ATRANES

XXXVI.* 1,1-DIOXOMOLYBDATRANIC ACIDS

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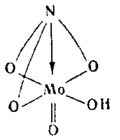
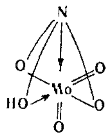
A study of the PMR spectra of 1,1-dioxomolybdatranic acids makes it possible to propose prototropic isomerization of their molecules in solutions, during which the Mo ← O coordinate bond is redistributed between the three oxygen atoms of the 2-hydroxyethyl groups, thereby averaging the three-dimensional and electronic structures of each of the atrane half rings. This sort of rearrangement is a bimolecular process, and its rate-determining step proves to be attack on the convalently bonded (with the molybdenum atom) oxygen by a solvated proton. The rate of isomerization depends substantially on the proton-acceptor capacity of the solvent.

We have obtained chelate compounds, to which we assigned the 1-hydroxy-1-oxomolybdatrane structure (I), by reaction of molybdenic anhydride, molybdenic acid, or ammonium molybdate with tris(2-hydroxyalkyl)amines [1].



I



II

(⌒ Denotes an unsubstituted or substituted $-CH_2CH_2-$group)

A subsequent x-ray diffraction investigation of the simplest compound of this type showed that the length of one Mo–OC bond (2.34 Å) is considerably greater than that of the other two Mo–OC bonds (1.91 and 1.94 Å). At the same time, the lengths of the two remaining bonds between the molybdenum and oxygen atoms are considerably less and almost identical (1.80 and 1.75 Å). This indicates that both of these bonds are Mo=O bonds and that the Mo–OH bond is not present in the molecule. On the basis of this, the compounds that we synthesized should be assigned the 1,1-dioxomolybdatranic acid structure (II).

The protonated hydrogen atom in crystals of compounds of this type remains bonded to the oxygen atom of the 2-hydroxyethyl group, which forms an elongated coordinate bond with the central molybdenum atom. Both of the coordinate bonds in the II molecule (Mo ← N and Mo ← O) are in the trans position relative to the Mo=O bonds. The $H[MoO_2(OCH_2CH_2)_3N]$ structure assigned to it in [2], which has a delocalized proton, is less likely, inasmuch as all three Mo–OC bonds should be approximately equivalent in this case.

1,1-Dioxomolybdatranic acid has weakly acidic properties (a 0.1 N aqueous solution has pH 5.5). We were able to isolate only a salt of this acid with piperidine – $C_6H_{13}MoNO_5 \cdot C_5H_{11}N$ – which was obtained as colorless crystals that decomposed without melting at ~280°C.

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*See [6] for communication XXXV.

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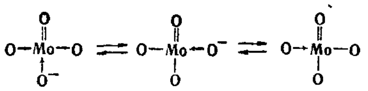
TABLE 1. Parameters of the PMR Spectrum of a 5% Solution of 1,1-Dioxomolybdatranic Acid in d_6-Dimethyl Sulfoxide

Chemical shifts, τ, ppm							J, Hz						
NCH_2	OCH_2	H^+	H_A	H_B	H_C	H_D	$J_{NCH_2CH_2O}$	J_{AB}	J_{CD}	J_{AC}	J_{AD}	J_{BC}	J_{BD}
6,99	6,35	6,63	6,79	6,44	5,55	5,32	5,4	12,5	10,4	3,7	5,6	6,5	8,2

The vibrations of the Mo=O bond in the IR spectra of acids II appear as a doublet at 900-930 cm^{-1}. This indicates the cis structure of the dioxo group of MoO_3 [3] and is in good agreement with configuration II, which was established by means of x-ray diffraction analysis.

Notwithstanding the x-ray diffraction data [2], which reveal the clearly increased length of one of the Mo—O bonds in the 1,1-dioxomolybdatranic acid crystal, the PMR spectrum* of an aqueous solution of it indicates equivalence of the three atrane half rings, the protons of which resonate as a single multiplet of the A_2B_2 type (τ_{CH_2N} 6.59 ppm and τ_{OCH_2} 6.05 ppm). This may be interpreted as a consequence of dissociation of the 1,1-dioxomolybdatranic acid molecule and its rapid intramolecular isomerization in aqueous solution, during which the Mo←O coordinate bond is redistributed between three oxygen atoms,

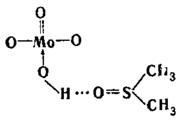


$H^+[O_2Mo(OCH_2CH_2)_3N]^-$

III

thereby averaging the three-dimensional and electronic structures of each of the half rings.

Consequently, the structure of 1,1-dioxomolybdatranic acid in aqueous solution can be represented by formula III. We had hoped that in dimethyl sulfoxide (DMSO) the formation of a quite strong hydrogen bond between the hydroxyl proton of the 1,1-dioxomolybdatranic acid molecule and DMSO would make it possible to localize the Mo←O coordinate bond and enable us to spectroscopically detect the nonequivalence of the atrane half rings.



In fact, the resonance of the protons of the two atrane half rings in the PMR spectrum† of 1,1-dioxomolybdatranic acid in anhydrous d_6-DMSO is represented by a multiplet of the ABCD type, while the resonance of the protons of the third atrane half ring is represented by two triplets of a degenerate A_2B_2 system. This constitutes evidence for a considerable three-dimensional and electronic difference between the atrane half rings with covalent and coordinate bonds between the molybdenum and oxygen atoms. In the latter of these, the geminal protons in the OCH_2 and CH_2N groups are equivalent because of averaging during rapid conformational transformations of the flexible half ring, which is formed by two coordinate bonds (O→Mo and N→Mo). In the two remaining half rings the magnitudes of the chemical shifts and the spin–spin coupling constants for the geminal protons are substantially different in both the OCH_2 groups and the CH_2N groups. The reason for this sort of nonequivalence may consist in the conformational rigidity of these nonplanar half rings. The shielding of their protons is appreciably lower (see Table 1) than is the case for the corresponding protons of the more flexible half ring of the molecule.

It is extremely important to note that the signal of the "hydroxyl" proton is very narrow without any hits of spin–spin coupling with the OCH_2 protons. This sort of coupling should be observed in the case of the formation of a strong hydrogen bond between the hydroxyl proton and the DMSO molecule. Consequently, our results repudiate the possibility of the retention of a covalent bond between the labile hydrogen and the oxygen atom of the 1,1-dioxomolybdatranic acid molecule, thereby providing evidence in favor of protonation of the DMSO molecules.

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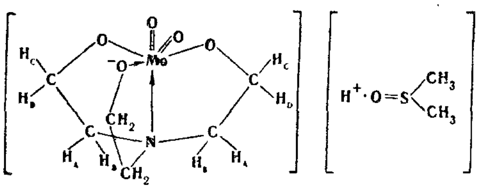
* The spectrum was obtained with a BS487B spectrometer with an operating frequency of 80 MHz.

† The PMR spectra were obtained with the participation of S. N. Tandura and M. F. Larin.

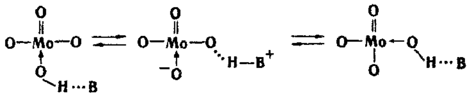
Thus prototropic rearrangement of the 1,1-dioxomolybdatranic acid molecule in a solution in dry DMSO occurs extremely slowly, and the molecule itself, due to the high proton-acceptor capacity of the solvent, exists exclusively in the dissociated form.



The addition of small amounts of D_2O (<0.5%) to a solution of 1,1-dioxomolybdatranic acid in DMSO slowly leads to smoothing out of the fine structure of the PMR spectrum (particularly for the OCH_2 protons). The subsequent addition of heavy water leads to a gradual broadening of all of the signals and then to merging of them into two triplets – for the CH_2N and OCH_2 protons. This indicates that the rate of prototropic rearrangement of the 1,1-dioxomolybdatranic acid molecule increases as the percentage of water in solution increases.

An increase in temperature also brings about the same effect. At ~150° the signals of all of the CH_2N protons in the PMR spectrum are united in a common triplet, while the signals of the OCH_2 protons are united in an unresolved triplet.* The broadening of the latter is apparently associated with the presence of spin–spin coupling of the OCH_2 protons with the labile proton, the position of which is averaged at high temperatures with respect to all of the oxygen atoms of the acid molecule. The chemical shifts of the OCH_2 and CH_2N protons are equal to the arithmetic mean of the values observed in the spectrum at room temperature. Cooling of the sample leads to restoration of the initial spectrograms.

The results make it possible to assume that prototropic isomerization of the 1,1-dioxomolybdatranic acid molecule is a bimolecular process; its rate-determining step proves to be attack on the covalently bonded (with the molybdenum atom) oxygen by a solvated proton.



1,1-Dioxomolybdatrane-3,7,10-trionic acid, which we also synthesized [4] and to which the II structure (⌒ = —$CH_2C(=O)$—) should also be assigned, is also a 1,1-dioxomolybdatranic acid derivative. Judging from the PMR spectrum of an aqueous solution of it, rapid prototropic isomerization is also inherent in its molecules. It is precisely this structure rather than the planar structure or conformational lability of the atrane half rings of this molecule, as was previously supposed [4, 5], that leads to equivalence of the geminal protons in the PMR spectrum of 1,1-dioxomolybdatrane-3,7,10-trionic acid, in contrast to derivatives of methyliminoacetic and ethylenediaminetetracetic acid [5], in which this sort of isomerization cannot occur.

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*Partial decomposition of 1,1-dioxomolybdatranic acid is observed at higher temperatures.