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A structural study of *D*-mannitolatodimolybdate(VI) complexes in aqueous solution

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Abstract

The structure of the *D*-mannitolatodimolybdate(VI) complex has been determined by means large angle X-ray scattering (LAXS) in aqueous solution at two pH values, 2.0 and 5.5. The two complexes have in principle the same structure in aqueous solution, two face-sharing molybdate(VI) octahedra connected to one *D*-mannitol ligand, as previously observed in the solid state. In the deprotonated form of the complex, pH=5.5, the *D*-mannitol ligand has lost a proton and as a result the Mo···Mo distance is 0.054 Å shorter than the protonated form, pH=2.0. This indicates that it is a proton on an oxygen shared by molybdate groups that leaves the complex at deprotonation and forces the molydate(VI) octahedra even closer to each other.

Keywords: molybdate, *D*-mannitol, structure, aqueous solution

Footnotes:

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Introduction

The molybdate(VI)-*D*-mannitol system in aqueous solution has been studied extensively as it has some very interesting properties. One is the high optical activity which increases by addition of strong acid [1-7]. This system has many similarities with pure anion hydrolysis systems and can be used as model system for these. A large number of potentiometric, polarimetric, conductometric and spectrophotometric investigations has been reported for this system [8]. The equilibria over the range $1 < -\log[H^+] < 10$ can be written as

$$pH^+ + q\,MoO_4^{2-} + r\,C_6H_8(OH)_6 \leftrightharpoons (H)_p(MoO_4)_q(C_6H_8(OH)_6)_r^{(p-2q)+}$$

where $C_6H_8(OH)_6$ is *D*-mannitol. It was found that complexes with the (*p*,*q*,*r*) compositions (0,1,0), (2,2,1), (3,2,1) are formed within well-defined regions of domination, Figure 1. The diagram was constructed using the equilibrium constants reported by Pettersson [8], determined at low molybdate(VI) concentrations in 3.0 M $Na(ClO_4)$ ionic medium. Attempts have been made to crystallize the predominating complexes using molar ratios of acid, molybdate(VI) ions and *D*-mannitol corresponding to the complex composition (*p*,2,1), with *p* = 2.0, 2.5, 3.0, 3.5, 4.0. However, the only crystalline phase obtained did correspond to the composition (3,2,1) and contained discrete dimeric $[Mo_2O_5\{O_3(OH)C_6H_8(OH)_2\}]^-$ anions [9], Figure 2. A striking feature is that the two Mo-octahedra in the solid phase are face-shared which is very uncommon.

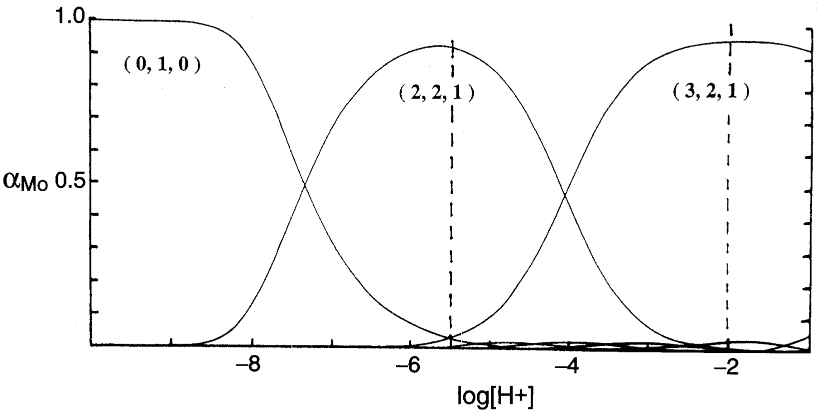

Figure 1. Complex distribution diagram of the dimolybdate(VI)-*D*-mannitol system in aqueous solution as function of acidity from reference 8

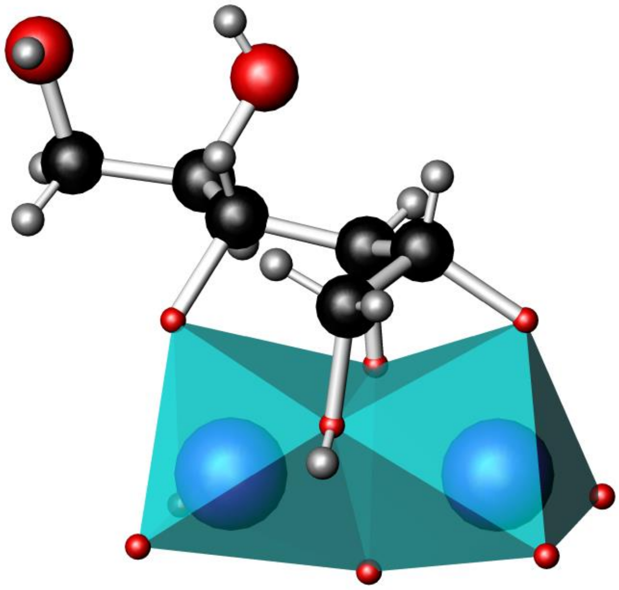

Figure 2. The structure of $[Mo_2O_5\{O_3(OH)C_6H_8(OH)_2\}]^-$ from the crystal structure used in the model calculation of theoretical contribution to the LAXS function.

The aim of this study is to determine whether the kind of structure reported in the solid state also is the dominating one in aqueous solution, and if the structure will change with degree of protonation. Large angle X-ray scattering (LAXS) experiments have been applied as this method gives information of all distances in the studied sample contrary to EXAFS where only the distances around the absorbing atom are observed. Furthermore, long and diffuse distances are detectable by LAXS, but not by EXAFS [10], which is of particular interest in the study of large complexes in solution as in this case. Measurements were made on two solutions with C_{Mo} = 1.50 mol·dm^{-3} and C_{Mannitol} = 0.76 mol·dm^{-3} at pH = 2.0 and 5.5 to maximize the content of the individual complexes $[Mo_2O_5\{O_3(OH)C_6H_8(OH)_2\}]^-$ and $[Mo_2O_5\{O_3(OH)C_6H_8O(OH)\}]^{2-}$ (vertical lines in the distribution diagram, Figure 1). To obtain the high concentration of the complexes needed for the LAXS measurements, lithium was used as counter cation. The compositions of the studied solutions are given in Table 1.

Experimental

Chemicals. D-mannitol, $C_6H_8(OH)_2$ (Difco Laboratories and Bakers, p.a.), molybdenum(VI) oxide, MoO_3 (E. Merck, p.a.), lithium molybdate(VI), Li_2MoO_4 (Aldrich, 99 %) and hydrochloric acid (E. Merck, p.a.) were used as purchased.

Preparation of solutions. Litium molybdate and freshly recrystallized *D*-mannitol were dissolved in water and hydrochloric acid was added to pre-decided concentrations and pH values, see Table 1. The selected concentrations were chosen to get as high concentrations of the complexes as possible without any risk of precipitation during the measurements. The pH values during the addition of hydrochloric acid at the preparation of the solutions were followed by a pH meter with a standard glass electrode. The chosen pH values are based on measurements reported elsewhere [8], where the ionic strength, 3.0 mol·dm^{-3} ($NaClO_4$) is slightly higher than in the studied solutions, 2.25 and 1.51 mol·dm^{-3} for solutions MoMa1 and MoMa2, respectively. This difference is relatively small and it is therefore assumed that the complex distribution as function of pH is similar in the solutions used in this study as in the potentiometric and spectrophotometric studies reported previously, Figure 1 [8].

Table 1. Concentrations in mol·dm^{-3} of the dinuclear molybdate(VI)-*D*-mannitol complexes $(H)_p(MoO_4)_q(C_6H_8(OH)_6)_r^{(p-2r)+}$ in aqueous solution used in the LAXS studies at ambient room temperature; MoMa1 and MoMa2 correspond to the complexes with *p,q,r* values of *2,2,1* and *3,2,1*, respectively.

Sample	pH	[Mo^{VI}]	[*D*-mannitol]	[Li$^+$]	[H$^+$]	[Cl$^-$]	[H_2O]	ρ/g·cm^{-3}	μ/cm^{-1}
MoMa1	5.50	1.500	0.760	1.500	0	0	45.965	1.2042	10.047
MoMa2	2.00	1.500	0.760	1.500	0.775	0.775	44.903	1.2000	10.184

Large angle X-ray scattering measurements. A large-angle θ-θ diffractometer was used to measure the scattering of Ag-Kα radiation ($\lambda = 0.5609$ Å) from the free surface of aqueous solutions of *D*-mannitolatodimolybdate(VI) complexes. The solutions were contained in a Teflon cuvette inside a radiation shield with beryllium windows. After monochromatization of the scattered radiation by a focusing LiF crystal, the intensity was measured by means of a scintillation counter at 450 discrete θ-values in step scan mode with an interval of Δθ of 0.10 ° for $0.5 < \theta < 30$ ° and 0.25 ° for $25 < \theta < 65$ ° of the scattering angle 2θ, accumulating at least 40,000 counts twice for angle, which corresponds to a statistical error of 0.5 %. The reflections from a gold plate were used to calibrate the scattering angle 2θ of the goniometer. The experimental set-up and the theory of data treatment and modelling have been presented elsewhere [11]. All data treatment was carried out by means of the KURVLR program [12]. The experimental intensities were normalised to a stoichiometric unit of volume containing one molybdenum atom, using the scattering factors *f* for neutral atoms, including corrections for anomalous dispersion [13], Δ*f*' and Δ*f*'', and values for Compton scattering [14]. Leastsquares refinements of the model parameters were carried out by means of the STEPLR program [15], where the expression $U = \sum w(s)[s\cdot i_{\mathrm{exp}}(s) - s\cdot i_{\mathrm{calc}}(s)]^2$ is minimised. The refinement of the model parameters was made for data in the high *s*-region where the intensity contribution from the long-range distances can be neglected [16]. In order to obtain a better alignment of the intensity function before the refinements, a Fourier back-transformation procedure was used to correct the $i_{\mathrm{exp}}(s)$ functions by removing spurious non-physical peaks below 1.2 Å in the experimental radial distribution function (RDF) [17]. The estimated standard deviations (esd’s) given within parenthesis in Table 2 include only statistical errors, while in the text the esd’s include also the systematic errors.

Results and Discussion

The LAXS data on two aqueous solutions of 0.750 mol·dm^{-3} *D*-mannitolatodimolybdate(VI) display very similar radial distribution functions with a mean Mo-O bond distances of 1.8 Å, and Mo-O/C distances and intramolecular distances within the *D*-mannitolatodimolybdate(VI) complex at 2.6, 3.1, 4.3 and 5.4 Å, Figures 1, 2 and S1. The applied coordinates in the model of the *D*-mannitolatodimolybdate(VI) complex were derived from the crystal structure of the protonated *D*-mannitolatodimolybdate(VI) complex [9], the Cartesian coordinates are given in Table S1, and all intramolecular distances in this complex were calculated by the KURVLR and STEPLR programs. The Mo···Mo distance in the two complexes is slightly different, Figure S1, and was determined by letting the z coordinate for the atom Mo2 be refined, Table S1. The Mo···Mo distance was determined to 3.075(6) and 3.129(6) Å for the (2,2,1) and (3,2,1) solutions, respectively. The large peak at 3.0 Å in the radial distribution function (RDF) contains also the O···O distance from the aqueous bulk, refined to 2.864(6) and 2.860(6) Å, respectively, which is in the expected range for such distances [18]. It has not been possible to determine the structure of the hydrated lithium ion. However, the Li-O bond distance has been set 1.945 Å, which is the mean distance of four-coordinate lithium ion with oxygen donor ligands [19]. The applied Li-O bond distance affects the determination of the structure of the studied *D*-mannitolitodimolybdate(VI) complex very little as the dominating distances do not coincide. The main contribution to the 3.1 Å peak originates from Mo···Mo interactions, and this short distance strongly supports the existence of a dimolybdate group with face-sharing octahedra in both solutions.

In the (2,2,1) solution, containing the non-protonated species, the Mo···Mo distance is 3.075(6) Å and l = 0.13(1) Å, where l is the atomic displacement factor. In the (3,2,1) solution the Mo···Mo distance is 3.129(6) Å and l = 0.15(1) Å. The latter distance is in close agreement with the one in the solid state, 3.1435(3) Å. The present study has shown that the structural feature of the solid face structure prevails in aqueous solution and the Mo···Mo distance increases when a proton is attached to a face sharing oxygen (Fig. 2).

The fits of the RDFs and intensity functions of the (2,2,1) and (3,2,1) solutions are given in Figures 3a and 3b, respectively, and the final structure parameters, besides those of the of *D*-mannitolitodimolybdate(VI) complex in Table S1. The experimental curves (Fig. 3a and 3b) show two distinct peaks at 3.1 and 4.2 Å in perfect agreement with the calculated intensity curve and radial distribution function, using the atomic coordinates from the X-ray structure.

Table 2. Mean bond distances, *d*/Å, number of distances, *N*, and temperature coefficients, *b*/Å^2, in the LAXS studies of the *D*-mannitolatodimolybdate(VI) complex in in aqueous solution at room temperature. The estimated standard deviations given within parenthesis include only statistical errors.

Species	Interaction	*N*	*d*	*b*
2,2,1	Mo···Mo	1	3.075(3)	0.0032(3)
Water bulk	O···O	2	2.863(4)	0.0217(4)
$Li(H_2O)_4^+$	Li-O	4	1.945	0.0075
3,2,1	Mo···Mo	1	3.129(3)	0.0039(3)
Water bulk	O···O	2	2.860(4)	0.0200(4)
$Li(H_2O)_4^+$	Li-O	4	1.945	0.0075

Figure 3a.

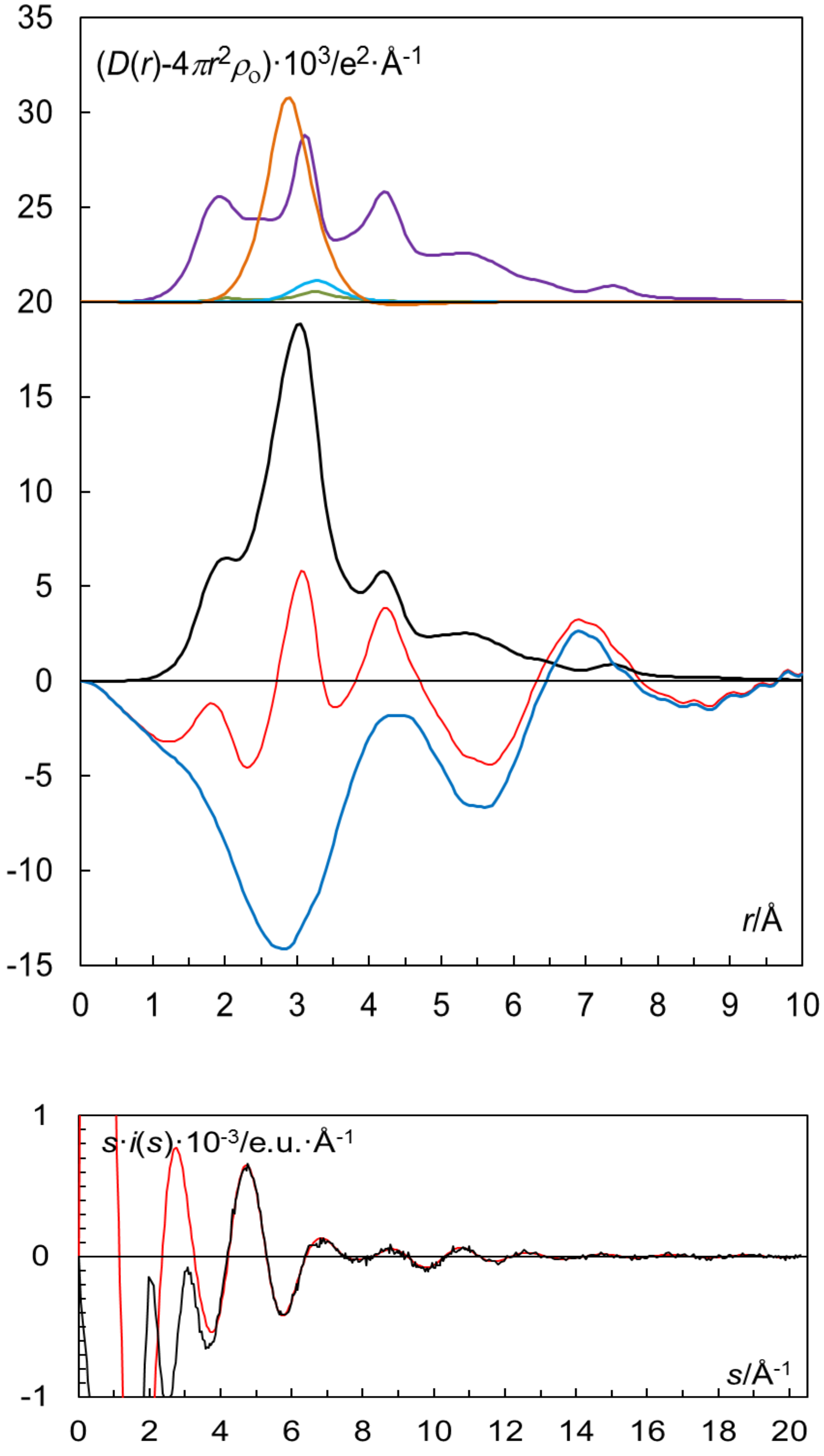
(D(r)-4πr²ρ₀)·10³/e²·Å⁻¹
35
30
25
20
15
10
5
0
-5
-10
-15
r/Å
0
1
2
3
4
5
6
7
8
9
10
s·i(s)·10⁻³/e.u.·Å⁻¹
1
0
-1
s/Å⁻¹
0
2
4
6
8
10
12
14
16
18
20

Figure 3b.

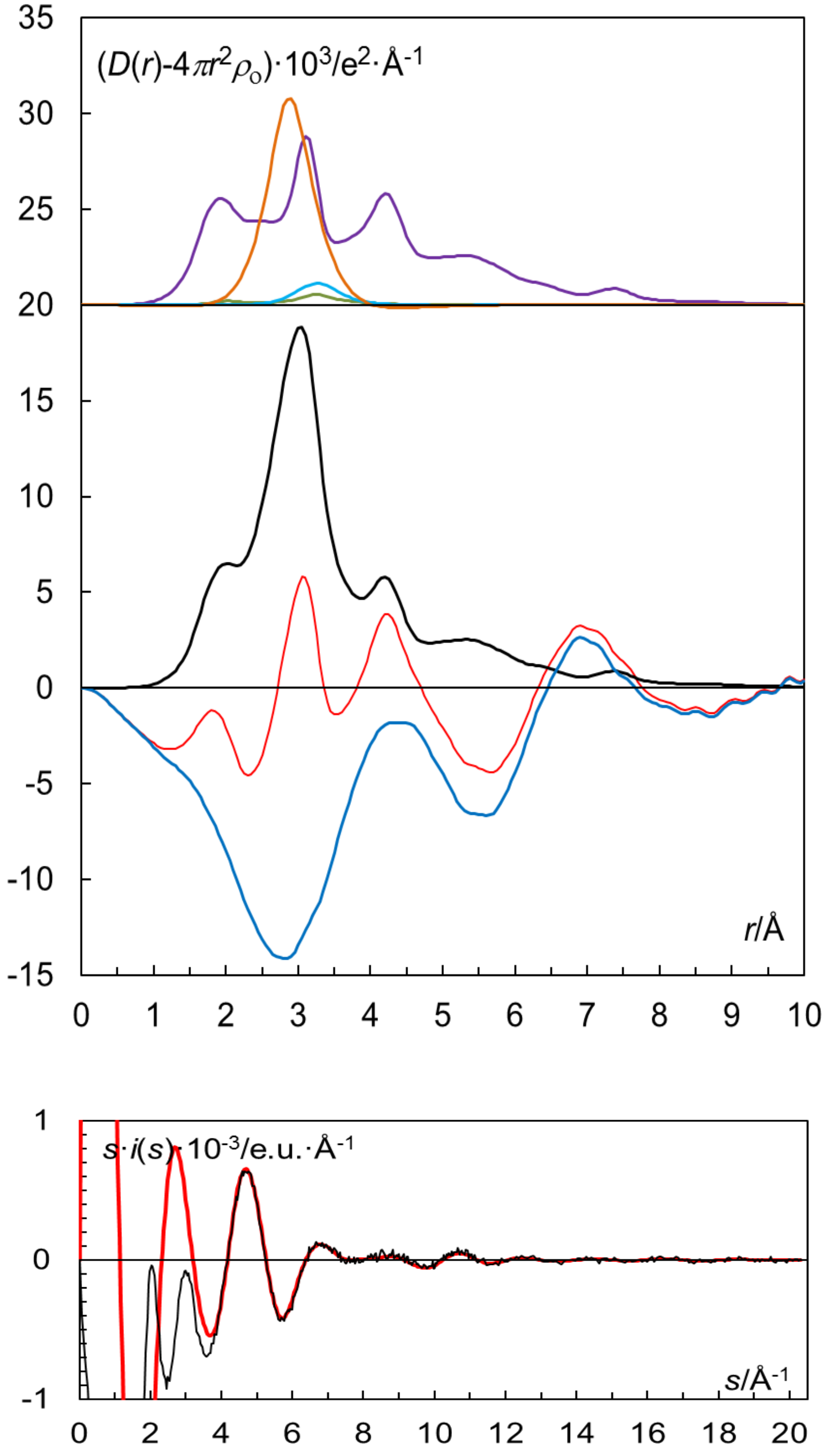
$(D(r)-4\pi r^2\rho_o)\cdot10^3/e^2\cdot Å^{-1}$
35
30
25
20
15
10
5
0
-5
-10
-15
r/Å
0
1
2
3
4
5
6
7
8
9
10
$s\cdot i(s)\cdot10^{-3}/e.u.\cdot Å^{-1}$
1
0
-1
s/Å^{-1}
0
2
4
6
8
10
12
14
16
18
20

Figure 3. Experimental and theoretical plots for the solutions. Top panel, upper part, offset 20, shows the separate model contributions: a/ (2,2,1) and b/ (3,2,1) *D*-mannitolatodimolybdate(VI) complexes – purple line, bulk water < 3.5 Å - orange line, $Li(OH_2)_4^+$ - green line, and hydrated chloride ion – light blue line. Top panel, lower part, shows the experimental radial distribution functions, $D(r) - 4\pi r^2\rho_o$ - red line, sum of the calculated peak shapes - black line, and the difference between the experimental and model functions – blue line. Bottom panel shows the reduced LAXS intensity functions, *si(s)* (black line), and calculated model contributions (red line).

Conclusion

The *D*-mannitolatodimolybdate(VI) complex has an unusual structure with two face-sharing molybdate(VI) octahedra connected to one *D*-mannitol ligand in solid state [9]. This study has proven that the structure remains also in aqueous solution. This complex loses a proton when increasing pH from 2.0 to 5.5, Figure 1. As the already very short Mo···Mo distance, 2.129(6) Å in the $H_3(MoO_4)_2(C_6H_8(OH)_6)^-$ complex at pH 2.0 decreases to 3.075(6) Å in the deprotonated complexes at pH 5.5, $H_2(MoO_4)_2(C_6H_8(OH)_6)^{2-}$ it strongly indicates that that proton on a *D*-mannitol ligand oxygen binding to both molybdenum atoms.

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