trations of the stock solutions were controlled by complexometric titrations and the acid contents by titrations of the hydrogen ion liberated from an ion-exchange column (Amberlite IR-120).

Apparatus and methods. The apparatus and methods were the same as described in a recent paper.[2] All measurements were carried out at 25 °C.

In the determination of the complex stability constants, several titrations were carried out at ionic strengths near 0.1 using different ligand-metal ratios. The initial estimates of the constants calculated from stoichiometric relationships were refined by a modified version of the programme SCOGS [7] on a Univac 1108 computer. An example of the calculations is presented in Table 2. The final values of the constants given are those obtained by interpolation to the precise value 0.100 of ionic strength.

The values of the naphtholic protonation constants of the ligands needed in the calculations were obtained from the following Debye-Hückel equations: for 2-nitroso-1-naphthol-4,6-disulfonic acid,[2]
$pK_3 = 6.507 - 3.054\sqrt{I}/(1 + 1.394\sqrt{I}) + 0.453\ I$
and for 2-nitroso-1-naphthol-4,7-disulfonic acid,[2]
$pK_3 = 6.451 - 3.054\ \sqrt{I}/(1 + 1.591\ \sqrt{I}) + 0.277\ I.$

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Multicomponent Polyanions. IX. On the Crystal Structure of a Protonized Mannitolodimolybdate Complex

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Investigations of equilibria

$$pH^+ + qMoO_4^{2-} + rC_6H_{14}O_6 \rightleftharpoons (H^+)_p(MoO_4^{2-})q(C_6H_{14}O_6)_r$$

where $C_6H_{14}O_6$ is D-mannitol, have shown that complexes (2,2,1) and (3,2,1) are formed (the complexes are given in (p, q, r) notation).[1] The study covered the $-\log\ [H^+]$ range $1 < -\log\ [H^+] < 9$.

In parallel with this investigation crystallization experiments using molar ratios of H^+, MoO_4^{2-}, and $C_6H_{14}O_6$ corresponding to the composition of the complexes, have also been carried out. Hitherto this preparative work has only resulted in crystals corresponding to a (4, 2, 1) complex, which has not been confirmed in the $-\log\ [H^+]$ range studied, but is assumed to appear at $-\log\ [H^+] < 1$.

X-Ray characteristics and a preliminary structure of this crystalline phase is reported in the present communication.

Crystal data.

$H_2Mo_2O_5C_6H_{10}O_6.3H_2O$
Monoclinic $P2_1$
$a = 12.2342(6)$ Å
$b = 6.9008(4)$ Å
$c = 8.3845(5)$ Å
$\beta = 99.740(6)°$

F.W. = 506.10
$V = 697.7(1)$ Å^3
$D_x = 2.409$ g cm^{-3}
$D_m = 2.40 \pm 0.01$ g cm^{-3}
(flotation method)
$Z = 2$

Experimental. Accurate unit cell dimensions were determined from X-ray powder photographs taken with a Guinier-Hägg camera using Cu$K\alpha_1$-radiation ($\lambda = 1.54051$ Å) with $Pb(NO_3)_2$ as internal standard ($a_{Pb(NO_3)_2} = 7.8575$ Å, 25 °C). Three-dimensional single crystal X-ray diffraction data were collected by the equi-inclination Weissenberg method, using Cu$K\alpha$-radiation ($\lambda = 1.5418$ Å). The intensities of 1414 independent reflexions from the $h0l - h6l$ layers were estimated visually using multiple film technique. Correction for Lorentz- and polarization effects was then applied.

From a three-dimensional Patterson synthesis the positions of the two Mo atoms were obtained. Since the y-coordinates for both atoms were the same (≈ 0.37), the phase angles computed were equivalent within the layers and restricted to multiples of $\approx \pi/4$. This resulted in a centre of symmetry induced in the space group $P2_1$, making both the complex and its mirror image appear in a following Fourier map.[2] To obtain non-equivalent phase angle values anomalous scattering was applied, and combined

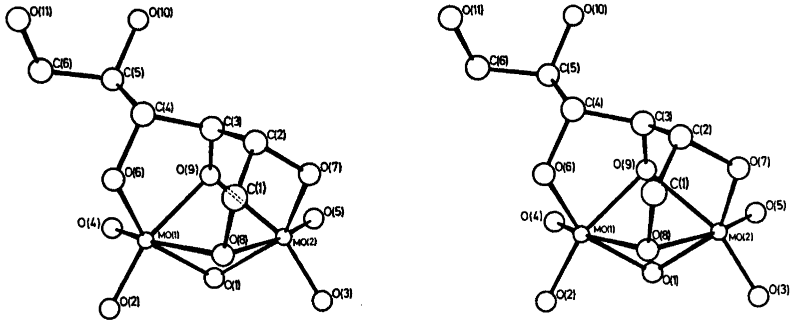

Fig. 1. A stereoscopic view of the non-hydrogen atoms in the $H_2Mo_2O_5C_6H_{10}O_6$-complex.

with very careful weighting of the material during the computational refinements. The positions of eleven oxygen and six carbon atoms of the complex and three water oxygen atoms were then determined stepwise from Fourier calculations. Full-matrix least squares refinement of positional and isotropic thermal parameters has so far yielded an R-value of 0.108, R being defined as $\sum||F_o|-|F_c||/\sum|F_o|$.

Structure description. The structure consists of uncharged mannitolodimolybdate complexes and water molecules linked together by hydrogen bonds forming probably a three-dimensional network. The mannitolodimolybdate complex consists of two MoO_6-octahedra which share a face. Four of the oxygen atoms in this dimolybdate unit are directly bonded to four adjacent carbon atoms in the D-mannitol chain, as shown in Fig. 1. Actually D-mannitol can be considered as a tetradentate ligand with respect to the dimolybdate group. Three five-membered chelate rings Mo(1) – O(9) – C(3) – C(4) – O(6), Mo(2) – O(7) – C(2) – C(1) – O(8), and Mo(2) – O(7) – C(2) – C(3) – O(9) are formed.

Besides these four mannitol-bonded oxygen atoms of the dimolybdate group there are five additional oxygen atoms, of which two are probably part of hydroxyl groups. At the present stage it is impossible to decide which of the oxygens that are protonized.

The Mo – Mo distance is 3.13 Å, considerably shorter than for MoO_6-octahedra which share an edge or a corner. For instance in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$ the average Mo – Mo distance is 3.39 Å when sharing an edge.[3] To our knowledge the coupling of octahedra by sharing a face has not earlier been reported for discrete dimolybdate units. However, for condensed heteropolyanions the occurrence of shared faces has been found in the crystal structure of $(NH_4)_2H_6(CeMo_{12}O_{42}).12H_2O$.[4]

The Mo – O distances can, in both octahedra, be divided into three groups, each containing two distances, the average of which are 1.69, 1.95, and 2.29 Å. They are in agreement with other Mo – O distances reported, for instance in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$[3] and $Na_6Mo_5P_2O_{23}(H_2O)_{13}$.[5]

In the D-mannitol chain the average C – C and C – O distances are 1.53 and 1.45 Å, respectively. The average angle C – C – C is 114° and C – C – O 106°. In the crystal structure determination of the β form of D-mannitol the corresponding distances reported are 1.516 and 1.437 Å.[6]

The variation in distances found in the complex and the corresponding distances in β-D-mannitol are possibly not significantly different from each other.

Collection of a new reflexion data set, measured by diffractometer, is in progress. This should not only permit higher accuracy in positional and thermal parameters, but should also allow an attempt to determine the hydrogen atom positions, of which the two protons of the hydroxyl groups previously mentioned are of special interest. A neutron diffraction study of the compound is also planned.

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