Structure of Xanthan Hydride

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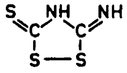
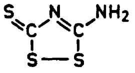
So far X-ray structure determinations of three unsaturated five-membered cyclic disulphides have been reported [1-3]. The relatively high stability of these compounds as contrasted with unsaturated ones, seems to be due to some aromatic character of the ring. This idea may be tested by a structure determination of the 1,2,4-dithiazolidine derivatives, rhodan hydrate [3] and xanthan hydride.

According to Hantzsch and Wolvekamp [4], xanthan hydride has structure I.



I



II

The unit cell and space group of xanthan hydride have been reported by Foss [5]. The crystals are monoclinic prismatic, $a = 4.05$ Å, $b = 10.59$ Å, $c = 12.78$ Å, $\beta = 97°$. The space group is $P2_1/c$.

The structure was solved by means of Harker-Kasper inequalities and systematic use of the "multiplication rule" [6]. This led to 8 sets of signs for the 45 strongest reflections in the a-axis projection. The molecule was recognised in one of the corresponding Fourier maps, and after three Fourier refinements the reliability factor R was 0.18. The electron density map is reproduced in Fig. 1. Two small maxima near to the exocyclic nitrogen atom are most likely hydrogen peaks. The heights correspond approximately to 1 e.Å^{-2}, and the distance from nitrogen is about 1 Å if the hydrogen atoms are assumed to lie in the plane of the molecule, thus making possible a π orbital overlap C—N as in thiuret hydroiodide [1]. The bond angles H—N—H and H—N—C would be *ca.* 120°, and the peaks are both situated between atoms where hydrogen bonding may be expected. Further refinement of the rhodan hydrate structure [7] also strongly indicates that the two hydrogen atoms in the molecule belong to the exocyclic nitrogen atom. It may therefore be more correct to assign both rhodan hydrate and xanthan hydride a structure of type II.

Table 1. Atomic coordinates, in fractions of corresponding cell edges.

	y	z
S_1	0.349	0.051
S_2	0.342	0.199
S_3	0.118	0.299
C_1	0.187	0.030
C_2	0.177	0.190
N_1	0.141	−0.055
N_2	0.125	0.105

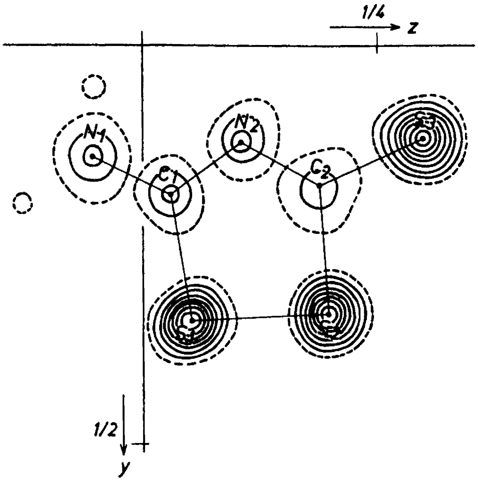


Fig. 1. Electron density projection of xanthan hydride along the a-axis showing one asymmetric unit. Plane group *pgg* and origin in center of symmetry. Contours at arbitrary but equal intervals.

Refinement of the xanthan hydride structure will be continued by means of $(F_o - F_c)$-technique.

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On Molybdenum Oxide Hydroxides Genotypic with MoO_3

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A series of molybdenum oxide hydroxides, which may be assigned the general formula $MoO_{3-x}(OH)_x$ have been prepared by Glemser *et al.*[1-4] by the reduction of crystalline MoO_3 with (*a*) Zn and HCl, (*b*) Mo powder in the presence of water, (*c*) atomic hydrogen, or (*d*) $LiAlH_4$. Four members of this series were prepared, namely those with $x = 0.5$, 1.0, 1.6, and 2.0, and in addition a compound $Mo_5O_8(OH)_8$, which may be formulated $MoO_{1.8}(OH)_{1.2}(H_2O)_{0.2}$. The close connection existing between these reduced phases and MoO_3, demonstrated by the possibility for stepwise reduction and oxidation, has led Glemser and Lutz to describe them as *genotypic with MoO_3* and to suppose that this chemical relationship would be reflected in their crystal structures [1].

Preliminary X-ray investigations have been made by the present authors in order to study the structural relationships within this genotypic series. Samples of MoO_3 were subjected to different degrees of reduction by methods (*a*), (*b*), and (*c*) above and the X-ray powder patterns of the products were recorded in Guinier focusing cameras with Cu*Ka* radiation using KCl as an internal standard ($a = 6.2921$ Å).

The existence of a number of different crystalline phases was verified. Their powder patterns, which are all very similar to that of MoO_3, could be interpreted in most cases, and the unit cell dimensions thus derived were seen to differ only slightly from those of MoO_3, *viz.* within 5 % for the *a* and *b* axes and within 10 % for the *c* axis. In some cases the cell is slightly monoclinically deformed, the *a* axis being the unique axis. It is thus evident, that the term "genotypic with MoO_3" is also appropriate when considering the structural relationships between these compounds.

Although no data for chemical analysis were available, one phase could be identified as the compound $Mo_4O_{10}(OH)_2$ ($x = 0.5$) described by Glemser and Lutz, since it could be prepared by method (*b*) above, specific for this compound, and its powder pattern (Table 1) was seen to agree with the data given by these authors. The orthorhombic unit cell has the dimensions: $a = 3.888$ Å, $b = 14.082$ Å, $c = 3.734$ Å, which may be compared with the values for MoO_3[5]:
$a = 3.963$ Å, $b = 13.855$ Å, $c = 3.696$ Å.

Table 1. X-Ray powder pattern of $MoO_{2.5}(OH)_{0.5}$. Cu*Ka* radiation.

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
m	0.01195	020	0.01199
v st	0.04219	110	0.04231
m	0.04797	040	0.04795
v st	0.05453	021	0.05460
w	0.06626	130	0.06628
st	0.08488	111	0.08492
v w	0.09059	041	0.09057
m	0.10802	060	0.10789
m	0.10895	131	0.10890
w	0.11430	150	0.11423
w	0.15066	061	0.15051
m	0.15719	200	0.15724
st	0.17051	002	0.17046
w	0.20519	240	0.20519
m	0.21173	221	0.21184
m	0.21276	112	0.21277
w	0.21846	042	0.21842
w	0.22885	171	0.22888
v w	0.23460	081	0.23442
v w	0.23677	132	0.23675
v w	0.24794	241	0.24780
v w	0.26509	260	0.26513
w	0.27846	062	0.27836
w	0.28474	152	0.28470

v = very, st = strong, m = medium, w = weak.