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THE STRUCTURE OF A COMPOUND OF UNEXPECTED CONFORMATION INVOLVED IN THE XYLOSE-LYXOSE EPIMERIZATION

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Abstract: The structure of a molybdenum(VI) complex of the sugar, lyzose, has been established by the X-ray method.

It is well known that monosaccharides adopt different conformations involving both pyranose and furanose forms. Early conformational studies of the latter suggested the existence of so-called twist (T) and envelope (E) arrangements[1-2]. However, these descriptions, based on the displacement of atoms out of the ring plane relative to the exocyclic oxygen atom were, of course, discrete. The more sophisticated treatment of Altona and Sundaralingam[3] now allows a continuous description of the conformation by means of the "phase angle of pseudo-rotation" which is obtained by measuring the bond rotation angles around the ring.

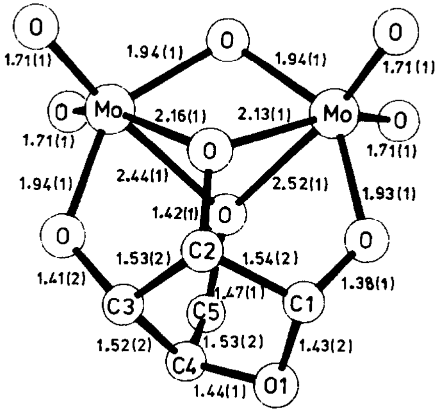
From the reaction between ammonium molybdate and the pentose, xylose, we have obtained crystals of a complex composed of two molybdate and one sugar moiety. It was difficult to envisage the sugar conformation or even its form in such a molecule in view of the known structural features of xylose[4] and of the known dinuclear molybdate complexes[5-14] and consequently an X-ray structural analysis was undertaken.

The complex crystallises in the space group $P2_12_12_1$ with four molecules in a cell of dimensions a = 8.0029(6), b = 19.853(1), c = 6.9178(9). Intensity data were collected on a Hilger and Watts 4-circle diffractometer using Cu-K_α radiation and a total of 1078 reflections with $I > 3\sigma(I)$ were recorded. The structure was solved by Patterson and Fourier methods and has been refined by the full-matrix least squares process to give R = ·039.

The molecule is illustrated in the figure together with relevant distances. The metal centre is dinuclear with a triple-oxygen bridge linking the two molybdenum atoms. All Mo-O distances are normal. The monosaccharide in the complex is in fact lyxose in an unusual furanose form. This contrasts with the pyranose configuration found for the uncomplexed sugar[15]. Bilik[16-18] has demonstrated that Mo(VI) will catalyse epimerization of pentose sugars at carbon(2), and, to a much lesser degree, at carbon(3) according to the following equilibria.

$$\begin{tikzcd}
\text{RIBOSE} \arrow[r, shift left] \arrow[d, shift right] & \text{[1,2-ANHYDRO-]} \arrow[l, shift left] \arrow[r, shift left] & \text{ARABINOSE} \arrow[l, shift left] \\
\text{[2,3-ANHDRO-]} \arrow[u, shift right] \arrow[d] & & \text{[2,3-ANHYDRO-]} \arrow[u] \arrow[d, shift left] \\
\text{XYLOSE} \arrow[r, shift left] & \text{[1,2-ANHYDRO-]} \arrow[l, shift left] \arrow[r, shift left] & \text{LYXOSE} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

In this instance the starting sugar xylose has established an equilibrium with its C2-epimer lyxose and this sugar has preferentially complexed with the metal centre.



The pseudo-rotation formulae have been applied to this furanose form of lyxose and a phase angle of 247.7° together with a normal amplitude of pucker (reflecting the degree of non-planarity of the ring) of 35.6° are calculated. (Torsion angles around the lyxose ring are $\tau_0 = 26.7$, $\tau_1 = -7.3$, $\tau_2 = -13.2$, $\tau_3 = +29.2$, $\tau_4 = -36.0°$.) The conformation is thus midway between the discrete descriptions $C_{4'}$-endo (^{4}E) and $C_{4'}$-endo/$O_{1'}$-exo ($^{4}_{O}T$)[3]. It is, as far as we are aware, a unique monosaccharide furanose ring conformation. The reasons, however, are plain. The oxygen atoms at C1, C2, and C3 bind normally across the dinuclear centre with no undue strain but, in order that the exocyclic oxygen O5 can bind, the attached carbon atom C4 must be pushed out of the ring in this direction. The small twist at O1 is by way of compensation for this extra strain.

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