171. *A Nuclear Magnetic Resonance Study of the Hydrates of Molybdenum Trioxide.*

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A combined proton magnetic resonance and infrared study has been made of the mono- and the di-hydrate of molybdenum trioxide. The results support the structures MoO_3,H_2O and $MoO_3,2H_2O$, the separation of the hydrogen nuclei in the water molecules being $1{\cdot}56 \pm 0{\cdot}03$ Å in both compounds.

Molybdenum trioxide dihydrate, $MoO_3,2H_2O$, forms as yellow crystals when a solution of ammonium molybdate in fairly concentrated nitric acid is stored for a long time. Its obvious formulation is either as the hydrate of molybdic acid, $MoO_2(OH)_2,H_2O$, or as a simple hydrate of MoO_3. However, a preliminary *X*-ray investigation of the crystal showed that the structure was similar to that of $BaUO_4$, suggesting the formulation $(H_4O)^{2+}MoO_4^{2-}$, although subsequent refinement of the data has not confirmed this structure.[1] The presence in the solid state of any large concentrations of H_4O^{2+} ions is extremely unlikely, and very strong confirmation of their presence would be required. The existence of a definite monohydrate has been established by both *X*-ray [2,3] and tensioeudiometric methods;[4] neither definitely establishes whether the structure is H_2MoO_4 or MoO_3,H_2O.

This paper discusses proton magnetic resonance experiments carried out on the monohydrate and dihydrate in an attempt to resolve these problems.[5] The general features of

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[1] Lindqvist, *Acta Chem. Scand.*, 1956, **10**, 1361; see also *idem*, *ibid.*, 1950, **4**, 650.

[2] Buerger, *Z. anorg. Chem.*, 1922, **121**, 224.

[3] Funaki and Segawa, *J. Electrochem. Soc. Japan*, 1950, **18**, 307.

[4] Hüttig, *Z. angew. Chem.*, 1922, **35**, 391; Hüttig and Kurre, *Z. anorg. Chem.*, 1923, **126**, 167.

[5] Maričić and Smith, *Acta Chem. Scand.*, 1956, **10**, 1362.

such investigations in the solid state have often been discussed;[6,7] the criterion we shall use here is that water molecules, if they exist in the crystal, should possess a characteristic proton resonance spectrum, very similar to those found in previous measurements on other hydrates[8] but different from that expected from an H_4O^{2+} ion, which should resemble the spectrum of the ammonium ion in ammonium chloride.

EXPERIMENTAL

The sample of $MoO_3,2H_2O$, kindly supplied by Dr. I. Lindqvist, had been prepared by crystallisation for some years from an acid solution of ammonium molybdate and had been about one year in air. Chemical analysis revealed the presence of 0·057% w/w of ammonium ion, which would not be expected to produce a detectable nuclear resonance signal under the experimental conditions.

Proton resonance measurements were made at 16·435 Mc./sec. in a radiofrequency bridge type of apparatus, details of which have been given previously.[9] Radiofrequency levels in the bridge were kept below saturation in recording the spectra and the 25 c./sec. modulation never exceeded an amplitude of 1·2 gauss, so that the corresponding corrections to the second moment[10] were less than 1½%. These corrections have been applied to all second-moment values quoted here. The lines were usually recorded with a sweep rate of about 3 gauss per min., and the final time constant on the recorder channel was 9 sec. The inhomogeneity and the fluctuations in the magnetic field were both of the order of 1 part in 10^4. Line shapes were recorded for samples ranging in composition from $MoO_3,2H_2O$ to $MoO_3,1{\cdot}1H_2O$, and at temperatures of 77° K and 290° K.

The infrared spectra of $MoO_3,2H_2O$, $MoO_3,1{\cdot}1H_2O$, and MoO_3 were recorded on a Grubb-Parsons S4 double-beam spectrometer. The samples were compressed in previously-ignited potassium chloride and the usual precautions were taken to exclude water.

The sample of MoO_3 was prepared from the dihydrate by ignition in air at 560° C and was pale ivory. The sample of composition $MoO_3,1{\cdot}1H_2O$ was prepared by slow dehydration of the dihydrate at room temperature in a vacuum desiccator at a pressure of about 2 mm. The process took over three weeks and the water lost corresponded to a residue of mean composition $MoO_3,1{\cdot}12H_2O$. Complete dehydration to the monohydrate would have taken at least another month unless the sample were heated. We assume here that the infrared and nuclear resonance spectra of this mixture of hydrates will be largely characteristic of the monohydrate.

RESULTS AND DISCUSSION

At 77° K the second moments of the absorption curves were $30{\cdot}7 \pm 1{\cdot}6$ gauss^2 for $MoO_3,2H_2O$ and $27{\cdot}6 \pm 1{\cdot}4$ gauss^2 for $MoO_3,1{\cdot}1H_2O$. These values, with their standard deviations, are the mean of at least five measurements. Typical derivative curves for the two hydrated samples are given in Figs. 1 and 2; the small double-headed arrow in each Figure indicates the peak-to-peak amplitude of the modulation. The curve for $MoO_3,1{\cdot}1H_2O$ is in many respects typical of that obtained from powdered gypsum,[11] with the exception of the small additional peaks at the centre of the curve. In order to provide additional confirmation of the hydrate structure, the theoretical curve for a water molecule was calculated by assuming a " rigid lattice " and an inter-proton distance of 1·58 Å (so that the value of the parameter $\alpha = \frac{3}{2}\mu r^{-3}$ is $5{\cdot}36_3$ gauss). Values of 1·58 Å have been found in $CaSO_4,2H_2O$,[11] 1·57 Å in Li_2SO_4,H_2O,[12] and 1·56 Å in $Ba(ClO_3)_2,H_2O$.[13] We used Pake's method of calculation[11] and computed two curves for values of the intermolecular broadening function, β^2, of 4·60 and 5·60 gauss^2. The comparison of the theoretical absorption curves with two sets of experimental data, given in Fig. 3, shows that better

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[6] Andrew, " Nuclear Magnetic Resonance," Cambridge University Press, 1955, chap. 6.

[7] Smith, *Quart. Rev.*, 1953, **7**, 279.

[8] Wertz, *Chem. Rev.*, 1956, **55**, 829.

[9] Smith, *Discuss. Faraday Soc.*, 1955, **19**, 207.

[10] Andrew, *Phys. Rev.*, 1953, **91**, 425.

[11] Pake, *J. Chem. Phys.*, 1948, **16**, 327.

[12] Soutif, Dreyfus, and Ayant, *Compt. rend.*, 1951, **233**, 395.

[13] Spence, *J. Chem. Phys.*, 1955, **23**, 1166.

agreement is obtained with the curve for which $\beta^2 = 5{\cdot}60$ gauss^2 except at the centre of the line, where a small additional peak appears. One possible impurity which might give rise to this narrow line is a small concentration of hydroxyl groups; less than 1% of the total hydrogen, an amount difficult to detect analytically, would be sufficient to give rise to the effect. Groups like NH_4^+ or H_3O^+ would not give rise to such a narrow line unless they were allowed considerable freedom of movement at 77° K. Whatever the origin of the central peak its effect on the second moment will be very small.

Rather similar experimental curves were obtained from $MoO_3,2H_2O$, but the signal-to-noise ratio was poorer. The best agreement with theory in this case was obtained with a curve calculated for a water molecule of the same inter-proton distance (1·58 Å) as in the monohydrate but with a value for β^2 of 7·70 gauss^2. A comparison of the two is given in Fig. 4. Again there is a poor fit at the centre of the curve, presumably arising from the same impurities that have been discussed in the case of the monohydrate. In this compound and possibly the monohydrate the high values of β^2 suggest that the water molecules approach quite closely.

FIG. 1. *Derivative curve of* $MoO_3,2H_2O$ *at* 77° K.

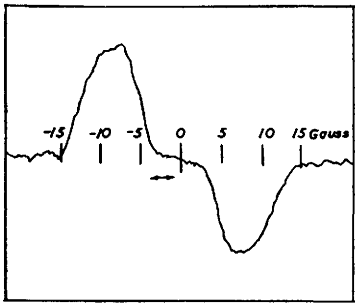


FIG. 2. *Derivative curve of* $MoO_3,1{\cdot}1H_2O$ *at* 77° K.

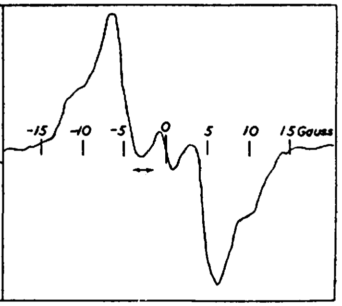


FIG. 3. *Comparison of the theoretical and experimental absorption curves for* $MoO_3,1{\cdot}1H_2O$ (*full line,* $\beta^2 = 5{\cdot}6$; *broken line,* $\beta^2 = 4{\cdot}6$ *gauss*^{2}).

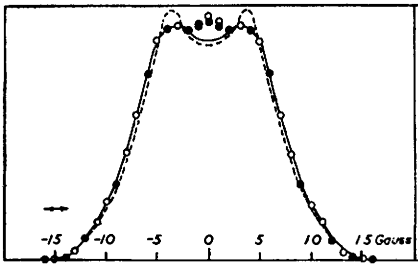
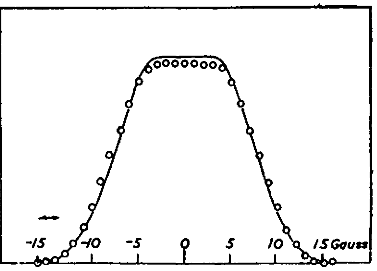


FIG. 4. *Comparison of the theoretical and experimental absorption curves for* $MoO_3,2H_2O$ ($\beta^2 = 7{\cdot}7$ *gauss*^{2}).



For example, if we take into account only nearest-neighbour interactions, an intermolecular broadening of 7·70 gauss^2 would be provided by two protons at 2·13 Å to each proton of the water molecule or from four protons at 2·39 Å, compared with the value of about 2·30 Å expected in ice. The most probable arrangement cannot be predicted without more accurate information on the location of the oxygen atoms in the crystal. This would also tell us to what extent the assumption of a two-spin system for the water molecules is correct.

The value of 1·58 Å as obtained above is subject to serious systematic errors due to the thermal oscillations of the protons. Corrections to allow for this have been given by

Deeley and Richards,[14] Gutowsky, Pake, and Bersohn,[15] and Ibers and Stevenson.[16] We shall use here the method due to the last-named, and the infrared data mentioned later. In calculating the correction due to the vibrations of the water molecule, for which only the antisymmetric stretching frequency (S_3 in ref. 17) need be considered, we took ν_3 as 3150 cm.$^{-1}$, r as 1·58 Å and ∠HOH as 104° 28′. Unfortunately, the magnitudes of the two torsional frequencies which change θ are not known, but for the purpose of this calculation we used the mean of the two lowest infrared frequencies observed, 909 and 926 cm.$^{-1}$, which are absent from the spectrum of MoO_3, so that our calculation still contains an uncertainty. The corrected value of $\langle r^3 \rangle^{\frac{1}{3}}$ is then 1·56 Å. The standard deviation of the random errors is $\pm$0·015 Å; allowing a reasonable value for the uncertainty mentioned above, we estimate the total s.d. to be $\pm$0·03 Å.

What agreement there exists between the theoretical and experimental results is not improved by assuming the structure $MoO_2(OH)_2,H_2O$. An analogous configuration occurs in oxalic acid dihydrate, $(CO_2H)_2,2H_2O$,[18,19] and the derivative curve of this compound shows significant differences from that of the present hydrate. A comparison of the two curves recorded under similar conditions at 77° K is made in Fig. 5. Measurements on the present equipment suggest that the second-moment values for oxalic acid dihydrate are higher than previously reported.[18] The mean of four measurements at 77° K is 23·4 ± 1·4 gauss^2 and $(\Delta H)_{\mathrm{m.sl}}$ is 13·4 gauss. The outer peaks of the curve, due largely to the water molecule, are similar in shape although different in separation, but the two curves behave quite differently near the centre where the contributions from the hydroxyl groups should predominate and be twice as great for the structure $MoO_2(OH)_2,H_2O$ as for $(CO_2H)_2,2H_2O$, so that the evidence from the line shape alone is fairly conclusive. A similar comparison of the line shapes of $MoO_3,2H_2O$ and $(H_3O^+)HSO_4^-$ [18] also rules out the formulation $(H_3O^+)MoO_3(OH)^-$.

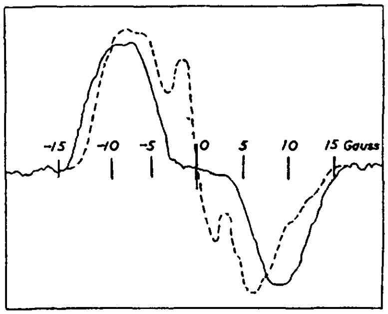


FIG. 5. *Comparison of the derivative curves of* $MoO_3,2H_2O$ *(full curve) and* $(CO_2H)_2,2H_2O$ *(broken curve) recorded at* 77° K.

If the crystal had contained H_4O^{2+} ions, a different line shape and second moment would have been expected, as can be shown by a calculation of what O–H distance would be required by the observed second moment. If we assume that the interaction between the groups of hydrogen atoms contributes 7·7 gauss^2 to the second moment, the contribution of the molecular groups themselves (the intramolecular second moment) whatever their nature is 23·0 gauss^2. As we have tried to show, this value is consistent with the presence of water molecules of an inter-proton distance of 1·56 Å. The exact relation between the

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[14] Deeley and Richard, *Trans. Faraday Soc.*, 1954, **50**, 560.

[15] Gutowsky, Pake, and Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.

[16] Ibers and Stevenson, Montreal Conference 1957; to be published in *J. Chem. Phys.* We are indebted to the authors for allowing us to see their paper before publication.

[17] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1945.

[18] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; Itoh, Kusaka, Kiriyama, and Yabumoto, *J. Chem. Phys.*, 1953, **21**, 1895.

[19] Pringle, *Acta Cryst.*, 1954, **7**, 716; Ahmed and Cruickshank, *ibid.*, 1953, **6**, 385.

intramolecular second moment and the inter-proton distance r_{jk} between the jth and kth proton for a rigid lattice is

$$\langle \Delta H^2 \rangle_{\text{intra}} = \frac{18\mu^2}{5N_s} \sum_{j>k} r_{jk}^{-6}$$

in which N_s is the number of nuclei in the molecular grouping and μ is the magnetic moment of the proton in ergs gauss^{-1}. The most recent value for the nuclear magneton [20] being used, this equation becomes

$$\langle \Delta H^2 \rangle_{\text{intra}} = \frac{716{\cdot}16}{N_s} \sum_{j>k} r_{jk}^{-6}$$

in which r_{jk} is in Å. If $N_s = 2$ and $\langle \Delta H^2 \rangle_{\text{intra}} = 23{\cdot}0$ gauss^2 ($= 4/5\alpha^2$), then r_{jk} comes to 1·58 Å. If $N_s = 4$ however, then for the same second moment (and a symmetrical H_4O^{2+} ion being assumed), $r_{jk} = 1{\cdot}90$ Å, corresponding to an O–H distance of 1·16 Å. In water vapour r_e is 0·958 Å, so that the O–H distance would have to expand by about 0·20 Å in forming H_4O^{2+}. In going from NH_3 to NH_4^+ (in NH_4F) the N–H distance expands by 0·027 Å from 1·014 to 1·041 Å [16, 21] and an expansion of seven times this amount in the case of H_4O^{2+} seems unlikely.

The infrared spectra of these hydrates provide some evidence for this view. The samples showed broad infrared absorption bands with maxima at the following frequencies (m medium, w weak, sh shoulder) (cm.$^{-1}$):

$MoO_3,2H_2O$	3100 m	2336 w	1592 m	963 m	909 m
$MoO_3,1{\cdot}1H_2O$	3200 m	2326 w	1600 m	1122 sh	926 m
MoO_3	2326 w	1140 sh	1081 sh	980 m	823 w

The pairs of frequencies 3100, 1592 and 3200, 1600 cm.$^{-1}$ are absent from the spectrum of MoO_3 and are therefore attributed to water frequencies characteristic of the hydrated crystals. (Potassium chloride pellets prepared under anhydrous conditions show weak lines at 3425, 2936, and 1616 cm.$^{-1}$,[22] but lines of these frequencies could not be detected in the spectrum of MoO_3.) The lines at 1592 and 1600 cm.$^{-1}$ in the dihydrate and monohydrate respectively are attributed to an O–H bending frequency and are little changed from the value in water vapour of 1600 cm.$^{-1}$. The maxima at 3100 and 3200 cm.$^{-1}$ are attributed to the stretching frequencies and are considerably removed from the values in water vapour of 3652 (ν_2) and 3756 (ν_3). Such shifts are well known to occur in hydrogen-bonded compounds and there is a general tendency for the O–H stretching frequency to decrease with a shortening of the O–H . . . O distance. From the values listed by Nakamoto, Margoshes, and Rundle [23] one would expect an O–H . . . O distance in the hydrates of MoO_3 of between 2·73 and 2·75 Å. If these hydrogen bonds linked oxygen atoms at least one of which were attached to molybdenum, the grouping Mo–O . . . H–O would produce a contribution to β^2 because of the nuclear moment of ^{95}Mo and ^{97}Mo which together are in about 25% abundance. Calculation shows this to be at least one hundred times smaller than the actual values of β^2 required to give a reasonable theoretical curve. This again suggests that the fairly large values of β^2 are due to close approach of the water molecules to each other.

The nuclear magnetic resonance results give us only the inter-proton distance (1·56 ± 0·03 Å) in the water molecule; the O–H distance is not derived until we know the HOH angle. However, if we assume that this angle is the same as that in water vapour (104° 28′), the proton resonance results give an O–H distance of 0·99 Å, which is very close

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[20] Cohen, Dumond, and Rollett, *Rev. Mod. Phys.*, 1955, **27**, 363.

[21] Drain, *Discuss. Faraday Soc.*, 1955, **19**, 200.

[22] Lucchesi and Glasson, *J. Amer. Chem. Soc.*, 1956, **78**, 1347.

[23] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

to the value of 0·98 Å suggested by the data assembled in ref. 23. If the O–H distance were 1·16 Å, the predicted frequency would be around 1900 cm.$^{-1}$, which is not observed.

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