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Scanning Tunneling and Atomic Force Microscopy of Heteropoly Oxometalates

Chemically modified electrodes are increasingly popular for use in various catalytic and electrocatalytic electrochemical processes. In this domain, we have demonstrated that isopoly and heteropoly oxometalates, which are soluble analogues of metal oxides, can be used to prepare particularly active surface structures [1]. Also they may offer a rare opportunity to study in detail the chemical and structural transformations of the catalyst on well-defined species. However, the geometric factors within the attached catalysts, their chemical transformations and their spatial distribution which all together may induce the observed catalytic properties, are not fully understood. In this context, the emerging family of scanning probe microscopes [2], several of which can be used in-situ during electrochemical experiments, may be very helpful in revealing topographical variations related to bulk properties in catalysts under operating conditions. The first step in this direction is to make sure that oxometalates could be imaged with high resolution. The present communication describes STM and AFM experiments on this class of compounds and stresses various aspects of this work which are not being published elsewhere [3-5].

Experimental

A Nanoscope II (Digital Instruments, Santa Barbara, California) was used throughout, in air and at room temperature. Pt/Ir wires were employed as tunneling tips for the STM images. The same instrument, properly implemented, was used for the AFM, in the constant force mode. It combines a microfabricated Si₃N₄ cantilever and integral tip with the optical lever deflection technique. The cantilever has a spring constant of approximately 0.58 N/m, and, during the imaging, exerted a force of approximately 10⁻⁸ newton on the surface of the sample. All images have been fast-Fourier transform filtered to remove high frequency noise.

Tungstophosphoric acid H₃PW₁₂O₄₀, abbreviated as PW₁₂ in the following, has been purchased from Fluka (Fluka puriss.) and used as received. Multifaceted yellow single crystals of sodium decatungstocerate (IV) of formula Na₆H₂CeW₁₀O₃₆·30H₂O, were grown, following the synthesis described by Weakley *et al.* [6, 7]. For STM experiments, the selected oxometalate was dissolved in methanol (typically 10⁻⁴ M). A drop of the solution was deposited on a freshly-cleaved surface of highly oriented pyrolytic graphite (HOPG) and the solvent allowed to evaporate at room temperature, then at 60 °C in an oven. For AFM experiments, crystals showing visually large flat terraces have been selected and glued onto the steel sample-holder with cyanoacrylate adhesives (Loctite[®] or Super Glue 3[™]). A particular situ-

ation may be encountered with thin crystals. Depending on the amount of solvent from the drop of glue, some of them may be soaked up to their surface. They are designated as "wet" crystals in the following. Although a "wet" crystal still appears visually as a single piece; it gives less regular AFM images than the "dry" crystal.

STM Study of H₃PW₁₂O₄₀ (PW₁₂)

Current mode STM images of PW₁₂ deposited on HOPG appear in figures 1a and 1b. A regular pattern is obtained which was found not to depend on bias for the small variations around the value of + 200 mV used in the present experiments. The images call for several remarks. The observed pattern is stable and cannot be mistaken as representing the underlying graphite. The pseudo-three dimensional display best visualizes the details of the surface structure. Thus, scrutiny of figure 1a reveals that the surface pattern contains regular arrays and also "faulted" areas. Such an observation is to be expected as the deposition technique of PW₁₂ may not give a uniform layer and also several layers may partly overlap. Figure 1b has been obtained by zooming in a relatively "unfaulted" area of figure 1a. The apparent period on the structure suggests that individual species are imaged. As a matter of fact, tungstophosphoric species, like most transition metal polyoxoanions, is a discrete, molecular compound, with its structure based on closed-packed oxygen arrays containing interstitial metal centers [8]. PW₁₂ is one of the prototypes of the well-documented Keggin structure [9-10]. It has a highly symmetrical structure and has been shown by crystallography to be easily accommodated in a sphere of 11 Å diameter [11]. In the present case, it is therefore expected that STM images should represent pure topography of the surface. Figure 2 shows a zoomed area of figure 1a and a section through such an area. The mean diameter from the two measurements on this figure is 9.4 ± 0.4 Å. Drawing of very numerous sections through various areas of the STM images resulted in a mean value which is 9.6 ± 0.4 Å. Several comments deserve emphasis. A point of interest concerns the geometric shape of PW₁₂ as suggested by STM images, in particular by figure 1b. This heteropolyanion is expected to be almost perfectly spherical [9-11]. It does appear that the image shows such a pattern. It is rewarding that very numerous size determinations revealed no asymmetry whatever the direction chosen for the sections. The mean diameter value, even though it is slightly smaller than known from crystallographic determinations, is however satisfactorily close to it. The accuracy is within the range expected from measurements on STM images. Among

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reasons which could explain this result, we stress the fact that the deposition technique from methanol should destroy, at least partly, the structuring of PW_{12} crystal by water molecules, thus inducing physical transformations which bring heteropolyanions much closer to each other than seen by crystallography. Also, it is not obvious that dimensions measured by other physical techniques should not be slightly different from those given by STM, which probes the electronic states of the sample. Other problems related to the present experiment are discussed elsewhere [3].

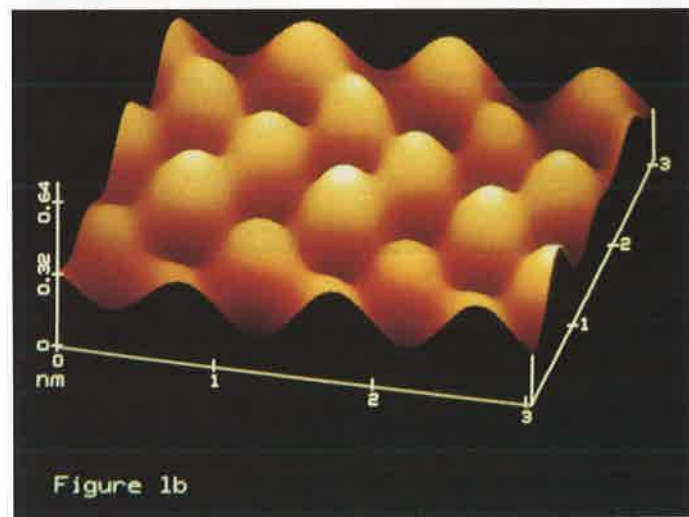
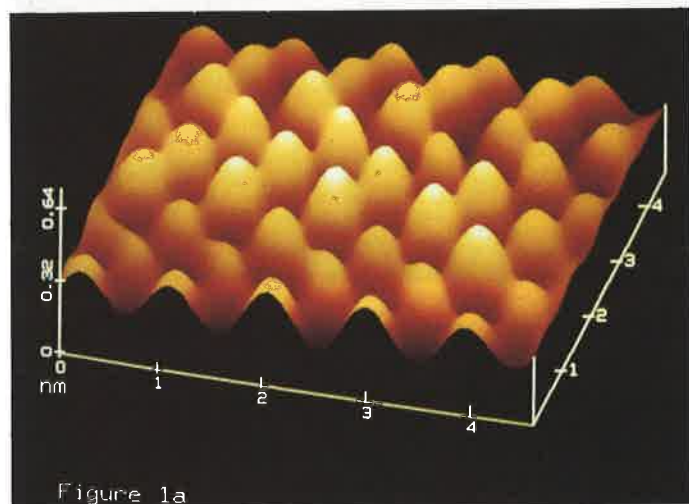


FIGURE 1. - Pseudo-three dimensional STM images, in air at 298 K, of $H_3PW_{12}O_{40}$ deposited on freshly-cleaved HOPG ($I = 1.1 \text{ nA}$, $U = 201.4 \text{ mV}$). The images have been filtered by two-dimensional fast Fourier transform. Pitch angle : 30° . Image (b) is a close-up on a part of figure 1a.

STM and AFM Study of Sodium Decatungstocerate

It was desirable to explore further the ability of STM and AFM techniques to show the shape of molecules and to help in size determinations. Sodium decatungstocerate (IV) was chosen as a new representative example in the oxometalate series. Among the advantages attached to this compound, is the possibility that it can be grown as a single crystal, perfectly stable in air at room temperature, without any need to control the ambient hygrometry. Also its crystal structure is known [7], and cannot be accommodated in a sphere but rather in an ellipsoid. Figure 3 is a space-filling model of this molecule, with the means values of

the major and minor axes of the ellipsoid. Thus, the size and the shape are distinctly different from the corresponding parameters of PW_{12} . Furthermore, a direct comparison of the results of the two techniques is obtained.

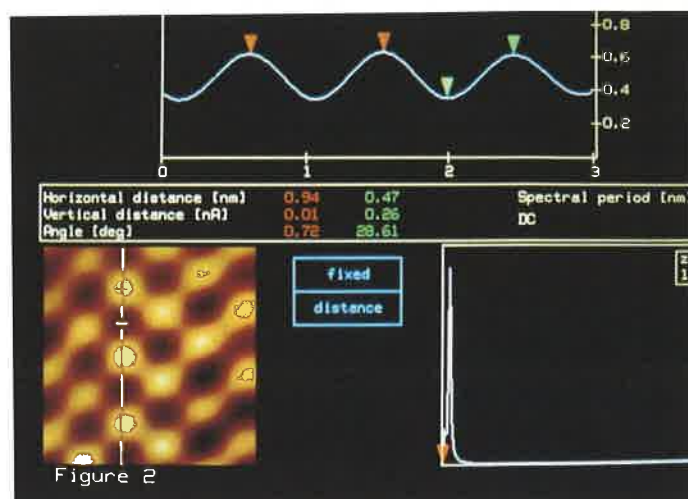


FIGURE 2. - Section through a zoomed area of figure 1a, showing an example of molecular size determination.

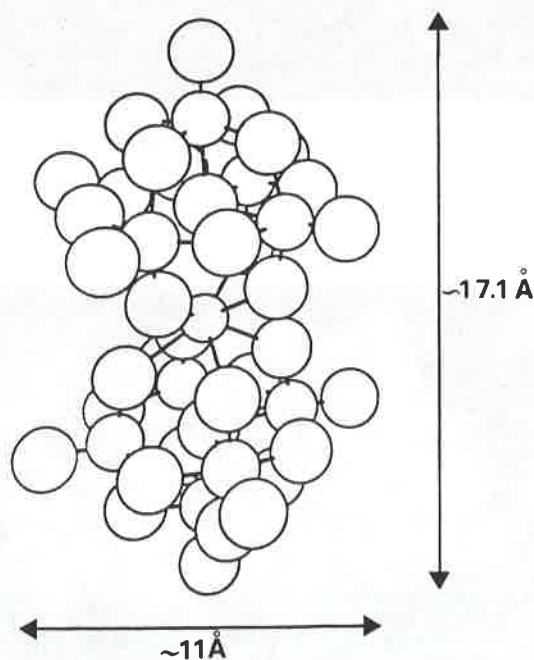


FIGURE 3. - Space-filling model of the structure of sodium decatungstocerate (IV), the spheres representing essentially close-packed oxygen atoms.

Figure 4 represents the pseudo-three dimensional STM image of sodium decatungstocerate (IV) deposited on HOPG. The presence of the oxometalate is revealed on the surface. A good organization, however, does only appear from place to place. In several domains, entities are observed which should be suitable for molecular size determinations from the images. Much the same pattern is observed on the AFM image of the "wet" single crystal as is displayed on Figure 5. One of the reasons for this relative disorder can, probably, be traced out to the very origin of the cohesion of the single crystal of sodium decatungstocerate. It is known that, contrary to some other salts of heteropolyanions in which the cations are essential in linking together the anions [7],

the cohesion of sodium decatungstocerate mainly depends on hydrogen bonds to water molecules. It is then conceivable that the wetting of the crystal by any other solvent should destroy the structuring forces, at least partly, and random individual molecules should be observed, much the same way as in STM. As a matter of fact, whatever the technique, figures 4 and 5 show, randomly but several times in any selected area of the surface, molecules isolated enough for their dimensions to be measurable. Routinely, the values mentioned on figure 3 have been obtained within 5 % error. Notice must be taken of the reproducibility of the structure observed by the two techniques, indicating a good correlation between them. In the present case, STM images can be considered as representing pure topography of the surface.

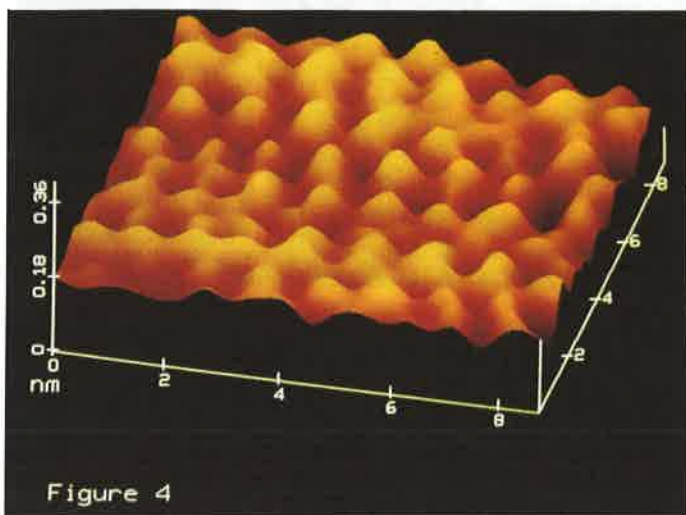


FIGURE 4. - Pseudo-three dimensional STM image of sodium decatungstocerate (IV) deposited on HOPG ($I = 0.76 \text{ nA}$, $U = 57.7 \text{ mV}$). The image has been filtered by two-dimensional fast-Fourier transform. Pitch angle : 30° .

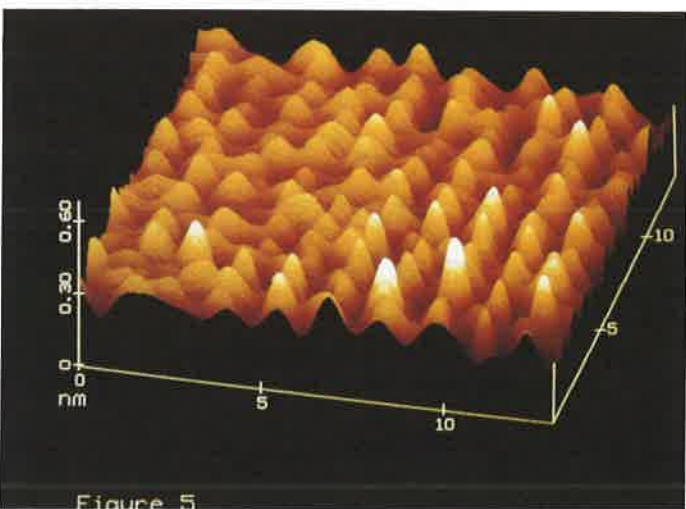


FIGURE 5. - Pseudo-three dimensional AFM image of the surface of a "wet" single crystal of sodium decatungstocerate (IV) in air at room temperature. The image has been filtered by two dimensional fast-Fourier transform. Pitch angle : 30° . For other conditions, see text.

AFM runs have also been performed on the surface of the "dry" single crystal. Figure 6a shows a strikingly regular array of molecules. On closer scrutiny, it can be noticed that slightly "faulted" areas exist, even though the whole pattern is largely dominated by a periodic arrangement. Figure 6b is a close-up image on a

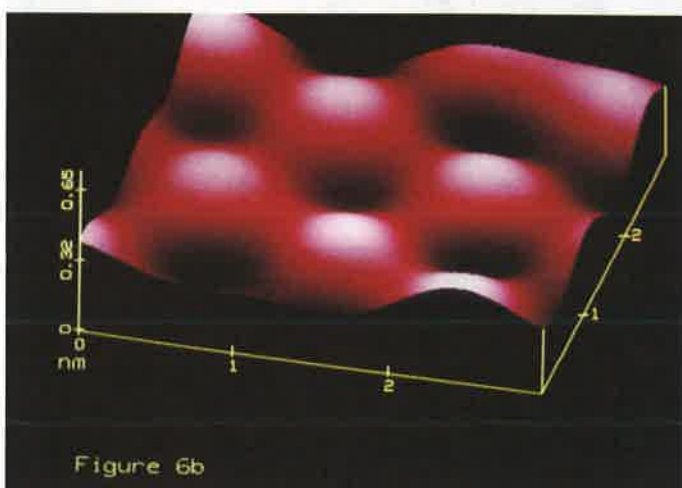
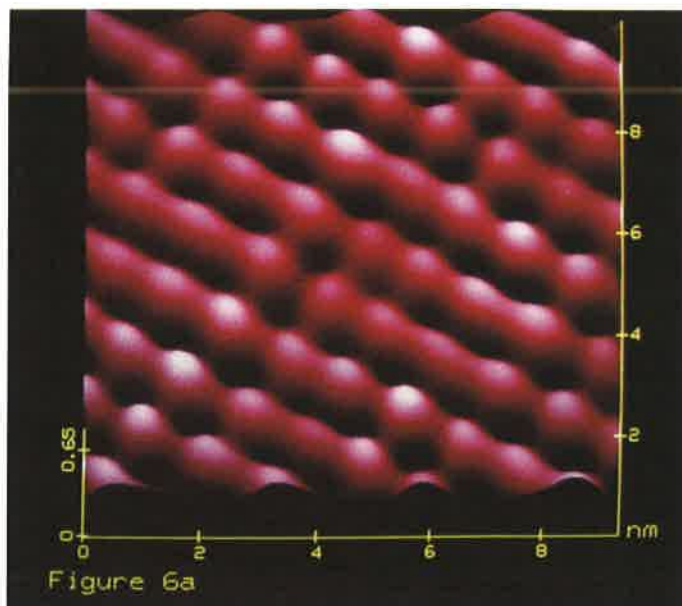


FIGURE 6. - AFM images of the surface of a "dry" single crystal of sodium decatungstocerate (IV) in air at room temperature. The image have been filtered by two-dimensional fast-Fourier transform. For other conditions, see text.

- (a) pitch angle 60°
 (b) zoom on a part of figure 6a. Pitch angle : 30° .

part of figure 6a. Obviously, AFM images the surface of this "dry" crystal down to molecular resolution. The shape of the molecule is clearly visible. This suggests that, despite water molecules which link the anions together, the main contribution to the atomic force measured by the AFM tips results from the contour shown in figure 3. Careful sections through figure 6a-6b and several other close-up images culled from figure 6a, have allowed to measure the dimension of each molecule with a satisfactory accuracy. As expected from the inspection of the figures, the measurements in the present case are very easy as there is no need to select particularly well-behaved areas or molecules. The very regularity of the observed pattern prompted us to try and fit the AFM images with the crystallographic arrangements of the molecules in the single crystal. Sodium decatungstocerate (IV) $\text{Na}_6\text{H}_2\text{CeW}_{10}\text{O}_{36}\cdot 30\text{H}_2\text{O}$ crystallizes with 30 water molecules and belongs to the monoclinic system [7], space group $C2/c$, $a = 18.14 \text{ \AA}$, $b = 18.62 \text{ \AA}$, $c = 18.51 \text{ \AA}$, $\beta = 95.9^\circ$, $Z = 4$. Figure 7a is a computer representation of the arrangement of the heteropolyanions in a projection along the b -axis. This arrangement has been chosen because it seems to correspond best to the AFM image. For clarity, only every other anion is represented. In each heteropolyanion, only the main interatomic bonds are shown, with the cerium atom at the center of the species. In figure 7a are

indicated the main distance parameters which have been deduced from X-ray analysis of the single crystal [7, 12]. It must be noticed that the conventional unit-cell is not represented, but only an apparent unit-cell with its vertices coinciding with cerium atoms. The fitting of this computer arrangement to a zoomed AFM patterns appears on figure 7b. Non linear effects of the piezo ceramics responses on this image are expected to be minimal, because the scanned area is small. With this in mind, it appears that the angles in the apparent unit-cell are slightly different from 90° , suggesting that the scanned area represent actually the (010) face of the single crystal. The experimental distances measured from the AFM image by drawing the appropriate sections through it appear, on figure 7b. In the particularly favourable example studied in this work, these experimental values deduced from AFM experiments appear to approach crystallographic determinations to within less than 5%. All these results together suggest strongly that the area imaged by the AFM is a simple termination of the bulk.

Concluding remarks

It is rewarding that the two oxometalates studied in this work could be imaged with molecular resolution both by STM and AFM. The molecular sizes and the shapes of the species are revealed with a good accuracy as compared to X-ray analysis determinations. In the present examples, the STM and AFM techniques give the same results and the STM images can be concluded to represent pure topography.

Acknowledgement

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References

- [1] B. Keita, L. Nadjo, *Materials Chemistry and Physics*, **1989**, 22, 77.
- [2] Y. Martin, C.C. Williams, H.K. Wickramasinghe, *Scanning Microscopy*, **1983**, 2, 3.
- [3] B. Keita, L. Nadjo, *Surf. Sci. Lett.*, in press.
- [4] B. Keita, L. Nadjo, K. Kjoller, *Surf. Sci. Lett.*, in press.
- [5] B. Keita, F. Chauveau, F. Theobald, D. Belanger, L. Nadjo, *Surf. Sci.*, submitted.
- [6] R.D. Peacock, T.J.R. Weakley, *J. Chem. Soc. A*, **1971**, 1936.
- [7] J. Iball, J.N. Low, T.J.R. Weakley, *J. Chem. Soc. Dalton Trans.*, **1974**, 2021.
- [8] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, Heidelberg, **1983**.
- [9] J.F. Keggin, *Proc. Roy. Soc. A*, **1934**, 144, 75.
- [10] G.M. Brown, M.R. Noe-Spirlet, W.R. Busing, H.A. Levy, *Acta Cryst. B*, **1977**, 33, 1038.
- [11] L.C.W. Baker, M.T. Pope, *J. Am. Chem. Soc.*, **1960**, 82, 4176.
- [12] C. Riche (ICSN, CNRS, UPR 2031, France) carried out the X-ray analysis of the single crystals and also provided us with representations of the arrangements of the heteropolyanion along several projection directions.

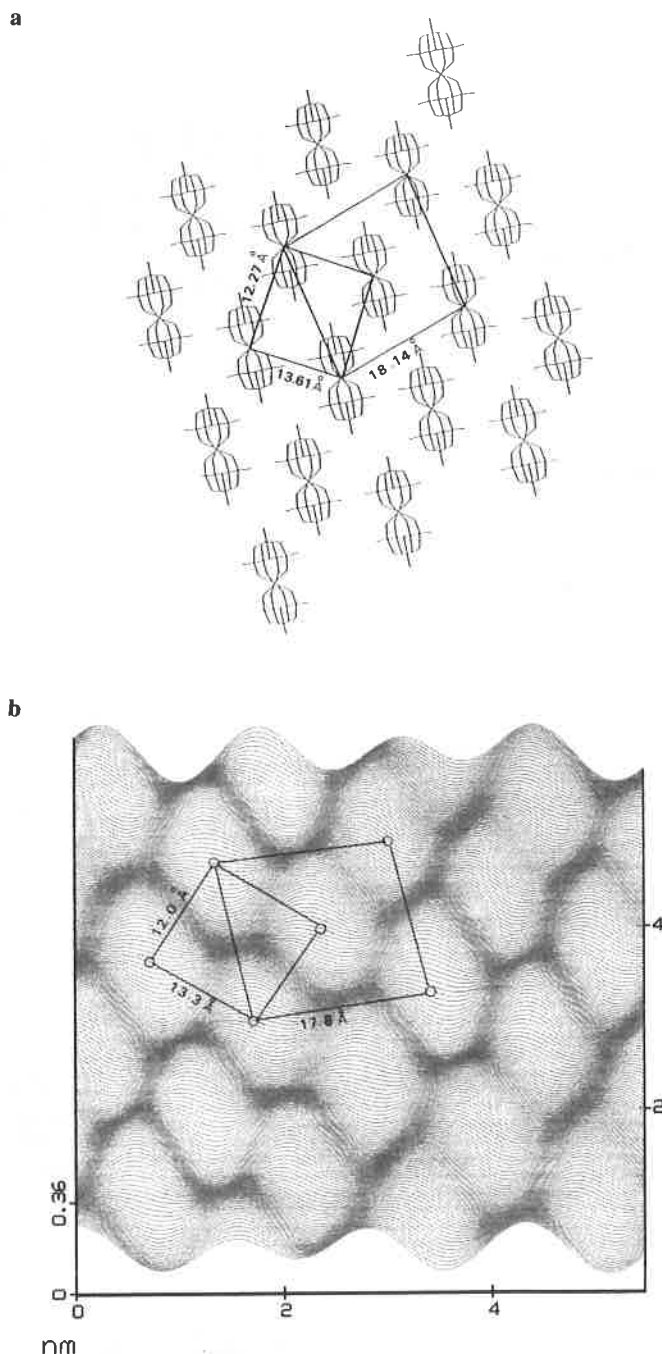


FIGURE 7. - (a) Computer representation of the arrangement of sodium decatungstocerate (IV) species in the (010) plane of the crystal. For clarity, every other anion has been represented. The main distance parameters obtained from X-ray analysis are indicated on the figure. (b) Zoomed AFM image of the surface of a crystal of sodium decatungstocerate, showing an apparent unit-cell, with the experimental distance parameters to be compared to those of figure 7a.