



Note

The crystal structure of a lyxose-bridged dimolybdate: a redetermination of the first monosaccharide–metal complex's structure

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ABSTRACT

The crystal structure of the first monosaccharide–metal complex ever reported, a β -D-lyxofuranose-bridged dimolybdate [Taylor, G. E.; Waters, J. M. *Tetrahedron Lett.* **1981**, 22, 1277–1278] was re-determined since the original work shows unbalanced charges, and thus an unclear protonation state of the lyxose ligand. As a result, the complex was found to be a monoanion whose charge is balanced by an ammonium counterion. The lyxose O5 atom is non-deprotonated, and the carbohydrate ligand is trianionic due to deprotonation of the O1, O2 and O3 hydroxy functions.

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In 1981, Taylor and Waters published their pioneering work on the first crystal structure determination of a monosaccharide–metal complex, a dinuclear molybdenum–lyxose complex.¹ For more than a decade, this crystal structure determination on a heteroleptic oxido-alkoxido complex remained the only one in the field. Not until 1995 did a work on a series of homoleptic, dinuclear mannose complexes expand the ever more rapidly developing field of metal complexation of reducing sugars.² Unfortunately, despite the fundamental significance of Taylor and Water's work, neither the original publication nor the corresponding entry in the Cambridge data base (LYXSMO) met the requirements for a state-of-the-art structure determination. Thus, the formula given in the data base, $C_5H_6Mo_2O_{10}$, corresponds to an entirely deprotonated lyxose tetraanion, which, together with five oxido ligands, results in a -14 charge of the anionic part which is not counter-balanced by the obvious oxidation state $+VI$ of the molybdenum central atoms. Since no hydrogen positions were reported, a check of the Mo–O atomic distances promises more insight from the anticipated detection of two non-deprotonated ligands. Only a single candidate results for a proton-bearing oxygen ligand, however, namely the lyxose-O5 atom which exhibits markedly elongated Mo–O contacts. Accordingly, Kováčik et al. have reported the detection of $C_5H_7Mo_2O_{10}^-$ monoanions in lyxose–molybdate solutions.³

The Chapelle–Verchère group has interpreted NMR and potentiometric data of lyxose–molybdenum complexes.^{4–7} After quite a bit of wavering with respect to the lyxose's configuration and protonation state, they now consider a 2:1:3 stoichiometry of MoO_4^{2-} , lyxose and H^+ for the main solution species which resembles $C_5H_7Mo_2O_{10}^-$ monoanions.⁴

In order to settle the situation, we are presenting here a re-evaluation of the 1981 structure determination. Unlike Taylor and Waters, who reacted ammonium molybdate with D-xylose and obtained the title compound by epimerisation of the aldopentose, we used a solution of D-lyxose directly and, with respect to the isolated product's stoichiometry, a slight excess of ammonium molybdate for crystallisation. Using the procedure described below, we obtained crystals of $NH_4[Mo_2O_4(\mu-O)(\beta-D-Lyx\eta^{1,2,3}H_3\text{-}\kappa O^{1,2,3,4})]$ (**1**, Lyx = lyxose) which gave the same reduced unit cell as reported by the above-mentioned authors. Figure 1 shows the molecular structure of the ion pairs that make up the crystal. The two negative excess charges of Taylor and Water's determination are coun-

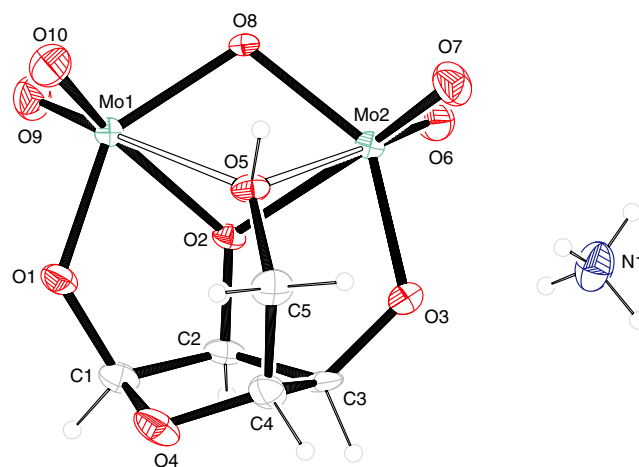


Figure 1.

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ter-balanced by an ammonium counter-ion and by the non-deprotonation of the O5 hydroxy function. Considering the lower precision of the former study compared to the present work, in terms of standard deviations, the molecular parameters of the complex are essentially the same.

Assuming that the slight heptamolybdate excess in our study does not markedly influence the proton balance, the mother liquor used here is similarly proton-deficient with respect to the isolated solid-state species as are Chapelle and Verchère's solutions. It may thus be assumed, in agreement with the mass-spectrometric result, that the monoanions of **1** are generally representative for the slightly acidic solutions in question (pH ca. 6).

The crystal structure of **1** is determined by hydrogen bonds (Table 1). A short donor–acceptor distance is found for an intermolecular O5–H···O8 bridge that concatenates the dimolybdate monoanions to ribbons along the crystallographic [100] direction. The ammonium ions combine these ribbons to layers that are separated along [001] by hydrophobic interfaces made up from the furanose rings' 'back sides' (the hemisphere opposite to the molybdenum atoms).

Related structurally characterised compounds that show coordination of a tetradentate polyolate trianion to an Mo₂O₅ core show close resemblance of significant structural parameters. Thus, both the erythritolate and the mannitolate trianion provide the typical O₄ rhomb that binds in an asymmetrical way to the Mo₂ couple due to the presence of a proton at one of the two bridging oxygen atoms.^{8,9} Structural resemblance in terms of intermolecular features is observed for **1** and the mannitol-derived dimolybdate.⁹ In both compounds, a strong intermolecular hydrogen bond between the non-deprotonated hydroxyl bridge as the donor and the alkoxido bridge as the acceptor concatenates the dimolybdate anions to polyanionic strands by the action of a 2₁ axis. The donor–acceptor distances underline the similarity: about 2.60 Å in the mannitolato-dimolybdate and about 2.62 Å in **1**.

1. Experimental

1.1. Material

D-Lyxose (0.015 g, 0.10 mmol) and (NH₄)₆Mo₇O₂₄·4H₂O (0.062 g, 0.05 mmol) were dissolved in 1 mL of water, and stirred for 2 h at 4 °C. Colourless crystals were obtained within one week at 10 °C.

1.2. X-ray study

Crystals suitable for X-ray crystallography were selected with the aid of a polarisation microscope, mounted on the tip of a glass fibre and investigated at room temperature on a Stoe IPDS diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SIR 97) and refined by full-matrix least squares calculations on F^2 (SHELXL-97). Anisotropic displacement parameters were re-

Table 1
Hydrogen bonds (Å and °)

D	H	A	D–H	H···A	D···A	D–H···A
O5	H5	O8 ⁱ	0.94(4)	1.69(4)	2.618(3)	165(3)
N1	H71	O3	0.85(6)	2.26(6)	3.093(5)	168(5)
N1	H72	O10 ⁱⁱ	0.85(6)	2.26(6)	3.082(5)	163(5)
N1	H73	O10 ⁱ	0.85(6)	2.13(6)	2.937(5)	159(5)
N1	H74	O9 ⁱⁱⁱ	0.85(5)	2.09(6)	2.857(5)	150(5)

Symmetry codes: (i) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $x, -1 + y, z$; (iii) $-1 + x, -1 + y, z$.

Table 2
Crystallographic data

Empirical formula	C ₅ H ₁₁ Mo ₂ NO ₁₀
M _r (g mol ⁻¹)	437.02
Crystal size (mm)	0.31 × 0.11 × 0.05
T (K)	293(2)
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a (Å)	6.9029(4)
b (Å)	7.9951(4)
c (Å)	19.850(1)
V (Å ³)	1095.5(1)
Z	4
ρ (g cm ⁻³)	2.650
μ (mm ⁻¹)	2.340
Absorption correction	Numerical
T _{min} /T _{max}	0.3614/0.7163
Refls. measured	10589
R _{int}	0.0404
Mean $\sigma(I)/I$	0.0286
θ range	2–28
Flack parameter	–0.06(6)
Refls. in refinement	2622
Observed refls.	2309
Parameters	181
Restraints	10
R(F _{obs})	0.0296
R _w (F ²)	0.0606
S	0.977
Shift/error _{max}	0.001
Max. res. density (e Å ⁻³)	0.425
Min. res. density (e Å ⁻³)	–1.037

fined for all non-hydrogen atoms. C-bonded H atoms were considered as riding on their pivot atoms. The O5-bonded H atom was located on a difference map; its coordinates and an isotropic U value were refined without applying restraints. A common isotropic U value and a common distance to N1 were refined for the ammonium H atoms. Both the refined distance and the common temperature factor indicate a librational disorder of the ammonium H atoms though they are all involved in hydrogen bonds (Table 1). Crystallographic data are listed in Table 2. Distances, angles and furanose puckering parameters¹⁰ are collected in the caption to Figure 1.

Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 703639. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.12.001.

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