Inorganica Chimica Acta, 198–200 (1992) 319–336

New trends in polyoxometalate chemistry, toward large polyanions, toward nitrosyl-substituted polyanions

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Abstract

The chemistry of polymolybdates and polytungstates demonstrates various facts which may be put together with some value. (1) The variety of compounds is quite large, even if the oxidation number of the metal is maintained at 6 and then provides an octahedral surrounding and a polyanion surface covered by oxygen. (2) Taking the case of molybdenum, and going from water toward non-aqueous solvents, it is clear that many other structures can be found or stabilized by using that type of solvent; also the occurrence of the tetrahedron becomes more frequent. (3) Molybdenum offers another facet of reactivity, due to its easy reduction. (4) The formal oxygen substitution of an M–O bond by a nitrogen or an oxygen containing ligand, such as nitrosyl, phenyldiazenido, alcoolate, oximate, amidoximate, an anion deriving from an organic acid, etc., opens the door to a wide range of reactions; moreover it provides some new structural types unknown for the unsubstituted polyanion. The catalytic effect of polyoxometalates has been often underlined and currently is under active study. There is no doubt that the development of polyoxometalate chemistry will help in the understanding of these complex catalytic reactions, and will maybe provide other efficient catalytic procedures.

Historical background and presentation of the subject

The first heteropolymetalate was very likely prepared by Berzelius in 1826 when he mixed ammonium molybdate and phosphoric acid [1]. However the accurate nature of the compound was not known. Today it is clear that $(NH_4)_3[PMo_{12}O_{40}]$ was prepared. The prefix hetero in the name heteropolymetalate is used to underline that there is another atom than tungsten or molybdenum encapsulated inside the polyanionic cage. Although the use of polymolybdates was introduced in chemical analysis quite early, the first correct description of its formula was given later by Marignac who studied in 1862 the analytical compositions of silicotungstic acids and their salts [2]. For many years heteropolytungstates or heteropolymolybdates were used either to determine quantitatively the content of a chemical sample in ammonium, in phosphorus, or in silicon.

The first attempt to propose a structure was made by Miolati and Pizzighelli who used Werner's idea on coordination [3]. This was extensively developed by Rosenheim. The basic idea was an hexaligated heteroatom surrounded by MO_4 or M_2O_7 groups. This was questioned by Pauling who realized that Mo^{6+} and W^{6+} have a radius ideal for hexacoordination with oxygen atoms as ligands [4]. However Pauling only considered the possibility of corner sharing octahedra and based a new structural proposal on the principle of octahedrally surrounded metal atoms. It was shown later to be wrong when Keggin made the first X-ray structure determination of the silicododecatungstic acid $H_4[SiW_{12}O_{40}]$; this work was a real accomplishment since it was based upon powder photographs [5].

Although several groups were concerned with the study of polyoxometalate in solution, using electrochemical methods quite extensively, the structural investigation developed very slowly. Nowadays, with the use of X-ray automated diffractometer and of NMR techniques, particularly on ^{183}W which has a 1/2 spin, it is much easier to provide a full and accurate description of homo- and heteropolytungstates. Quite a number of groups are active in the field. However the synthesis is still a difficult problem and the identification of compounds in solution remains a challenge because equilibria between several compounds often, not to say always, occur. There are two constant difficulties, to adjust the concentration and to adjust the pH if water is used as a solvent. Moreover the general question may be raised about the true relationship between a crystallized species and compounds actually existing in

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solution. A very nice review of the field is given in ref. 6.

The Keggin structure is based upon a set of twelve octahedra sharing edges and corners and wrapped around a central heteroatom which may be silicon, phosphorus, arsenic, germanium, boron... In the case of arsenic, it may be arsenic(III) as well as arsenic(V). If arsenic(III) is involved in the formation of a heteropolymetalate, then the cage of twelve octahedra cannot be completed because of the lone pair of arsenic. The obtained compound $[HAs^{III}W_9O_{33}]^{6-}$ contains only nine metal atoms [7].

One then may think about using $[As^{III}W_9O_{33}]^{6-}$ as a building block to get larger structures. Indeed it is known that two '$P^VW_9O_{34}$' groups make the so-called Dawson structure by condensation [8]. One then could think about a somewhat similar procedure starting from $[As^{III}W_9O_{33}]^{6-}$ to build large structures.

This review will first describe arseno(III)polyoxotungstates, following as a conducting thread an increasing As^{III}/W ratio. Then, because compounds with a large number of tungsten atoms will be encountered, the case of phospho(V)polyoxotungstate will be looked at and very large species will be described. In other words, one could give a secondary title to this review: "How large can a polytungstate be?".

The Keggin structure and derived compounds

The preparation of the basic heteropolytungstate is very simple. Tungstate is mixed with phosphate. The solution is acidified and one gets immediately the tetracontaoxophosphododecatungstate(3−) $[PW_{12}O_{40}]^{3-}$ [1]. It clearly contains phosphorus(V).

$$12WO_4^{2-} + H_3PO_4 + 21H^+ \longrightarrow [PW_{12}O_{40}]^{3-} + 12H_2O$$

It will be recognized that the condensation actually occurs in rather acidic medium. The same compound may be prepared with arsenic(V) but it is sensitive to hydrolysis. In a similar way, when the pH of a mixture of tungstate and silicate is lowered, one gets the tetracontaoxosilicotungstate(4−) [9].

$$12WO_4^{2-} + SiO_3^{2-} + 20H^+ \longrightarrow [SiW_{12}O_{40}]^{4-} + 10H_2O$$

This synthetic method is straightforward and quite general.

However it turned out that Souchay *et al.* prepared an isomer of $[SiW_{12}O_{40}]^{4-}$. This new compound was formed by changing the order of reagents. The silicate was added after the acid instead of adding the acid after the silicate [10a].

To understand this, one first must explain where the isomery comes from, i.e. one must discuss the structure of the Keggin polytungstate, and one then will come back and look carefully at synthetic conditions.

The structure of the Keggin polytungstate consists of four W_3O_{13} groups arranged around the heteroatom, P^V, As^V, Si, Ge, by sharing vertices in such a way that the resulting species has a T_d symmetry (Fig. 1(a)) [5]. In the W_3O_{13} group, tungsten atoms are octahedrally surrounded by oxygen atoms, and the three octahedra share edges, two by two, so that they have a common oxygen vertex which also is a vertex of the oxygen tetrahedron surrounding the central heteroatom. Four W_3O_{13} groups bring four such oxygens which are then bridging four atoms, three tungstens and the central heteroatom.

Some chemists prefer to give a preferential role to the central heteroatom, considering that it is ligated by twelve WO_6 octahedra. We prefer to adopt the opposite view, that is to consider the cage made by twelve octahedra which is then filled up by the heteroatom. The first view has the advantage of remaining close to the synthetic pathway. The second one is preferred because the twelve octahedra cage may be built up without the heteroatom inside; actually it then

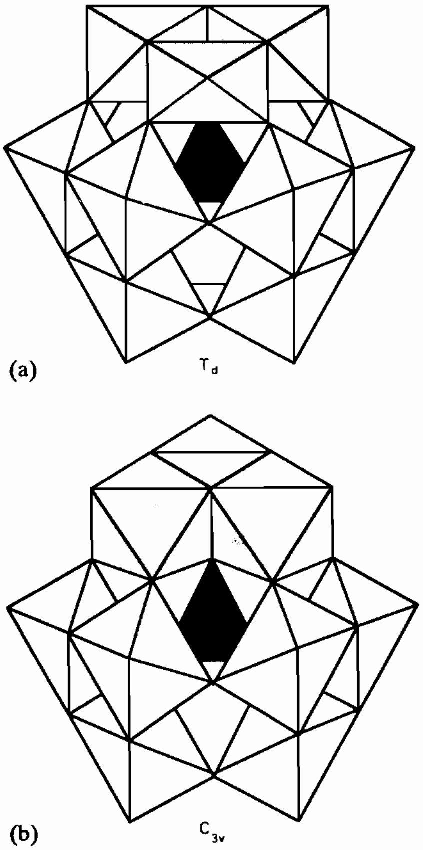

Fig. 1. Drawings of both α- and β-isomers $[XW_{12}O_{40}]^{n-}$: (a) the Keggin structure of T_d symmetry; (b) the Sasaki structure of C_{3v} symmetry. The central XO_4 tetrahedron is darkened. There is a turn of 60° of the shadowed W_3O_{13} group between both isomers.

contains two hydrogen cations which cannot be exchanged with the surrounding solution, being then trapped in, and the species is given the formula $[H_2W_{12}O_{40}]^{6-}$ [11].

This Keggin structure is also commonly called the α-isomer.

The size of the octahedron WO_6 and oxygen–oxygen distances are such that one W_3O_{13} group may be rotated by 60° (Fig. 1(b)). Each octahedron of this turned group is now joined to two octahedra of another W_3O_{13} group. The symmetry of the polyanion is consequently lowered to C_{3v}. This structure was solved by Sasaki and coworkers [10b] and it is commonly called the β-isomer.

Of course one might think about formally turning the three other W_3O_{13} groups also by 60°, one after the other one. This would lead to the other isomers called γ, δ, and ϵ. Although it is not in the scope of this paper to discuss this point, it is worth mentioning it and underlining that four isomeric structures are known, α, β, γ, ϵ.

Now we can return to the synthetic method. Actually the synthesis starts with a fairly high pH and goes down to a fairly low pH. Looking carefully at the various stages of acidification, one can establish the occurrence in solution of a range of compounds, some of them can be isolated and crystallized, some of them being just characterized by their electrochemical properties.

It turns out that the first step of acidification is $[HSiW_9O_{34}]^{9-}$ which has the β-structure [12]. This means that it formally derives from the β-$[SiW_{12}O_{40}]^{4-}$ by withdrawing three tungsten atoms from three different 'normal' W_3O_{13} groups, i.e. these three withdrawn tungsten atoms are on the opposite side with respect to the 60° rotated group which remains complete (Fig. 2). Consequently the four vertices of the central tetrahedron surrounding the heteroatom are still occupied by oxygen atoms bridging the heteroatom and tungsten atoms, one μ_4-bridge, and three μ_3-bridges. It is possible to isolate the α-form of $[SiW_9O_{34}]^{10-}$; however the synthetic pathway is different, we shall come to this point later on. The complete Keggin structure is formed from β-$[SiW_9O_{34}]^{10-}$ by adding tungsten atoms. It has been proposed that at the β-$[SiW_{11}O_{39}]^{8-}$ stage, the internal migration of one tungsten atom transforms the β-$[SiW_{11}O_{39}]^{8-}$ structure into α-$[SiW_{11}O_{39}]^{8-}$. If then one tungsten atom is added to β-$[SiW_{11}O_{39}]^{8-}$ before internal migration, one gets the β-isomer isolated by Souchay and studied by Sazaki [10]. If one tungsten atom is added to α-$[SiW_{11}O_{39}]^{8-}$, that is after the internal migration, one gets the α-isomer described by Keggin.

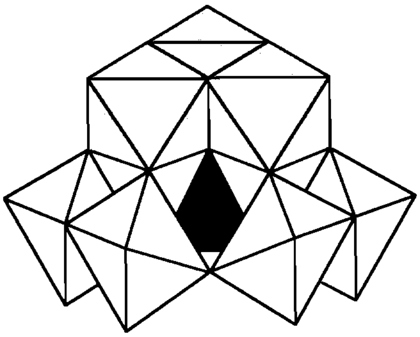

Fig. 2. $[SiW_9O_{34}]^{10-}$ polytungstate derived from the β-isomer by removing three tungsten atoms from the side opposite to the turned W_3O_{13} group.

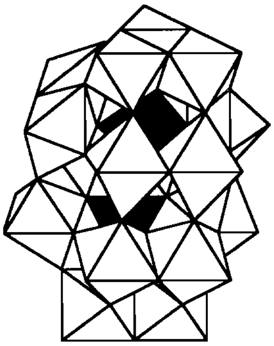

Fig. 3. $[P_2W_{18}O_{62}]^{6-}$ polytungstate called Dawson structure. PO_4 tetrahedrons are darkened.

Now, taking α-$[SiW_{12}O_{40}]^{4-}$, and by gently increasing the pH in a very controlled manner, it may be degraded into α-$[SiW_9O_{34}]^{10-}$ [13]. As for the β-isomer $[SiW_9O_{34}]^{10-}$ discussed above, three tungsten atoms belonging to three different W_3O_{13} groups have been withdrawn.

In the case of phosphorus(V) two such $[PW_9O_{34}]^{9-}$ are fused to build up the so-called Dawson structure by further condensation (Fig. 3) [8]. Of course three isomers are possible, depending on the turn of the W_3O_{13} top group, i.e. no turned top group isomer, one turned top group isomer, two turned top groups isomer. This will not be discussed herein any further.

In all preceding cases, the central heteroatom is tetrahedrally surrounded by four oxygen atoms. This is no longer possible if arsenic(III) is involved since the lone pair of arsenic(III) must remain free and needs some space. Consequently the acidification of a mixture of WO_4^{2-} and As_2O_3 yields $[As^{III}W_9O_{33}]^{6-}$ (Fig. 4). Rosenheim first isolated that polyanion as a potassium salt [7]. In solution, using various divalent metals or an excess of tungsten, it may further condensate to yield a larger species. This is what we are now going to consider, following as a guideline an increasing As/W atom ratio.

Ratio As/W=1/18. The $[AsH_2W_{18}O_{60}]^{7-}$ polyanion

A mixture of tungstate WO_4^{2-} and of arsenic(III) oxide As_2O_3 in a ratio As/W = 1/20, expressed in atoms,

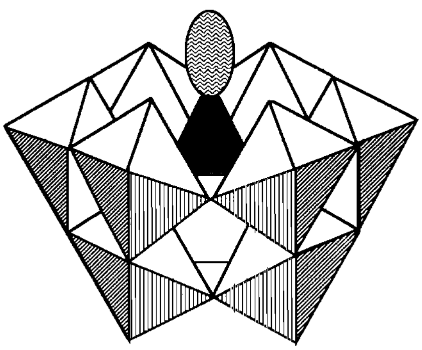

Fig. 4. $[As^{III}W_9O_{33}]^{9-}$ polytungstate; the arsenic(III) lone pair prevents the closing of the structure by a W_3O_{13} group. The nine tungsten atoms are distributed in two layers, one with three tungsten atoms, the other one with six tungsten atoms located at the vertices of an hexagon.

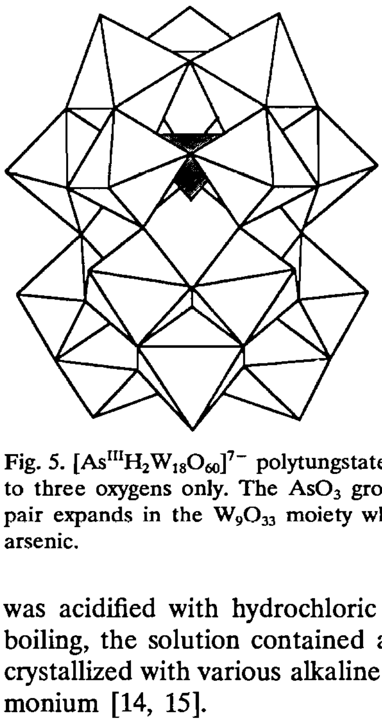

Fig. 5. $[As^{III}H_2W_{18}O_{60}]^{7-}$ polytungstate; the arsenic(III) is bound to three oxygens only. The AsO_3 group is darkened. The lone pair expands in the W_9O_{33} moiety which does not contain any arsenic.

was acidified with hydrochloric acid to pH = 4. After boiling, the solution contained a polyanion which was crystallized with various alkaline cations, including ammonium [14, 15].

$$36WO_4^{2-} + As_2O_3 + 58H^+ \longrightarrow 2[H_2AsW_{18}O_{60}]^{7-} + 27H_2O$$

An X-ray study was carried out on the ammonium salt for which chemical analysis gave the $7NH_4/1As/18W$ composition.

The crystallographic study showed that the polyanion is made of one unit AsW_9O_{33} and one unit W_9O_{33} (Fig. 5). They are fused and share six oxygen atoms. The polyanion $[AsW_{18}O_{60}]^{9-}$ has a C_{3v} symmetry. The existence of seven ammonium cations revealed by chemical analysis raised an electroneutrality problem. In order to establish the electroneutrality, it was necessary to consider the occurrence of two hydrogen cations which were obviously not seen by X-rays. Unfortunately it was also impossible to find them by chemical titration with a base. It was then assumed that they were trapped inside the moiety which does not contain arsenic. To check this, a ^1H NMR study was undertaken on a dimethyl sulfoxide (99.95 deuterated) solution of selected single crystals. Three lines showed up at chemical shifts of 4.5, 2.7 and 1.0 ppm with respect to the DMSO proton, with relative intensities 14:1:16. This fits well with the formula $(NH_4)_7[AsH_2W_{18}O_{60}] \cdot 16H_2O$. Clearly there was a separate peak at 2.7 ppm for those two hydrogen atoms displaying their special nature. In order to check further the structure of the compound, a ^{183}W NMR study on the same solution was carried out. Each W_9 group, the As containing one as well as the H containing one, is made of one group of three equivalent tungsten atoms and one group of six equivalent tungsten atoms. Those groups are in planes perpendicular to the ternary axis of the polyanion. One then should get four peaks, two of relative intensity 1 and two of relative intensity 2. This is what was observed [15].

Although the moiety $H_2W_9O_{33}$ has three oxygen atoms looking toward the inside of the W_9 basket, there are only two hydrogen atoms, so that strictly speaking the polyanion has no ternary axis. The equivalence of hydrogen atoms and this one of tungsten atoms on the NMR time scale suggest that those two hydrogen atoms move around in the cavity. However they cannot be attracted outside it by OH^- anions, as mentioned earlier.

The size of a hydrogen atom is such that the H_2W_9 moiety looks rather empty in front of the AsW_9 moiety so that the arsenic lone pair can find enough space to expand. It is clear that, due to steric hindrance of two lone pairs facing each other, it is not possible to make the $[As_2W_{18}O_{60}]^{6-}$ compound.

To be accurate, one must say that polyanions were disordered in the crystal and arsenic appeared with a 50% occupancy in both W_9 moieties. Of course it could be argued that the crystal was actually made up of a 50–50 mixture of $[H_4W_{18}O_{60}]^{8-}$ and $[As_2W_{18}O_{60}]^{6-}$. This would also fit the NMR results. However it can be ruled out for the following reasons:

- $[H_4W_{18}O_{60}]^{8-}$ is not known
- there would not be enough space for two arsenic lone pairs since the As–As distance, in the case of a double occupancy, would be 2.68 Å, to be compared with the As–As bonding distance (2.52 Å) and the As–As non-bonding distance (3.12 Å) in the α-form of arsenic [16]
- why is there exactly a 50–50 mixture? One should find a variable composition typical of mixed crystals from one analysis to another one, which was not the case.

Ratio As/W=2/21. The $[As_2W_{21}O_{70}]^{6-}$ polyanion

If one bridges two AsW_9O_{33} units by inserting additional atoms, arsenic(III) atoms are kept apart and the steric hindrance originated by lone pairs disappears.

This can be done by adjusting the ratio As/W to about 1/11 in the reaction mixture and by lowering the pH to about 4 with hydrochloric acid.

$$21WO_4^{2-} + As_2O_3 + 34H^+ \longrightarrow [As_2W_{21}O_{70}]^{8-} + 17H_2O$$

A yellow compound $H_2Rb_6[As_2W_{21}O_{70}] \cdot 34H_2O$ can be crystallized [17].

Its structure determined by X-ray diffraction reveals two AsW_9O_{33} moieties separated by three tungsten atoms so that it has an apparent threefold axis of symmetry (Fig. 6).

Each moiety has a crown of six tungsten atoms; each tungsten is bonded to one oxygen atom which is actually bridging this tungsten and an inserted tungsten atom. A crown of six tungstens contains six oxygens and may be divided into three groups of two. Each group of two oxygens with the corresponding group of two oxygens of the other AsW_9O_{33} moiety makes a basal square plane of an octahedron, roughly parallel to the ternary axis, the plane at the centre of which is located the inserted tungsten atom. There are then three such inserted atoms. The question now is, how the surrounding of those tungsten atoms is completed. Indeed it seems hard to assume that they are all three octahedrally surrounded since each octahedron would then have an oxygen vertex located inside the polyanion. Obviously a steric hindrance between those three oxygens would arise inside the polyanion, because the basal planes are parallel to the threefold axis.

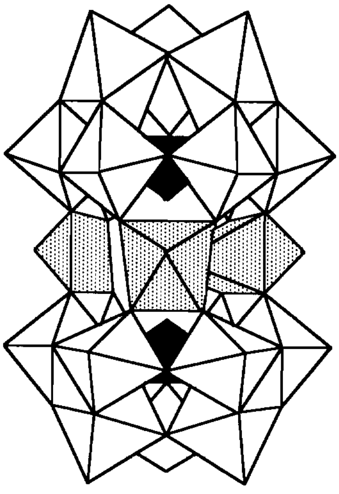

Fig. 6. $[As^{III}_2W_{21}O_{69}(H_2O)]^{6-}$ polytungstate. Two square pyramids and one octahedron keep separate the two $As^{III}W_9O_{33}$ moieties, providing space for arsenic(III) lone pairs. AsO_3 groups are darkened.

A Fourier map computed in the plane of those three intermediate tungsten atoms, that is in a plane perpendicular to the threefold axis, actually shows more peaks than expected which suggests that there is a disorder.

The interpretation is as follows. Only one tungsten atom has an octahedral surrounding, the two others have a square pyramidal surrounding, and they are disordered around the threefold axis. Consequently, one sees at each position 1/3 of octahedral surrounding and 2/3 of square pyramidal surrounding. This last environment is quite rare for tungsten, and in this case it is a forced situation.

There is another problem. The octahedrally surrounded inserted tungsten atom should complete its octahedron with two W=O bonds *trans* to each other because its basal plane of oxygens connects the two AsW_9O_{33} moieties. However this has not yet been observed. Only the *cis* case is known. Consequently it has been thought that one of those oxygen atoms actually is a water molecule and the two hydrogen atoms accounted in the above formula for setting electroneutrality actually belong to that water molecule. Indeed the corresponding W–O distance is quite long, 2.1 Å, which is more typical of a W–OH_2 bond rather than of a W=O bond. Therefore the threefold axis actually does not exist and one would then write the formula as $[As_2W_{21}O_{69}(H_2O)]^{6-}$.

Since the square pyramidal tungsten surrounding is very exceptional and because it induces the loss of the threefold axis in the polyanion structure, a ^{183}W NMR study was performed by dissolving selected crystals into deuterated dimethyl sulfoxide. As shown in Fig. 7 where

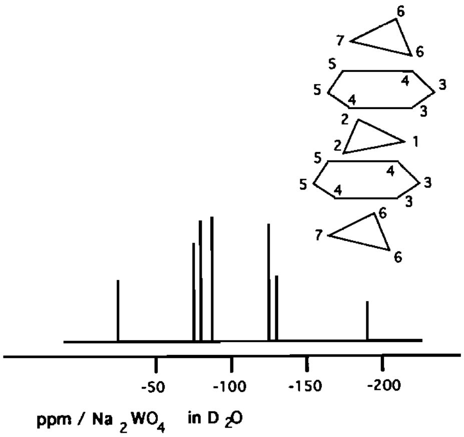

Fig. 7. Sketched NMR spectrum of $[As^{III}_2W_{21}O_{69}(H_2O)]^{6-}$. The diagram of three triangles and of two hexagons represents planes in which tungsten atoms are located. The inserted octahedrally surrounded tungsten atom is marked 1. Consequently one gets seven types of tungsten atoms marked 1, 2, 3, 4, 5, 6, 7 and seven lines, the heights of which fit with respective number of tungsten atoms of each type. The ^{183}W resonance frequency was 10.42 MHz.

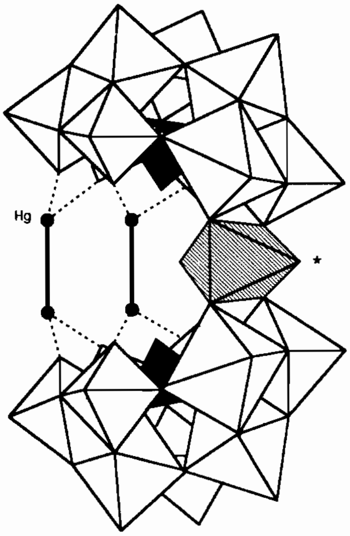

Fig. 8. $[As^{III}_2(Hg^I_2)_2W_{19}O_{67}(H_2O)]^{10-}$ polyanion. AsO_3 groups are darkened. The octahedron joining the two AsW_9O_{33} moieties is dashed. The linkage of both $(Hg^I_2)^{2+}$ cations to oxygen vertices is represented by dashed lines. The location of the water molecule is shown by an asterisk.

only tungsten atoms are represented in planes orthogonal to the longest axis of the molecule (the crystallographic threefold axis), there are seven types of tungsten atoms (1:2:3:4:5:6:7) which should give peaks with relative intensities (1:2:4:4:4:4:2). The observed spectrum which looks like a textbook example, is in full agreement with the X-ray structure.

Those three interleaved tungsten atoms keep separate the two AsW_9O_{33} moieties. This could be achieved in many other ways. First of all, one does not need three tungsten atoms, two or even one are enough. Indeed $[As_2W_{19}O_{68}]^{14-}$ and $[As_2W_{20}O_{69}]^{12-}$ have been described [18, 19, 6]. One could also use other transition metals and for instance the following compounds are known: $[As_2Cu_3W_{18}O_{66}(H_2O)_2]^{12-}$ where three copper have been inserted, $[As_2V_2W_{19}O_{70}]^{8-}$ and $[As_2Co_2W_{19}O_{70}]^{6-}$ where one tungsten and two other metal atoms (vanadium, cobalt) have been inserted. Although there is strong evidence that this assumption is correct, it remains an hypothesis, valuable indeed, but an hypothesis as long as there is no structure determination. However in the case of copper, a structure determination was carried out [20]. Copper atoms occupy expected locations, joining both $AsWO_{33}$ units. Two coppers have a square pyramidal surrounding with one water molecule on each copper, at a Cu–O distance of 2.39 Å, one copper is square planar. It is also remarkable that in this copper case the two $AsWO_{33}$ units are not exactly one above the other. Projections of arsenic atoms on the three copper atoms plane are 0.27 Å apart. This shift provides more space for arsenic lone pairs.

Another possibility was tried, i.e. using mercury(I), knowing its affinity for oxygen. Two solutions were prepared; one at pH = 5 using nitric acid, which contained sodium tungstate and diarsenic trioxide in the appropriate molar ratio As/W = 1/9, and another one at pH = 4 using also nitric acid which contained Hg_2^{2+} so that the molar ratio Hg/As is of 2/1. By mixing them one obtained a new polyanion which was easily separated. Single crystals were obtained and the structure was determined [21].

$$19WO_4^{2-} + As_2O_3 + 2Hg_2^{2+} + 24H^+ \longrightarrow [As_2Hg_4W_{19}O_{67}(H_2O)]^{10-} + 11H_2O$$

It has been said earlier that the fragment AsW_9O_{33} looks like a basket containing an arsenic atom. In this new polyanion two such baskets face each other (Fig. 8). It has also been said that such a AsW_9O_{33} fragment has six oxygen atoms pointing up. Two oxygen atoms are bound to one tungsten atom, two other oxygen atoms are bound at nearly equal distances to the first dimercury cation, and the two last oxygen atoms are bound similarly to the second dimercury cation. Each mercury of a Hg_2^{2+} cation makes a connection between the AsW_9O_{33} moieties. There are two such Hg_2^{2+} connections. The O–Hg–Hg–O assembly is very similar to those found for other mercury(I) salts, such as nitrate, perchlorate, bromate, sulfate, etc. [22–25]. As far as the joint tungsten octahedron is concerned two oxygen atoms from each fragment, i.e. four oxygens, are used to make the basal square plane of the octahedron surrounding it, as in the $[As_2W_{19}O_{69}(H_2O)]^{6-}$ compound; this octahedron is completed by another oxygen making a W=O double bond and a water molecule *trans* to this oxygen atom, as in the $WO_5(H_2O)$ octahedron joining the two AsW_9O_{33} in $[As_2W_{21}O_{69}(H_2O)]^{6-}$.

The crystal structure contains two polyanions $[As_2Hg_4W_{19}O_{67}(H_2O)]^{10-}$ which are located one in front of the other, however with a rotation of 90°. This means that the four linear Hg_2^{2+} cations are in two groups of two, perpendicular when the two polyanions are considered together. It is interesting to note that the non-bonding Hg···Hg distances inside a polyanion are equal, within experimental error, to the non-bonding Hg···Hg distances which separate two polyanions. The eight mercury atoms altogether are located at the vertices of a distorted cube; edges are alternately a long non-bonding Hg···Hg distance, slightly longer than twice the 1.5 Å van der Waals radius, and a short bonding Hg-Hg distance (Fig. 9). There is no bond between arsenic and mercury since Hg–As distances range from 3.71 to 3.80 Å while a bond would be close to 2.5 Å.

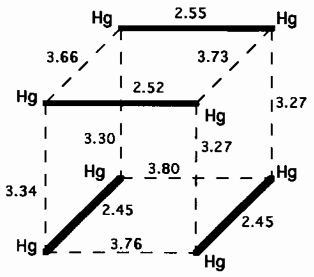

Fig. 9. The asymmetric unit contains two polyanions $[As^{III}_2(Hg^I_2)_2W_{19}O_{67}(H_2O)]^{10-}$ at 90°. The eight mercury atoms are at vertices of a distorted cube; intra and inter polyanionic Hg···Hg non-bonding distances are nearly identical.

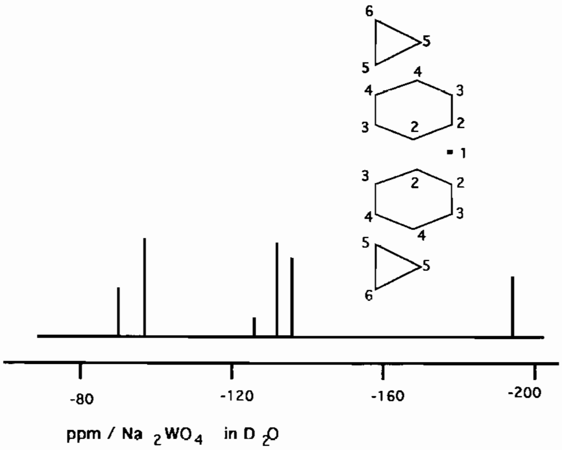

Fig. 10. Sketched NMR spectrum of $[As^{III}_2(Hg^I_2)_2W_{19}O_{67}(H_2O)]^{10-}$. The diagram presents the six different types of tungsten atoms marked as 1, 2, 3, 4, 5, 6, numbering 1 the octahedrally surrounded tungsten atom joining the two AsW_9O_{33} moieties. The ^{183}W resonance frequency was 16.67 MHz.

To complete this study, the ^{183}W NMR spectrum of this compound was obtained by dissolving selected crystals into deuterated dimethyl sulfoxide. Because of the occurrence of the tungsten atom serving as a joint between both AsW_9O_{33} moieties, it is easy to recognize that there are six types of tungsten atoms 1:2:3:4:5:6 which should give peaks with relative intensities 1:4:4:4:4:2. This is just about what was observed (Fig. 10).

In summary it is possible to associate two $As^{III}W_9O_{33}$ units provided that some space is given to arsenic lone pairs to expand. This can be achieved by inserting some atoms between the two units. It can be one tungsten atom, two tungsten atoms, three tungsten atoms; it can also be three copper atoms and in that case the two AsW_9O_{33} moieties are slightly shifted one with respect to the other to provide more space for arsenic lone pairs; it can also be one tungsten atom and two dimercury cations.

Ratio As/W=1/10. The polyanion $[As_4W_{40}O_{140}]^{28-}$

By still increasing the ratio As/W to a value 1/10, and using a solution with a pH in the range 3–7.5, one can get a new species having the formula $[As_4W_{40}O_{140}]^{28-}$ [26, 27].

$$40WO_4^{2-} + 4AsO_2^- + 56H^+ \longrightarrow [As_4W_{40}O_{140}]^{28-} + 28H_2O$$

The structure is based upon four AsW_9O_{33} units which are joined two by two by WO_6 octahedrons so that altogether it forms a ring (Fig. 11). These WO_6 joints differ from the preceding case of $[As_2W_{21}O_{68}(H_2O)]^{6-}$ since the four vertices with two AsW_9O_{33} groups (twice two oxygens) in common are no longer at the basal plane vertices of the octahedron. Thus the two left oxygen vertices of the octahedron make an angle O=W=O roughly equal to 90°, and there is consequently no need for a water molecule.

One can immediately recognize that these four WO_6 joints are actually flexible. Let us call these AsW_9O_{33} units 1, 2, 3 and 4. The use of a model shows that if 1 and 3 move up, the two others 2 and 4 move down. This allosteric effect is a very special feature of this heteropolyanion.

Let us now return to synthetic conditions. Once the compound was prepared, one realized that its solution was not very stable. It decomposed yielding the $[As_2W_{19}O_{67}(H_2O)]^{14-}$ polyanion mentioned earlier.

$$4H_2O + [As_4W_{40}O_{140}]^{28-} \longrightarrow 2WO_4^{2-} + 2[As_2W_{19}O_{67}(H_2O)]^{14-} + 4H^+$$

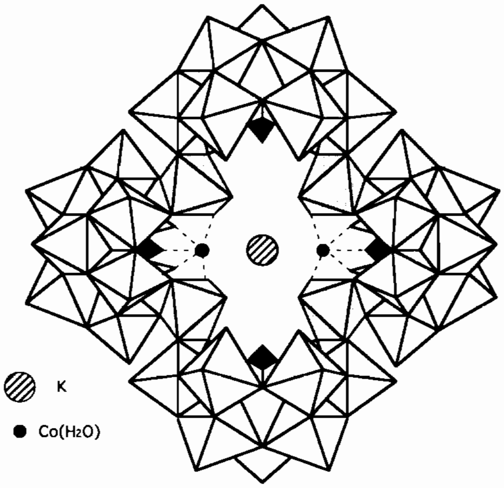

Fig. 11. $[As^{III}_4Co_2KW_{40}O_{140}]^{28-}$ polyanion. The four AsO_3 groups are darkened. Cobalt atoms are shown by large black dots. The potassium atom is at the centre of the polyanion and shown by a dashed circle. The four WO_6 octahedrons joining the four AsW_9O_{33} moieties and providing the flexibility to the whole structure, are shadowed.

It is actually a hydrolysis the rate of which was found to be highly dependent on the nature of the alkaline cation of the starting tungstate. One can roughly set up experimentally the following scale: $\mathrm{Li} < \mathrm{Na} < \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$. Obviously the size of the alkaline cation plays a major role in this hydrolysis, or in other words on the stability of the polyanion. The rate actually ranges from a few minutes up to several days. This suggested some other cations should be investigated and divalent transition metals were tried, with very different results. Two cobalt atoms are very easily added to form a greenish stable compound which has been crystallized with potassium and ammonium as counter cations. The full formula is $K(NH_4)_{23}[As_4Co_2W_{40}O_{140}] \cdot nH_2O$. The exact number of water molecules is not certain. The structure of this polyanion was actually determined using the cobalt containing compound.

The structure shows how cobalt atoms are incorporated with an octahedral surrounding. The two cobalt atoms are ligated to units 1 and 3, being attached to the arsenic lone pair. The AsW_9O_{33} unit, as underlined earlier, has six oxygen atoms pointing up. Twice two of them were used for the two WO_6 joints. Two are left which are ligated to cobalt. The two WO_6 joints also have an oxygen ligated to cobalt. That makes five vertices; As and two O from the AsW_9O_{33} unit, one O from one WO_6 joint, and one O from the other WO_6 joint. The sixth vertex of the octahedron is occupied by a water molecule.

In order to achieve correct Co–As and Co–O bond distances, it is necessary that some moves around the WO_6 joints take place. The cavity where cobalt is imbedded adopts the adequate size to ligate the cobalt atom. The allostery then is an essential feature of this compound. It may easily be seen from a model that the two cavities incorporating cobalt become smaller and that consequently the two other cavities become larger, so that any further addition of cobalt is not possible, as observed experimentally. However a larger atom could be added to fill the empty cavities. For instance silver may be used and one may demonstrate the occurrence of the two equilibria:

$$[KAs_4Co_2W_{40}O_{140}]^{23-} + Ag^+ \longrightarrow [KAgAs_4Co_2W_{40}O_{140}]^{22-}$$

$$K = 7.2 \times 10^8$$

$$[KAgAs_4Co_2W_{40}O_{140}]^{22-} + Ag^+ \longrightarrow [KAg_2As_4Co_2W_{40}O_{140}]^{21-}$$

$$K = 8.9 \times 10^8$$

If only silver was used and reacted on $[As_4W_{40}O_{140}]^{28-}$, four larger silver atoms are incorporated following the series of four successive equilibria:

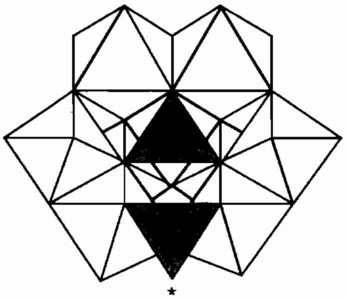

Fig. 12. $[As^{III}_2W_8O_{30}(OH)]^{7-}$ polyanion. AsO_3 groups are darkened. Both lone pairs of arsenic(III) expand in the same direction, perpendicularly to the figure plane. The OH group is located at the free vertex of the AsO_3 group which is at the bottom of the figure and marked by an asterisk.

$$[KAg_{i-1}As_4W_{40}O_{140}]^{(28-i)-} + Ag^+ \longrightarrow [KAg_iAs_4W_{40}O_{140}]^{(27-i)-}$$

$$K_1 = 1.2 \times 10^9, \quad K_2 = 1.7 \times 10^8,$$

$$K_3 = 4.2 \times 10^7, \quad K_4 = 6.0 \times 10^6$$

Finally it is worth pointing out that a potassium ion is located exactly at the centre of the polyanion (Fig. 12). It has eight oxygen neighbours and it is now easy to understand that the size of this central hole where the potassium lies, corresponds roughly to the ionic radius of that particular cation. This explains why the hydrolysis depends on the nature of the alkaline cation. The lowest rate of decomposition observed for potassium is related to a cavity the size of which is ideal for this cation.

Ratio As/W=1/4. The $[As_2W_8O_{30}(OH)]^{7-}$ polyanion

As mentioned earlier, a mixture of tungstate and arsenic(III) oxide yielded arseno(III)nonatungstate if the pH is close to 9. Addition of sodium chloride precipitates the salt described by Rosenheim, that is $Na_8H[AsW_9O_{33}]$. However addition of an excess of arsenate(III) formed quite a different compound which is the only one occurring in solution as shown by polarography. To prepare it, one combined tungstate WO_4^{2-} and dihydrogenarsenate(−) $AsO_3H_2^-$ in a atomic ratio As/W = 1/2. One got a solution the pH of which was adjusted to 8 by using hydrochloric acid.

$$8WO_4^{2-} + 2AsO_3H_2^- + 11H^+ \longrightarrow [As_2W_8O_{30}(OH)]^{7-} + 7H_2O$$

A new polyanion was separated and the chemical analysis led to the formula 7K:2As:8W [28]. One immediately realizes that the excess of arsenic yielded a new compound containing more arsenic since the ratio now is 1/4.

Since single crystals were obtained, the crystal structure was solved (Fig. 12). Although the drawing may look rather simple, it is a bit more difficult to explain. One may consider the structure as derived from the Rosenheim structure in which the three groups W_3O_{13} are equivalent. Let us rotate one of them by 60°, like in the Sasaki isomer. One would then end up with an octahedron of the turned group, being joined to two neighbouring tungsten octahedrons and to the central arsenic(III). Actually, this tungsten is eliminated and one gets an eight tungsten containing structure. On the other side of the structure, there are two tungsten–oxygen bonds pointing up. Those two oxygen atoms build two W–O–As bridges involving a second arsenic(III) atom. When solving the structure, it turned out that only seven potassium cations were located in the lattice, which meant that a H cation had to be added somewhere. It was proposed that this hydrogen ion was attached on the third free vertex of the pyramid surrounding the second arsenic atom, making it an OH group and the true formula of the polyanion is now written as $[As_2W_8O_{30}(OH)]^{7-}$. The geometrical surrounding of both arsenic atoms is such that both lone pairs expand in the same direction.

This is a rather unusual structure since it was the first time that one group of tungsten atoms turned by 60° was found in a low tungsten containing polyanion, with two independent arsenic(III) atoms.

Ratio As/Mo=1/1. The $[As_3Mo_3O_{15}]^{3-}$ polyanion

Moving further down to a ratio in atom As/Mo = 1/1, a mixture of As_2O_3 and MoO_3 was put into boiling water at a pH of *c.* 7 set up by addition of sodium carbonate. On cooling the solution pale yellow single crystals of $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$ were obtained in a yield of 70%.

$$6MoO_4^{2-} + 3As_2O_3 + 6H^+ \longrightarrow 2[As_3Mo_3O_{15}]^{3-} + 3H_2O$$

The same compound may be prepared when starting from WO_3, however the yield then is only 37% [29]. It must be pointed out that Gibb [30] and later Ephraim and Feidel [31] explored for the first time this range of low As/W ratio in solution adding some divalent metals and gave a list of possible compounds only on the basis of chemical analysis.

An X-ray study revealed an interesting feature. The structure may be described as being made of two fused units, a Mo_3O_{13} one and a As_3O_7 one (Fig. 13). The first unit is a trimolybdenum group Mo_3O_{13} often postulated as a building block for heteropolyanions. However its occurrence in solution as a free entity has not really been directly fully demonstrated. There are two previous other examples found by Zubieta and coworkers showing such a trimolybdenum unit associated either with a triolate, i.e. $[Mo_3O_7\{CH_3C(CH_2O)_3\}]^{2-}$ [32], or with a squarate, i.e. $[Mo_3O_7(OCH_3)(C_4O_4)]^{3-}$ [33].

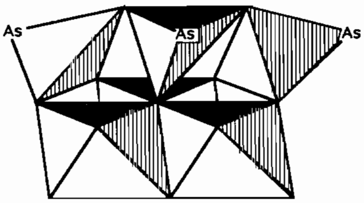

Fig. 13. $[As^{III}{}_3Mo_3O_{15}]^{3-}$ polyanion. The three arsenic(III) form a chained anion $O_2AsOAs(O)OAsO_2^{5-}$ anion stretching above the Mo_3O_{13} group and sharing with it five oxygen atoms.

The second unit is even more interesting because such a linear triarsenate $O_2AsOAs(O)AsO_2$ has never been described, either free or associated with something else. This triarsenate(III) shares five oxygen atoms with the trimolybdate fragment. The central As atom of the triarsenate(III) shares an oxygen with the three molybdenum atoms. Both terminal arsenics have two oxygen atoms, each of them connecting arsenic with one molybdenum atom. In other words, one can say that both terminal AsO_2 groups occupy the place of the two Mo_3O_{13} groups which would build $[AsMo_9O_{33}]^{6-}$ by formally adding them to a Mo_3O_{13} group.

It is clear that each arsenic(III) has a free lone pair. Looking at Fig. 13, one immediately realizes that the central arsenic atom of the triarsenate ligand has its lone pair pointing in the same direction as two oxygen atoms doubly bonded to molybdenum. This makes a triangle of three lone pairs, i.e. an octahedron face, one from arsenic and two from oxygens. This is similar to the $[As_4Mo_{40}O_{140}]^{28-}$ site in which the cobalt atom was inserted [26]. The similarity is more striking if the triangle of As–O distances is considered. They are 3.104 and 3.160 Å for $[As_3Mo_3O_{15}]^{3-}$, and 3.06 and 3.43 Å for $[As_4W_{40}O_{140}]^{28-}$.

One could then predict that a $[As_3Mo_3O_{15}]^{3-}$ would behave as a tridentate ligand L toward Co^{2+}, and one could expect to prepare a $[CoL_2]^{4-}$ complex anion. When cobalt(II) was added to a solution of $[As_3Mo_3O_{15}]^{3-}$ a change of color suggested that a reaction occurred, and orange single crystals were easily obtained [29].

Unfortunately, the behaviour of $[As_3Mo_3O_{15}]^{3-}$ was not as expected. The X-ray structure shows a different but quite interesting compound. It is based upon an Anderson structure $[M_7O_{24}]^{n-}$ [34], the central octahedral cavity of which is occupied by the cobalt atom which remains in the oxidation state II. On both sides, there is a cyclic triarsenate(III), which is also a unique example in arsenic(III) chemistry. This cyclic triarsenate shares three oxygen atoms with the Anderson fragment in such a way that each shared oxygen bridges one arsenic atom, the cobalt atom, and two molybdenum atoms (Fig. 14). Counterions were potassium and hexa-aquacobalt(2+).

As a consequence, the reaction which yielded this compound, is very neat.

$$Co^{2+} + 2[As_3Mo_3O_{15}]^{3-} \longrightarrow [As_6CoMo_6O_{30}]^{4-}$$

It must be pointed out that this reaction does not work with tungsten.

Figure 15 presents angles and distances for the two cyclic and linear triarsenate(III).

In conclusion to this part, it is interesting to repeat that neither M_3O_{13} nor As_3O_7 exist free; however they make each other stable when assembled in one compound. Clearly the As_3O_7 chain prevents the fusion of M_3O_{13} blocks.

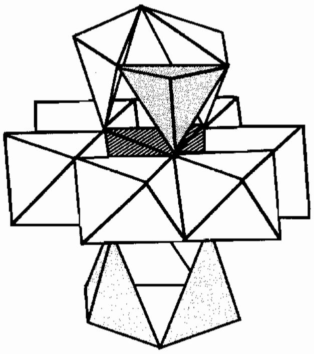

Fig. 14. $[As^{III}{}_6CoMo_6O_{30}]^{4-}$ polyanion. The cobalt atom is at the centre of the darkened octahedron located inside the Mo_6O_{24} crown. Arsenic(III) atoms are involved into two cyclic anions $As_3O_6{}^{3-}$ anions which share three oxygen atoms each with the polymolybdate.

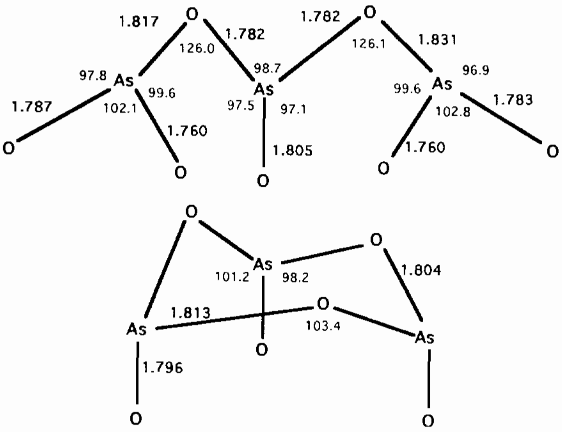

Fig. 15. Bond distances and angles in both triarsenate(III) anions.

Using a phosphorus(V) containing fragment

By condensation, AsW_9O_{33} groups are able to form larger species. It has been seen that upto four groups may be put together with some additional tungsten atoms to yield a species containing forty tungsten atoms. Condensation means that oxygen atoms are shared between tungsten octahedrons. This condensation takes place because the starting building block is actually an 'unsaturated' species, such as a degraded Keggin structure, that is a structure which has lost some of its tungsten atoms to become an open structure, in contrast to the Keggin structure itself which is regarded as a closed structure. Similarly the $[AsW_9O_{33}]^{9-}$ may be considered as an 'unsaturated' structure.

One could now raise the following question. Would it be possible to build up other large species by using other building blocks, that it other 'unsaturated' species, containing another heteroatom such as phosphorus(V).

The starting point should be an 'unsaturated' species, keeping in mind the preceding remark. In this respect it is known that the Dawson structure $[P_2W_{18}O_{62}]^{6-}$ can be progressively degraded by increasing the pH in a very controlled manner. There is strong evidence, NMR and chemical, that a $[P_2W_{12}O_{48}]^{12-}$ species occurs in solution [35–37]. It is made of two PW_6O_{26} units which share four oxygen atoms. This PW_6O_{26} unit may be described as derived from α-$[PW_9O_{34}]^{9-}$. Three tungsten atoms have been withdrawn (Fig. 16).

From an experimental point of view, by putting $H_2[P_2W_{12}O_{48}]^{12-}$ in a solution buffered around pH=5, one gets a $[P_8W_{48}O_{184}]^{40-}$ polytungstate with a yield of 50%.

$$4H_2[P_2W_{12}O_{48}]^{12-} + 16H^+ \longrightarrow [P_8W_{48}O_{184}]^{40-} + 8H_2O$$

It was isolated as white single crystals $K_{28}Li_5H_7$-$[P_8W_{48}O_{184}]\cdot 92H_2O$ and studied by X-ray diffraction [38, 39].

The polyanionic structure is an assembly of four $P_2W_{12}O_{48}$ groups which form a large ring. In contrast

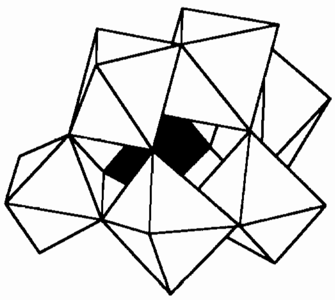

Fig. 16. Hypothetical '$P^VW_6O_{26}$' group involved into the $[P^V{}_2W_{12}O_{48}]^{14-}$ polyanion prepared by degradation of $[P^V{}_2W_{18}O_{62}]^{6-}$. The central PO_4 tetrahedron is darkened.

to $[As_4W_{40}O_{140}]^{28-}$ the central cavity now is empty, being too wide to incorporate an alkaline ion.

This structure $[P_8W_{48}O_{184}]^{40-}$ may be drawn in a simplified way by just showing solid octahedrons (Fig. 17). It is herein shown how $P_2W_{12}O_{48}$ is made of two PW_6O_{26} groups which are geometrically limited by two planes perpendicular to the figure plane; they make an angle of 72°, as can be checked from crystallographic data (the exact value is 72.1°).

Five times 72° makes 360°. Thus one should expect the occurrence of a polytungstate containing five phosphorus atoms and thirty tungsten atoms. Actually this compound may be found in the literature since its preparation was described earlier [40]. However its structure remained unknown and puzzling, until recently when single crystals were obtained. It can be prepared by adding a large excess of phosphoric acid to sodium tungstate (*c.* 6:1 moles). Transparent crystals were obtained as an ammonium salt [41a, 42].

$$5PO_4^{3-} + 30WO_4^{2-} + Na^+ + 60H^+ \longrightarrow [NaP_5W_{30}O_{110}]^{14+} + 30H_2O$$

The role of sodium will be discussed later.

The polyanion has an internal fivefold axis of symmetry. Figure 18 represents the polyanion looking down this symmetry axis. From atom coordinates, it appears that the polyanion has a plane of symmetry perpendicular to this symmetry axis. The five phosphorus atoms are located in this symmetry plane at the vertices of a regular pentagon. Tungsten octahedrons may be grouped in four rings, two of five octahedrons and two of ten octahedrons. In each ring tungsten atoms are in a plane which is perpendicular to the symmetry axis. Thus, going down this axis, one finds a planar ring of five octahedrons, a planar ring of ten octahedrons, a planar ring of ten octahedrons, and a planar ring of five octahedrons.

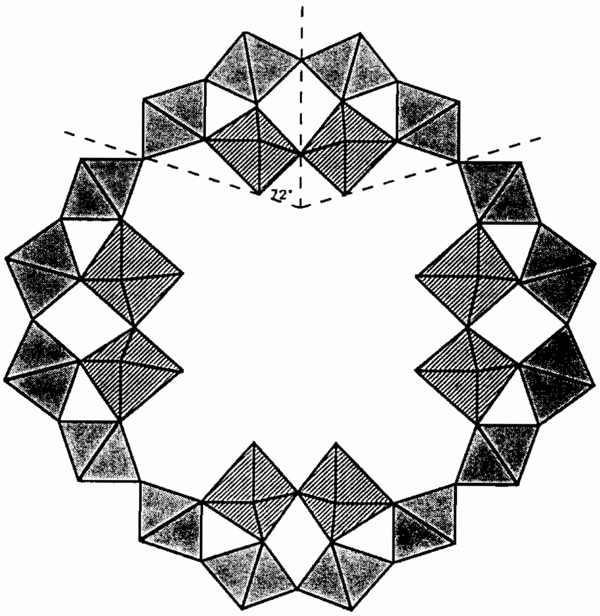

Fig. 17. Projection of the $[P^V{}_8W_{48}O_{184}]^{40-}$ polyanion. Octahedrons are not transparent; one half of them is seen, each octahedron hiding another one located underneath. Phosphorus atoms are represented by black dots. PW_6O_{26} group is limited by two planes which make a dihedral angle of 72°. Four $P^V{}_2W_{12}O_{48}$ groups make a large ring.

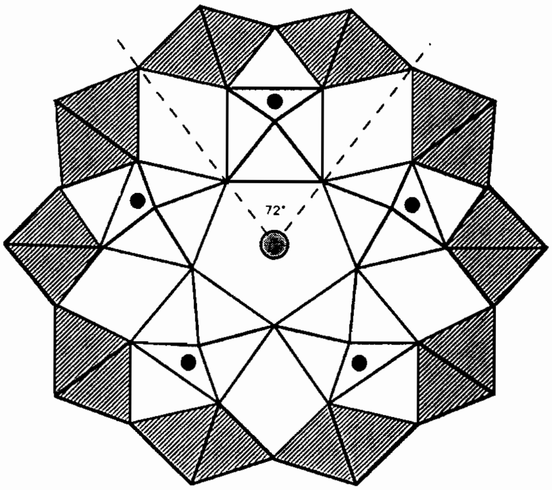

Fig. 18. Projection of the $[NaP^V{}_5W_{30}O_{110}]^{14-}$ polyanion. Octahedrons are not transparent, only one half of them is seen, each octahedron hiding another one located underneath. Phosphorus atoms are represented by black dots. The sodium atom is shown as a shadowed circle. The whole polyanion is a rare example of a species with a fivefold axis of symmetry perpendicular to the figure plane. Tungsten atoms are distributed into four planes, two of five tungsten atoms, two of ten tungsten atoms.

Consequently, from a ^{183}W NMR point of view, one would expect only two types of tungsten atoms in a ratio 1:2 (the two five octahedrons rings, the two ten octahedrons rings). However, when the ^{183}W NMR spectrum was recorded, it displayed four peaks with intensity ratios 1:1:2:2. Clearly rings having the same number of tungsten atoms are not equivalent (Fig. 19). A similar study was performed earlier by Baker and co-workers who found the same pattern of four peaks [41b].

Returning to the crystallographic study, it has been found that inside the polyanion there was one sodium cation located on the fivefold axis. However this cation is not at the centre of the polyanion. It is actually at the centre of one ten octahedrons ring. The dissymmetry is sufficient to make non-equivalent tungsten atoms belonging to rings having the same number of metal atoms, since one ten tungsten atoms ring has a sodium cation at its centre, the other has not.

It is interesting to look at sodium oxygen distances. In the ring where the sodium is, there are five oxygen atoms at 2.66 Å, which are closest neighbours. On each

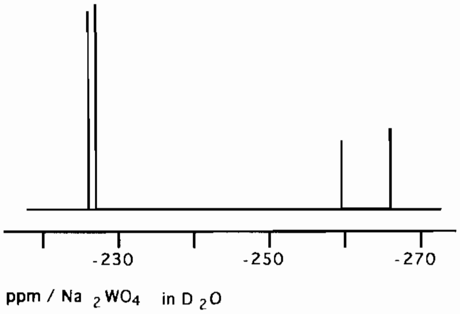

Fig. 19. Sketched NMR spectrum of $[NaP^{V}_{5}W_{30}O_{110}]^{14-}$. Because sodium is at the centre of a ten tungsten atoms ring, those two ten tungsten rings are not NMR equivalent, as well as those of the two five tungsten rings. Consequently there are four peaks with 1–1–2–2 heights. The ^{183}W resonance frequency was 16.67 MHz.

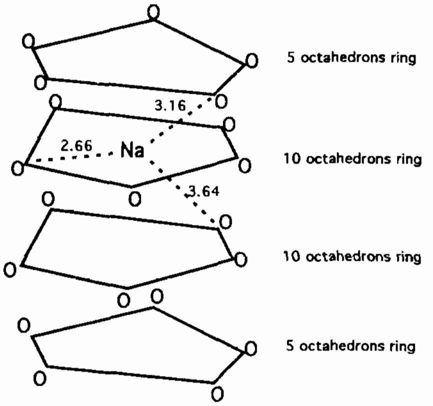

Fig. 20. Location of the oxygen atoms of the four tungsten rings which are inside the polyanion. It shows the sodium location and the 15 oxygen atoms surrounding sodium with Na–O distances.

side of this plane, one finds two other rings, one is the ten octahedrons ring, the other one is a five octahedrons ring. Each of them has five oxygen atoms at equal distances to sodium, 3.16 Å for the five octahedrons ring, and 3.64 Å for the ten octahedrons ring (Fig. 20). Thus sodium has fifteen neighbours altogether, five at 2.66 Å, five at 3.16 Å, and five at 3.64 Å. Taking into account the ionic radius of the sodium cation for a coordination of nine, as given by Shannon [43], it is interesting to compute the sum (ionic radius of sodium) + (ionic radius of oxygen), i.e. $1.32+1.40=2.72$ Å, which compares well with the 2.66 Å observed value.

From a geometrical point of view, the polyanion looks like a ball. The sodium is physically located at the centre of one of the ten octahedrons ring. But it crystallographically appeared disordered, that is five electrons at the centre of each of the ten tungsten atoms rings. There was indeed a very faint peak in the Fourier series computed along the fivefold axis, which could be questioned particularly in a structure having so many heavy tungsten atoms.

In order to cross-check, the ^{23}Na NMR spectrum (^{23}Na, $I=3/2$) was recorded using a D_2O solution. The probe was made of two concentric tubes, the internal one being a reference containing a sodium nitrate solution. The concentrations of the sample tube and of the reference tube were computed in such a way that both tubes contained approximately the same number of nuclei, based on the expected formula $[NaP_5W_{30}O_{110}]^{14-}$. Although the sodium spectrum displayed a broad peak for the sample (470 Hz half-width) at -19.27 ppm with respect to the reference, integrated peaks were in good agreement.

This suggests that it is preferable to write the formula of this polyanion as $[NaP_5W_{30}O_{110}]^{14-}$. In conclusion to this part, it is worth pointing out that the size of sodium fits precisely the size of the internal cavity of the polytungstate. Attempts to make the same 30 tungsten atoms compound with lithium, or any other alkaline cation, or copper(I), or a rare earth of similar dimension, failed.

General remarks on the construction of large polyanions

It has been shown how 'unsaturated' polyanions may be used as building blocks to prepare larger species by condensation.

The use of arsenic(III) makes the formation of a closed Keggin type structure impossible. The lone pair of arsenic(III) needs space to expand. The obtained compound $[AsW_9O_{33}]^{9-}$ can then be considered as an 'unsaturated' building block and used as such.

- One $[AsW_9O_{33}]^{9-}$ group may be used with an empty $[W_9O_{33}]^{12-}$ moiety to build up a $[AsH_2W_{18}O_{60}]^{7-}$; the empty moiety gives space to the lone pair.
- Two $[As_8W_9O_{33}]^{9-}$ groups may be used, but some intermediate atoms must still be inserted between both groups, to give space to lone pairs; if it is tungsten one gets $[As_2W_{21}O_{69}(H_2O)]^{6-}$; if it is copper(II), one gets $[As_2Cu_3W_{18}O_{66}(H_2O)_2]^{12-}$; if it is mercury(I) one gets $[As_2(Hg_2)_2W_{19}O_{67}(H_2O)]^{10-}$.
- Four $[As_8W_9O_{33}]^{9-}$ may be used, and the 'crown' compound $[As_4W_{40}O_{140}]^{28-}$ is formed; there is now so much space for lone pairs that it can even be used to ligate either two cobalt atoms yielding $[KAs_4Co_2W_{40}O_{140}(H_2O)_2]^{23-}$, or to four silver atoms yielding $[KAs_4Ag_4W_{40}O_{140}]^{23-}$.

Taking now a phosphorus(V) unsaturated group derived form the Dawson structure $[P_2W_{18}O_{62}]^{6-}$, one can also prepare large species.

- Four P_2W_{12} groups may be assembled into a ring shaped polyanion $[P_8W_{48}O_{184}]^{40-}$.

- Four PW_6 groups may be assembled in a ball shaped polyanion $[NaP_5W_{30}O_{110}]^{14-}$.

Other high nuclearity species might quite possibly be prepared provided one starts from other 'unsaturated' species. Indeed this method has already been successfully applied to the synthesis of large species containing antimony or boron as an heteroatom.

An overview of nitrosyl derivatives of polyoxomolybdates

The perceived analogies of polyoxoanions to metal oxide surfaces provide a current focus of interest in the chemistry of these species [6, 44]. A number of organic derivatives of polyoxometalates, mainly polyoxomolybdates, have been synthesized with the aim of developing models for the interaction of organic substances with catalytic oxide surfaces. Typical examples include methoxo [45], formyl [46], acetal [47], hydrazido [48], diazenido [49], imido [48b, 50] pyridine [51] and cyclopentadienyl [52]. In addition, a number of organometallic oxide clusters has been prepared and characterized by the groups of Klemperer [53], Isobe [54] and Finke [55]. They may be classified into two categories: organometallic units supported by polyoxoanions, organometallic units incorporated into a polyoxoanion.

As a part of our interest in derivatized polyoxometalates and in the chemistry of Mo–N multiple bonds, we have explored the chemistry of nitrosylpolyoxomolybdates with the aim of (i) assessing the change of the electronic structure of the oxomolybdate cluster arising from the replacement of the terminal π-donor oxo ligand by the very strong π-acceptor nitrosyl ligand, (ii) looking for models for catalytic oxygenation of NO_x on metal oxides.

Recent reviews on transition metal nitrosyl complexes are available [56]. The reaction of hydroxylamine, as a common source of NO, on Mo^{VI} oxoanions was first investigated by Hofmann and co-workers [57] who described various Mo^{VI} complexes with hydroxylamine. The Mo^{VI} reduction in that reaction was debated until it was recognized independently by Wieghardt *et al.* [58] and Sarkar and Müller [59] that these products are nitrosyl complexes of molybdenum(II). A variety of such complexes has been characterized [58–62]. Most of them are diamagnetic mononuclear complexes containing either the $Mo(NO)^{3+}$ [58, 59, 60a, b, e–g, 61a, c, 62] or the $Mo(NO)_2^{2+}$ [60a, 62] group while a few are paramagnetic containing the $Mo(NO)^{2+}$ group [62c]. A few polynuclear nitrosyl molybdenum complexes have also been characterized [60c, h, i]. None of these complexes contain oxomolybdenum centers together with nitrosylmolybdenum groups. However, in the absence of any other reagents MoO_4^{2-} and $NH_2OH \cdot HCl$ are known to yield a poorly characterized compound used as a starting material for preparing mononuclear nitrosyl complexes [61c, 63].

Despite the obvious analogies between RN_2^+ and NO^+ [64], and numerous reports on organodiazenido derivatives of isopolymolybdates [49], nitrosyl derivatives of oxomolybdates were unknown till the report of Zhang *et al.* on $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}] \cdot 42H_2O$ [65]. This compound was obtained by reacting $Na_2MoO_4 \cdot 2H_2O$ and $NH_2OH \cdot HCl$ in a refluxed acidified aqueous solution. We have recently found that the reaction of hydroxylamine with oxomolybdates in non-aqueous solvents provides a convenient route to nitrosyl derivatives of polyoxomolybdates which we are now going to discuss.

Nitrosylating reduction of polyoxomolybdates

Although we have been searching for nitrosyl derivatives of polyoxomolybdates for some time, such a compound was first obtained by serendipity while reacting hydroxylamine and $(NBu_4)_2[Mo_4O_{12}\{N{\equiv}CCH{=}CHC(NH_2)NO\}_2]$ in methanol with the aim of transforming the nitrile group into amidoxime. The mixture of hydroxylamine and tetramolybdate was refluxed for a few hours. Violet crystals formed readily from the filtrate and they were identified as $(NBu_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}] \cdot 3MeOH$ (**1**) on the basis of an X-ray structure determination (Fig. 21) [66].

It was then recognized that this stable compound may be obtained most conveniently by reacting hydroxylamine and $(NBu_4)_4[\alpha\text{-}Mo_8O_{26}]$ (yield *c.* 50%). Actually a variety of polyoxomolybdates may be used as starting materials; for instance $(NBu_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}] \cdot 3MeOH$ was obtained from $(NBu_4)_2[Mo_6O_{19}]$, $K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**) was obtained from $K_8[Mo_{36}O_{112}(H_2O)_{16}] \cdot 40H_2O$ [67], $(NMe_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (**3**) was obtained from $(NBu_4)_3[Mo_5VO_{19}]$ [68] or $(NBu_4)_4[\alpha\text{-}Mo_8O_{26}]$ in the presence of tetramethylammonium bromide.

The initial step of the reaction in methanol could be the formation of oxomethoxo species which subsequently reacted on hydroxylamine with simultaneous cluster dissociation and reaggregation to yield the pentanuclear species. Although no kinetic study of the nitrosylating step has so far been carried out, the following scheme may be suggested [69].

$$[Mo^{VI}O]^{4+} + NH_2OH \longleftrightarrow [Mo^{VI}O(NH_2O)]^{3+} + H^+$$

$$[Mo^{VI}O(NH_2O)]^{3+} \longrightarrow [Mo(NO)]^{3+} + H_2O$$

The ethoxo derivative $(NBu_4)_2Na[Mo_5O_{13}(OEt)_4(NO)] \cdot x EtOH$ (**4**) was similarly prepared by reacting

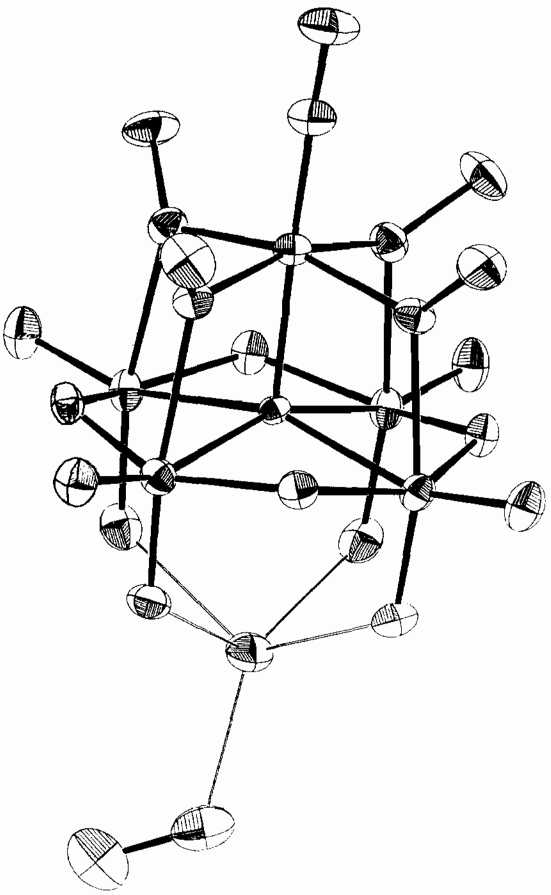

Fig. 21. Molecular structure of the anion $[Mo_5(NO)O_{13}(OMe)_4\{Na(MeOH)\}]^{2-}$ (**1**). The Na(MeOH) group sits at the position of the MoO group of a closed Lindqvist structure.

hydroxylamine and $(NBu_4)_2[Mo_4O_{12}\{N{\equiv}CCH{=}CHC(NH_2)NO\}_2]$ or $(NBu_4)_2[\alpha\text{-}Mo_8O_{26}]$ in ethanol.

The ethoxo species is somewhat unstable in solution and transforms readily into $[Mo_6O_{18}(NO)]^{3-}$. The methoxo species is more stable but gives $[Mo_6O_{19}]^{2-}$ when slightly acidified in methanol. Although $(NBu_4)_3[Mo_6O_{18}(NO)]$ (**5**) is easily obtained on recrystallization of $(NBu_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ from dichloromethane or acetonitrile solutions, it is more conveniently prepared in a one pot synthesis by reductive nitrosylation of $(NBu_4)_2[Mo_2O_7]$ with $NH_2OH\cdot HCl$ in acetonitrile. Base degradation of $[Mo_6O_{18}(NO)]^{3-}$ in methanol gives back the five molybdenum lacunar species $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$. As an example $(NBu_4)_2(C_6H_5NH_3)[Mo_5O_{13}(OMe)_4(NO)]\cdot C_6H_5NH_2$ (**6**) has been isolated using aniline in methanol.

Reactions of nitrosylmolybdenum(II) complexes

Reactions with isopolyoxomolybdates

The reactions of oximes and amidoximes toward a variety of oxomolybdenum compounds have been investigated in aqueous or non-aqueous solutions. It has been found that a number of amidoxime $RC(NH_2)NOH$ ($R=CH_3$, C_2H_5, $ClCH_2$...) reacted with $[MoO_2(acac)_2]$ to yield mononuclear nitrosylmolybdenum(II) complexes $[Mo(NO)(acac)_2(\{RC(NH_2)NO\}]$ containing a side-on ligated amidoximate(*N*,*O*) ligand. Acetone oxime reacted similarly with $[MoO_2(acac)_2]$ to give $[Mo(NO)(acac)_2(Me_2CNO)]$ in refluxing methanol while a tetranuclear oxocluster $[Mo_4O_{10}(OMe)_4(Me_2CHNO\}_2]$ (**7**) was formed at room temperature. The reaction of acetone oxime with $(NBu_4)_2[Mo_6O_{19}]$ in refluxing ethanol gave a mixture of $(NBu_4)_2[Mo_4O_{12}(Me_2CNO)_2]$ (**8**) and $[\{Mo(NO)(\mu\text{-}OEt)(Me_2CNO)_2\}_2]$ (**9**). A dissymmetrical dinuclear molybdenum(II) species $[Mo_2(NO)_2(Me_2CNO)_2(Me_2CNHO)Cl(\mu\text{-}Me_2CNO)(\mu\text{-}OMe)_2]$ (**10**) was obtained by reacting $(NBu_4)_2[Mo_4O_{12}(Me_2CNO)_2]$ with an excess of acetone oxime in methanol acidified with HCl. Reactions of those mononuclear and polynuclear molybdenum(II) species with $(NBu_4)_2[Mo_2O_7]$ in methanol yielded nitrosylpolyoxomolybdates $[Mo_4O_{10}(OMe)(NO)(Me_2CNO)_2]^{2-}$ (**11**) (Fig. 22), $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ (**12**) or $[Mo_6O_{18}(NO)]^{3-}$ (**5**), depending on reaction conditions. $[Mo_4O_{10}(OMe)(NO)(Me_2CNO)_2]^{2-}$ (**11**) is a highly unsymmetrical compound. First of all it contains a MoO_4 tetrahedron and three octahedrally surrounded molybdenum atoms. The methoxo group bridges three molybdenum atoms, one of them being the reduced $Mo^{II}(NO)$ one. One acetone oximate is O,N-side-on ligated to $Mo^{II}(NO)$. The other acetone oximate is bonded by oxygen which bridges

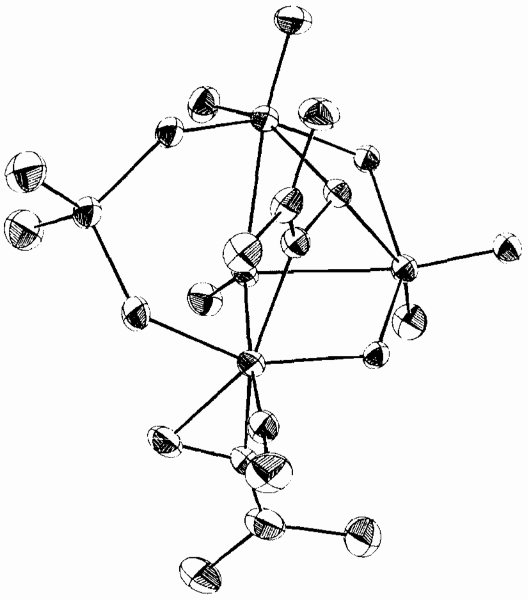

Fig. 22. Molecular structure of the anion $[Mo_4(NO)O_{10}(OMe)(Me_2CNO\}_2]^{2-}$ (**11**). The $Mo^{II}(NO)$ group is side-on ligated to one acetone oximate, while the other one bridges three molybdenum atoms. There is one MoO_4 tetrahedron.

two octahedrally surrounded Mo^{VI} atoms, and by nitrogen to the $Mo^{II}(NO)$ group.

Reduction of $(NBu_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$

The easy reduction of molybdenum is well known. Although there is already a Mo^{II} in this compound, one may think about adding more electrons. Actually this opens the door to new compounds although this compound is not electrochemically reducible. The reaction of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ with reductants including $MoCl_5$, $MoCl_4$ and VCl_3 in methanol yielded blue products which displayed similar properties. Actually the reaction afforded a mixture of compounds which has proved to be quite difficult to separate. However two derivatives have been identified by X-ray diffraction as $(NBu_4)_2[Mo_{10}O_{24}(OMe)_7(NO)]$ (**13**) (Fig. 23) and $(NBu_4)[Mo_{10}O_{25}(OMe)_6(NO)]$ (**14**) (Fig. 24). Reduction by hydrazine dichlorhydrate proceeds more cleanly and either one of the previous decamolybdates, or $(NBu_4)_2[Mo_{10}O_{20}(OMe)_9(NO)_3]$ (**15**) (Fig. 27), a decamolybdate of a new type containing three $Mo(NO)^{3+}$ units, is formed depending on reaction conditions. Those compounds are all mixed valence decanuclear polyoxomolybdates.

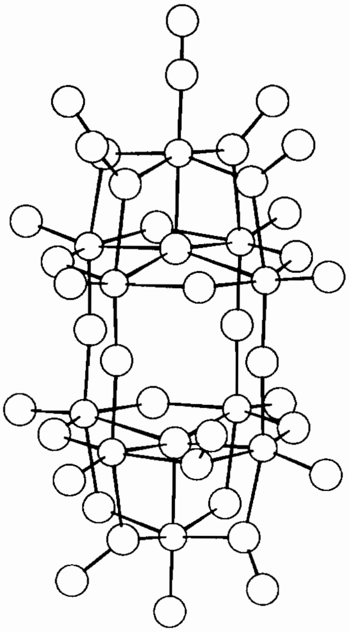

Fig. 23. Molecular structure of $[Mo_{10}O_{24}(OMe)_7(NO)]^{2-}$ (**13**). It is made of two moieties, sharing four oxygen atoms engaged in four linear Mo–O–Mo bonds. One moiety is the $Mo_5O_{13}(OMe)_4(NO)$ part of compound **1**, the other half is $Mo_5O_{14}(OMe)_3$ deriving from the Lindqvist structure by removing one MoO group.

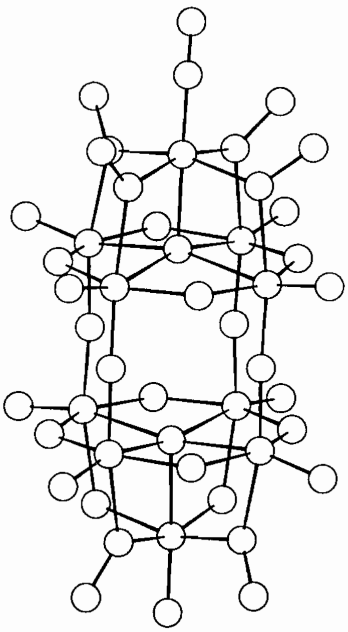

Fig. 24. Molecular structure of $[Mo_{10}O_{25}(OMe)_6(NO)]^-$ (**14**).

Molecular structures of nitrosyl derivatives of polyoxomolybdates

Lacunar Lindqvist structures

The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ framework has been characterized by X-ray diffraction in:

$(NBu_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ (**1**)
(Fig. 21)

$K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**)
$(NMe_4)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (**3**)
$(NBu_4)_2(C_6H_5NH_3)[Mo_5O_{13}(OMe)_4(NO)]\cdot C_6H_5NH_2$ (**6**)
$[(SC_4H_3)C(NH_2)_2]_3[Mo_5O_{13}(OEt)_4(NO)]$ (**16**)
$(NBu_4)_2[Ce\{Mo_5O_{13}(OMe)_4(NO)\}_2]\cdot xMeOH$ (**17**)
(Fig. 25)

They are all viewed as lacunar Lindqvist structures with approximate C_{4v} symmetry. The linear $Mo(NO)^{3+}$ moiety is opposite to the missing MoO^{4+} group and is bridged to the four MoO_2 neighbouring groups by four alkoxo ligands. The four Mo^{VI} centers lie in a plane. The central oxygen is displaced by *c.* 0.4 Å from the four Mo^{VI} plane toward $Mo^{II}(NO)$. The alkoxo bridges are asymmetric, $Mo^{II}–O = 1.99$, and $Mo^{VI}–O = 2.28$ Å (average over **1**, **2** and **3**).

The only other lacunar Lindqvist structure is found in $[Ce(W_5O_{18})_2]^{6-}$ where the lacunar group is stabilized by ligation to cerium [70]. The lacunar $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ species is herein stabilized by interaction either with inorganic cations (Na^+, Li^+,

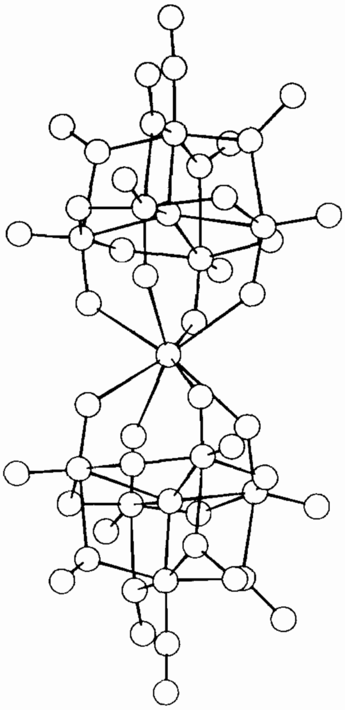

Fig. 25. Molecular structure of the anion $[Ce\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{2-}$ (**17**). This compound contains twice the $Mo_5O_{13}(OMe)_4(NO)$ part of **1** which behaves as a ligand to cerium in the same way as W_5O_{18} in $[Ce(W_5O_{18})_2]^{8-}$.

Ce^{4+}, Eu^{3+},...), or with organic cations ($ArNH_3^+$, $RC(NH_2)_2^+$). For instance its ligating capabilities provided straightforward synthesis of $(NBu_4)_2[Ce\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ (**17**) by reacting cerium sulfate and $(NBu_4)_2]Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}] \cdot 3MeOH$ in methanol (Fig. 25).

In complexes **1** and **3**, the sodium cation interacts with the four axial terminal oxygen atoms of Mo^{VI} centers. In **1** Na^+ attains coordination number 5 through ligation to a methanol molecule. Three hydrogen-bonded solvent molecules form a chain which bridges the sodium atom of one $[NaMo_5O_{13}(OMe)_4(NO)]^{2-}$ and a Mo–O–Mo oxygen atom of another anion; this results in chains. In **2** Na^+ attains coordination number 7 through ligation to one water molecule, to one methanol molecule, and to one axial terminal oxygen of a second anion. This results in dimeric units with which K^+ interacts with building ribbons. In **3** Na^+ attains coordination number 6 through coordination to one water molecule and to one axial terminal oxygen atom of another anion.

The anilinium cation of **6** interacts with the four axial terminal oxygen atoms. As there are only three hydrogen atoms in anilinium cationic function, the N–H...O network is disordered as observed for the phenyl ring.

The three amidinium cations of **16** are linked to the four axial oxygen atoms of one anion through six NH...O bonds and each anion is connected to three other anions through NH...O bonds involving equatorial atoms.

The cerium atom of **17** exhibits a square antiprism environment as in $[Ce(W_5O_{18})_2]^{8-}$.

Closed structures

The X-ray structure of $(NBu_4)_3[Mo_6O_{18}(NO)]$ (**5**) revealed a Lindqvist type structure with a disorder of the anion since it has an inversion center. The disorder could arise as well from a statistical distribution of $[Mo_6O_{17}(NO)_2]^{4-}$ and $[Mo_6O_{19}]^{2-}$ in the crystal; this was ruled out by cyclic voltammetry measurements in acetonitrile. A similar type of disorder was exhibited by $(NBu_4)_2[Mo_6O_{17}(OMe)(NO)]$ (**18**) which was obtained by reacting SO_4Me_2 and $(NBu_4)_3[Mo_6O_{18}(NO)]$ in acetonitrile. The use of an excess of dimethyl sulfate resulted also in the formation of $(NBu_4)_3[SMo_{12}O_{40}]$ which has a Keggin structure.

$[Mo_6O_{18}(NO)]^{3-}$ and $[Mo_6O_{17}(OMe)(NO)]^{2-}$ (Fig. 26) are further members of the $[Mo_6O_{18}L]^{n-}$ family structurally related to $[Mo_6O_{19}]^{2-}$ by the replacement of one terminal oxo group by a nitrogen ligated ligand such as diazenido [49i, j], hydrazido [48b], imido [48b, 50] or nitrido [48b]. Other related compounds include $[VMo_5O_{19}]^{3-}$ [70], $[CpTiM_5O_{18}]^{3-}$ (M=Mo, W) [71], *cis*-$[Nb_2W_4O_{19}]^{4-}$ [72] and its organic and organometallic derivatives [53], hexavanadate derivatives [54] and $[Cp^*{}_2W_6O_{17}]$ [52].

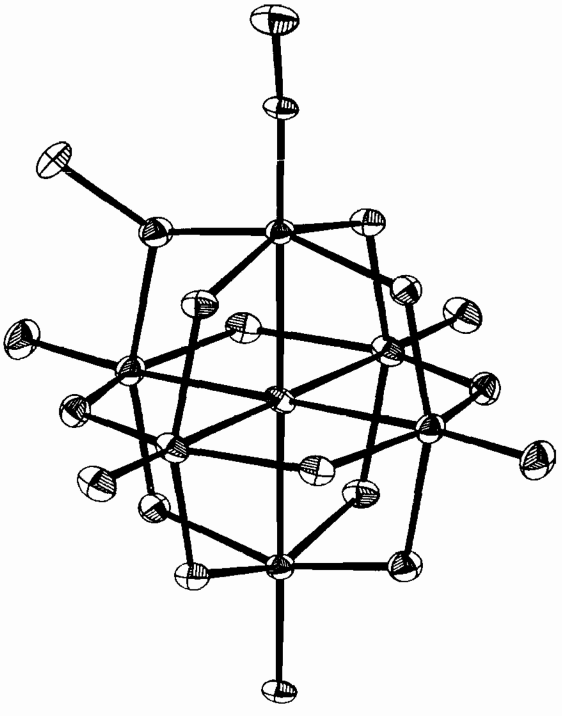

Fig. 26. Molecular structure of $[Mo_6O_{17}(OMe)(NO)]^{2-}$ (**18**) which derives from the Lindqvist structure by substituting one terminal oxygen by NO and one bridging oxygen by OMe.

Studied decamolybdates were $(NBu_4)_2[Mo_{10}O_{24}(OMe)_7(NO)]$ (**13**), $(NBu_4)[Mo_{10}O_{25}(OMe)_6(NO)]$ (**14**), $(NBu_4)_2[Mo_{10}O_{20}(OMe)_9(NO)_3]$ (**15**) (Fig. 27).

The structures of **13** and **14** are related to that of decatungstate $[W_{10}O_{32}]^{4-}$ (Figs. 23 and 24) [73]. The two halves of the anion are connected by almost linear Mo–O–Mo bridges. **13** and **14** are four and two electron reduced species of the mononitrosyl derivative of the hitherto unknown decamolybdate $[Mo_{10}O_{32}]^{4-}$. They can be viewed as containing five or seven Mo^{VI} centers, four or two Mo^{V} centers, and one $Mo^{II}(NO)^{3+}$ center. However it must be underlined that there is still some doubt about the exact composition of **14**, which shows how sometimes the full characterization of those compounds remains difficult. Compound **15** contains nine octahedrally and one tetrahedrally surrounded molybdenum atoms (Fig. 26). Zubieta *et al.* prepared a $[Mo_8O_{24}(OMe)_2]^{4-}$ polyanion where there are four tetrahedrally surrounded and four octahedrally surrounded molybdenum atoms [45c, d]; two tetrahedrons are bound by one oxygen to one molybdenum and two tetrahedrons are bridging two molybdenum atoms. In compound **15** the MoO_4 tetrahedron bridges two $Mo^{II}(NO)$ groups. The third $Mo^{II}(NO)$ group is actually a $Mo(NO)(OMe)O_4$ octahedron, two of its oxygens each bridging a Mo^{V} pair. It is thus a brown mixed valence compound with localized reduced atoms, in contrast to the two other decamolybdates which are blue. There are three Mo^{VI}, four Mo^{V} and three $Mo^{II}(NO)$ centres. The four Mo^{V} atoms make two Mo–Mo metal–metal bonds with a 2.57 Å bond length. Recently Zubieta *et al.* described a cyclic octamolybdate $[Mo_8O_{16}(OMe)_8(C_2O_4)]^{2-}$ containing an oxalate ligand [74]. This compound contains only Mo^{V} atoms which are bound two by two with a 2.578 Å distance.

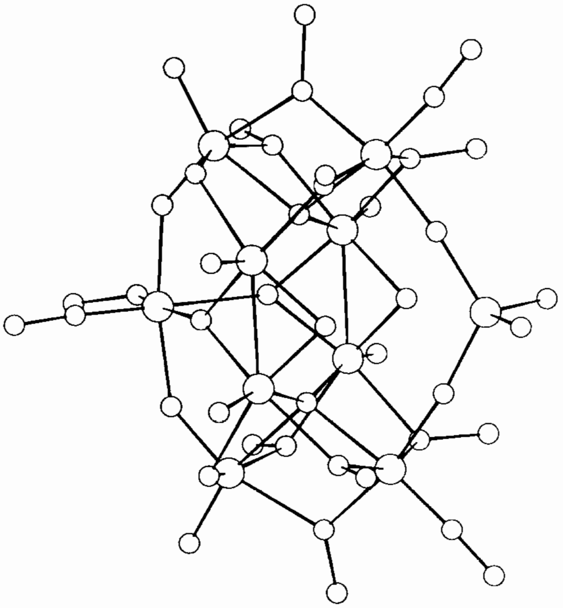

Fig. 27. Molecular structure of the anion $[Mo_{10}O_{20}(OMe)_9(NO)_3]^{2-}$. It contains one MoO_4 group. There are four Mo^{V} bonded two by two with a 2.57 Å Mo–Mo distance. There are three $Mo^{II}(NO)$ groups. One of them is in a $Mo(NO)O_4(OMe)$ octahedron, two oxygens of which each bridge a Mo^{V}–Mo^{V} bonded pair.

Acknowledgements

We would like to express our gratitude to our coworkers for their participation to this work which could not have been developed without their efforts, particularly R. Contant, M. Leyrie (†), J. Martin-Frère, P. Gouzerh, F. Robert, S.-G. Roh, A. Tézé, J. Zubieta and Q. Chen. We would also like to thank C. Brévard, Bruker Company, who kindly put to our disposal some NMR equipment and who assisted us in spectra interpretation.

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