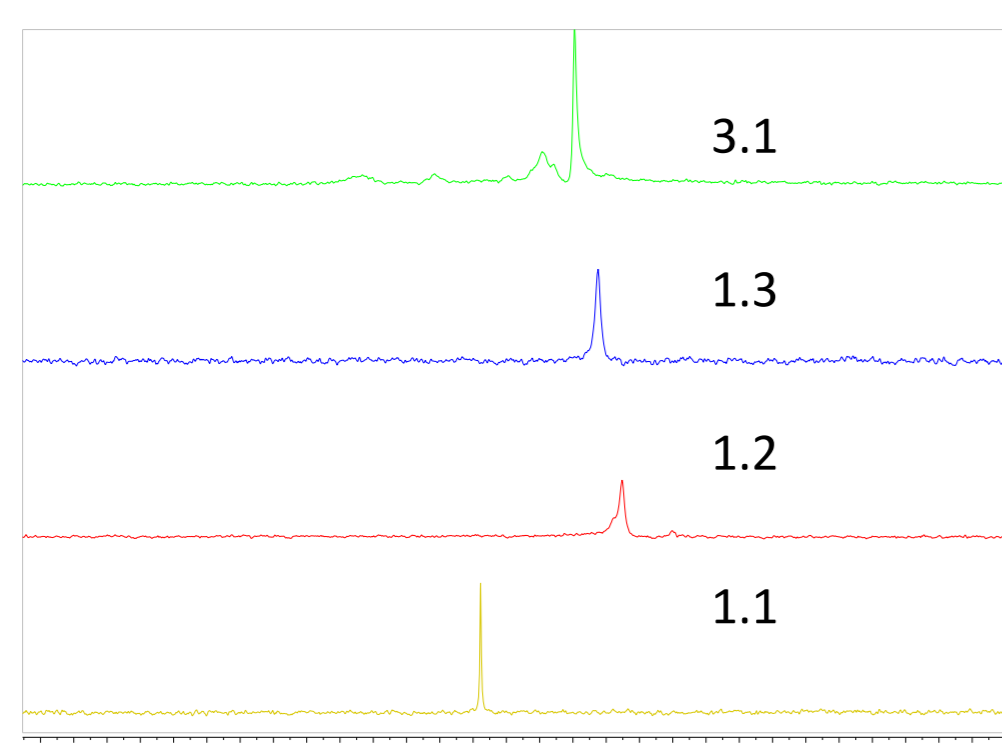


Figure 2. ^{31}P NMR spectra

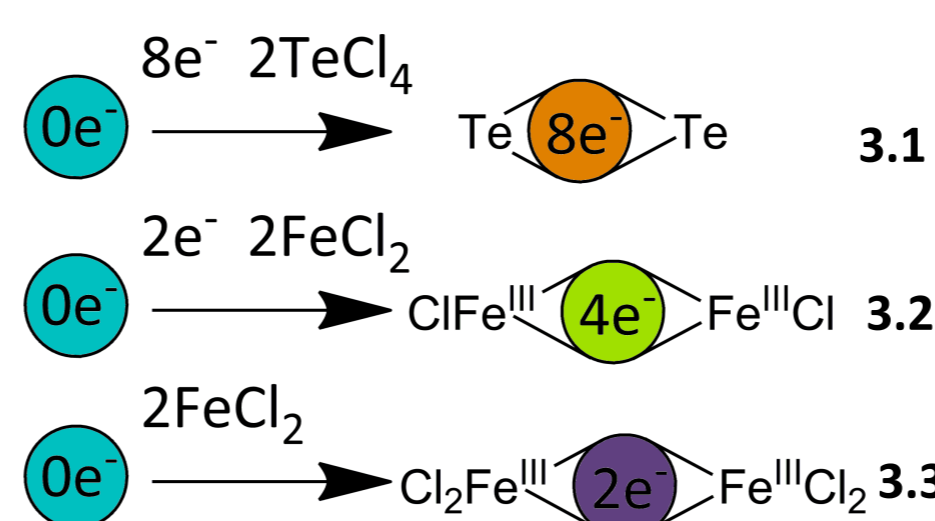


Figure 3. Schematics of the attempted reactions and targeted products.

FeCl_2 was found to reduce the POM in the absence of metal amalgam.

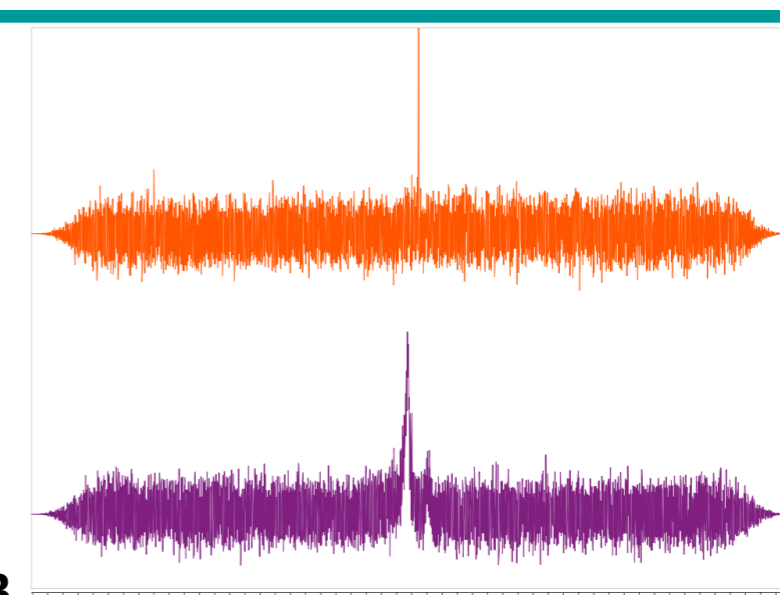


Figure 4. NMR spectra of products from reactions 3.2 (upper) and 3.3 (lower).

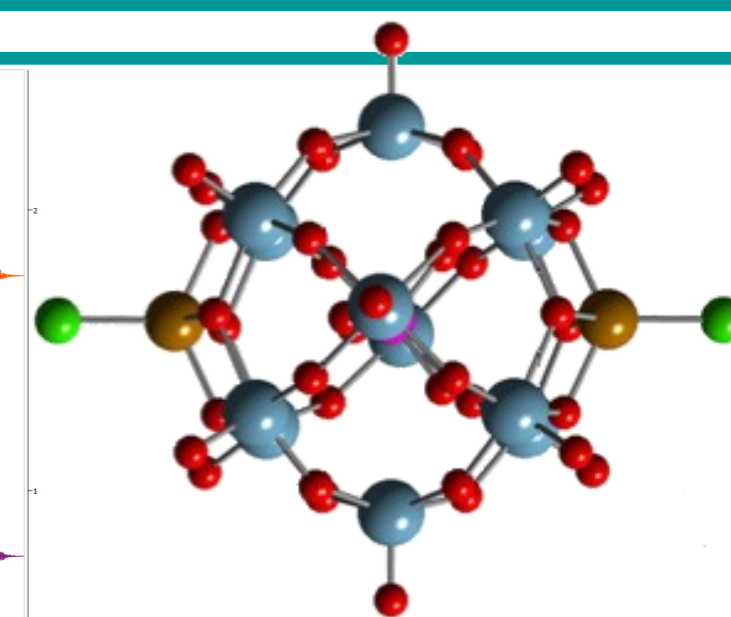


Figure 5. Structure of isolated species $[\text{PMo}_{12}\text{O}_{40}(\text{FeCl})_2]^{4-}$

Key to Atom Colours

- Red—Oxygen
- Blue—Molybdenum
- Purple—Phosphorus
- Yellow—Chlorine
- Brown—Iron

Redox Reactions for Spintronics

The further reduction of the $[\text{PMo}_{12}\text{O}_{40}(\text{VO})_2]^{3-}$ by addition of 2 more electrons to the core theoretically should give a species with the vanadium spins ferromagnetically coupled.

Equation

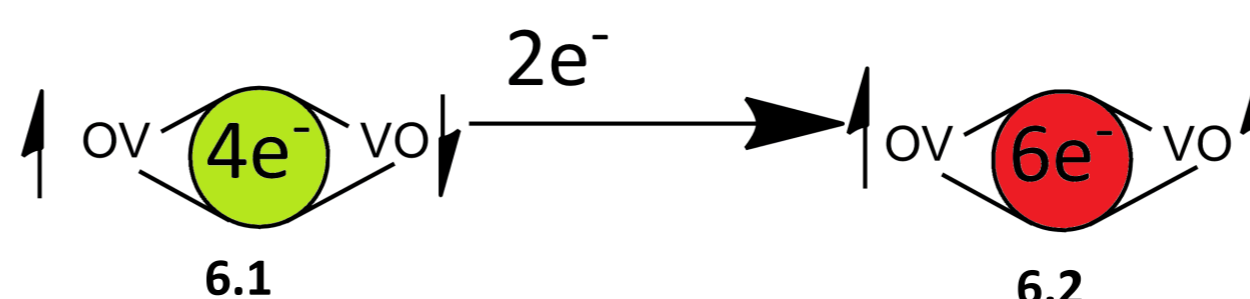
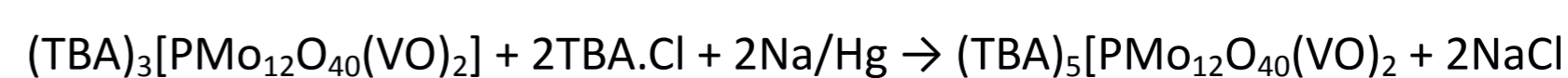
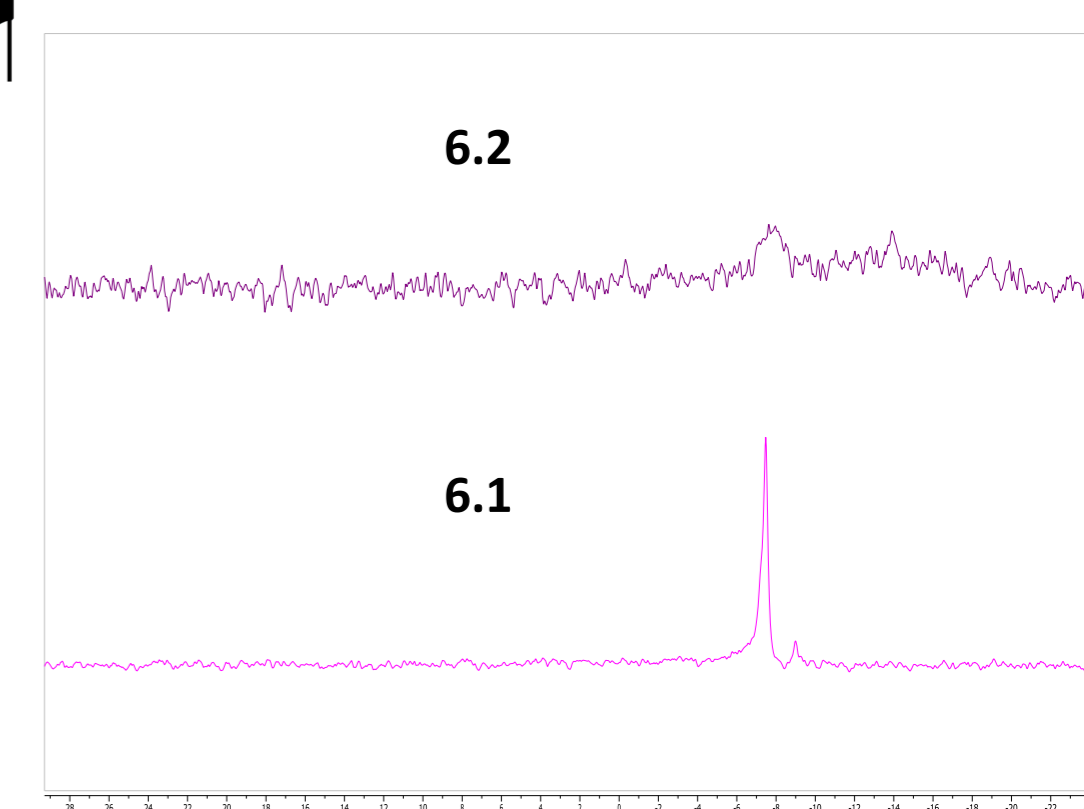


Figure 6 (Above). Schematic of the reduction of the Vanadium capped POM by 2 electrons showing the ferromagnetic coupling of the spins.

Figure 7 (Right). ^{31}P NMR spectra of 6.1 and reduction product 6.2. The line broadening suggests that the magnetism of the sample has increased.



The ability to switch spin states of the POM (antiferromagnetic to ferromagnetic) by injecting or removing charge from the core provides access to molecular computing and storage devices using spintronics.

Results and Further Work

The addition of electrons to $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ followed by the addition of the metal halides provided access to capped POMs which were air sensitive and prone to oxidation in air.

An issue arose with the scale up of the vanadium reaction as it was more difficult to control the degree of reduction (i.e. Redox state). This requires further investigation, and could be due to kinetics.

The reduction of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ with FeCl_2 was an interesting result and should provide access to new chemistry of these systems. Further work is underway to fully characterise the product.

The ^{31}P NMR of the further reduction of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ to $[\text{PMo}_{12}\text{O}_{40}]^{5-}$ indicated that we had been successful in adding the electrons to the core. Magnetic measurements will be carried out at ICMol in Valencia by the Coronado group.

Acknowledgements

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References:

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