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Proton Magnetic Resonance Study of the Crystal Structure of Magnesium Thiosulphate Hexahydrate, $MgS_2O_3.6H_2O$

By S. Visweswaramurthy

Department of Physics, Indian Institute of Science, Bangalore-12, India

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A proton-magnetic resonance study of $MgS_2O_3.6H_2O$ undertaken in order to locate the protons in the water of hydration is presented. A discussion of the hydrogen bonds (O–H ··· O) formed in the crystal structure follows. The hydrogen bonds are asymmetric and slightly non-linear. The H–H distance obtained is =1·54 Å, which is slightly smaller than the usual range of values 1·56 to 1·61 Å given by Silvidi & McGrath (1961) for hydrates.

Introduction

Magnesium thiosulphate hexahydrate, $MgS_2O_3.6H_2O$, contains no paramagnetic ions and is a convenient substance for proton magnetic resonance (PMR) study since the protons in the water molecules are the only nuclei with non-vanishing spin, and hence with a magnetic moment.

The crystals belong to the orthorhombic class. The structure is known through the X-ray investigations of Brunt (1946) and the later correction by Nardelli, Fara & Giraldi (1962). The unit cell contains four molecules, the cell dimensions being

$$a=9{\cdot}32\pm0{\cdot}01,\ b=14{\cdot}36\pm0{\cdot}04,\ c=6{\cdot}87\pm0{\cdot}01\ \text{Å}\,.$$

The other structural details are:

$$U=919\ \text{Å}^3.$$

Space group (from systematic absences):

$$Pnma\,(D_{2h}^{16})\ \text{ or }\ Pn2_1a\,(C_{2v}^{9})\,.$$

The structure as a whole is built up of alternating layers of $Mg(H_2O)_6$ octahedra and S_2O_3 tetrahedra. The layers are parallel to (010) and succeed each other at intervals of $\frac{1}{4}b$.

The X-ray data are insufficient to determine the distribution of H atoms. However, an attempt has been made (Nardelli *et al.*, 1962) to ascertain the approximate location of the protons by simple consideration of hydrogen bonding. The following PMR study was undertaken to get the more exact proton locations and the *P–P* vector orientations. The 24 water molecules in the unit cell conveniently fall into three groups of eight similar molecules each so that we have in effect only three orientations of *P–P* vectors of the water. (By 'similar', we mean that their *P–P* vectors are parallel. The similarity can be concluded by a study of the X-ray diffraction pattern).

Preparation

The substance was first described by Rammelsberg (1855).

The magnesium thiosulphate hexahydrate crystals used in our experiments were prepared by a method starting from sodium thiosulphate. First, saturated solutions of sodium thiosulphate and barium chloride are mixed and warmed, and a white precipitate of barium thiosulphate is formed (Debus, 1882):

$$Na_2S_2O_3+BaCl_2 = BaS_2O_3\downarrow+2NaCl\,.$$

The solution is filtered off and the precipitate collected. To this precipitate is added a saturated solution of magnesium sulphate; magnesium thiosulphate is formed and, being highly soluble, remains in solution. Barium sulphate remains as a precipitate (Mellor, 1937):

$$BaS_2O_3+MgSO_4 = MgS_2O_3+BaSO_4\downarrow\,.$$

The solution is filtered off and the filtrate is slowly evaporated over concentrated sulphuric acid to get good orthorhombic crystals of $MgS_2O_3.6H_2O$. The crystals are long along the *c* axis and are translucent.

Experimental

The NMR absorption spectrometer used in these experiments has been described elsewhere (Visweswaramurthy, 1961); it uses a slightly modified and improved version of the Pound-Knight marginal oscillator.

The crystal used in our experiment was a good rectangular parallelepiped of dimensions 2 × 0·7 × 0·4 cm. The longest side was the *c* axis, the side of 0·7 cm length was the *a* axis, and the side of length 0·5 cm was the crystallographic *b* axis.

The crystal was fixed to the crystal head by means of a small quantity of Araldite (Ciba) adhesive, so that its *c* axis, the axis of crystal rotation in our experiment, was vertical. The PMR spectra of the crystal were taken for different orientations of the crystal with respect to the direction of the static high magnetic field, starting from the initial position of the [100] axis parallel to the magnetic field.

The relative disposition of the crystallographic axes and the magnetic field direction is shown in Fig. 1.

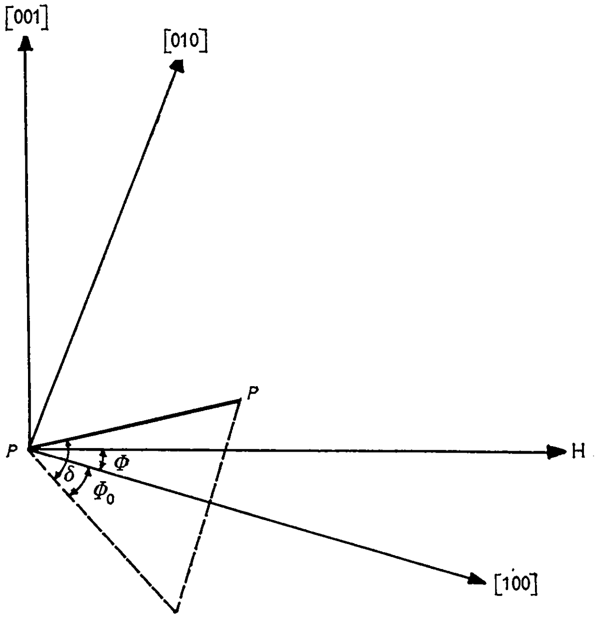

Fig. 1. The relative orientations of the crystallographic axes, the direction of the P–P vector, and the direction of the magnetic field.

In our calculations, the angle Φ is reckoned positive for rotation in the clockwise direction, away from the positive direction of the [100] axis.

The location of the protons requires that Φ_0, δ and the P–P distance r be determined from the spectra obtained.

The experiment for each orientation was repeated thrice and the mean values used to draw the spectra. The experimental conditions were $\nu_0 = 14{\cdot}74$ Mc.sec^{-1}, $H = 3473$ gauss, modulation field $= 1{\cdot}8$ gauss, sweep rate $= 1{\cdot}5$ gauss.min^{-1}, time constant $= 20$ seconds. (Peak-to-peak.) The r.f. level was low enough to prevent saturation of the sample.

Analysis of the spectra

The spectra obtained are more complicated than the ones that can be got with single or double P–P vector systems. The analysis of the spectra requires that they should first be resolved each into three 'unit' derivative curves, each derivative curve being the contribution from one P–P vector in that orientation. The size of the 'unit' derivative curve was found by a study of the spectra for $\Phi = 0$ and $\Phi = 20°$ which were somewhat better resolved. Three such 'units' were written on tracing paper pieces and these were slid on the experimental spectra to get the best fit. The peak separations of the pairs (equal to twice the distance in gauss from the centre of the resonance pattern to the zero of the concerned derivative unit) are collected in Table 1.

Table 1. *Rotation about the* [001] *axis*

Peak separations in gauss for different orientations

Φ	$(2\Delta H^1)$	$(2\Delta H)^2$	$(2\Delta H)^3$
0°	17·4 gauss	−5·0 gauss	−9·6 gauss
20	20·0	−12·0	−4·8
40	10·2	−5·4	−1·0
60	3·6	0·8	8·0
80	−2·0	7·2	14·0
90	−3·6	9·6	15·6
100	−7·0	11·6	14·4
120	−8·0	15·0	12·0
140	−1·8	10·0	8·0
160	10·8	−2·0	−6·0

The assignment of the correct values to each P–P vector can be done with certainty only by drawing the Pake curve (Fig. 2) of peak separation *versus* Φ. In drawing the Pake curve, the sign of the separation is changed everytime it passes through the zero value.

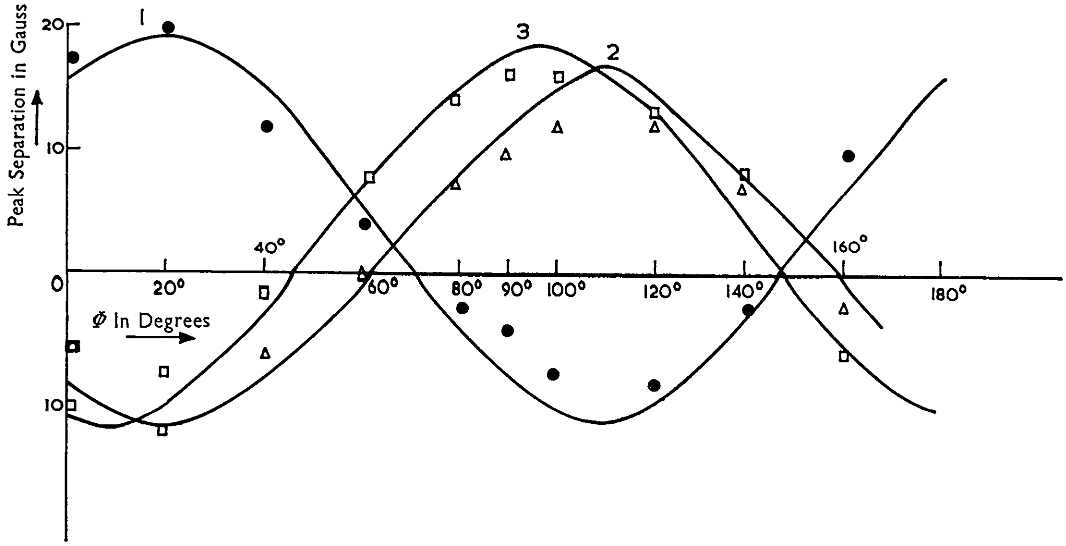

Fig. 2. Pake curves for $MgS_2O_3.6H_2O$; rotation about the [001] axis.
Φ Positive when measured clockwise from the +ve direction of the [100] axis.

Results

From a study of the Pake curves, it is found that the *minimum* peak separation in our case is slightly higher than 10·8 gauss, the value obtained by Pake (1948) in the first study of gypsum. The average value of $(2\Delta\mathbf{H})_{\min}$ in our case is $2\alpha = 11{\cdot}5$ gauss. Fitting the equation

$$2\Delta\mathbf{H} = 2(\tfrac{3}{2}\mu/r^2)[3\cos^2\delta.\cos^2(\Phi_0+\Phi)-1]\ \text{gauss}\,,$$

with the experimental results at a number of points for each curve, the values of Φ_0, δ and $\alpha = \frac{3}{2}\mu/r^3$ are got for each *P–P* vector. The values of Φ_0, δ and α thus obtained for each *P–P* vector are:

$$\Phi_0^1 = -20^\circ;\quad \delta_1 = 20^\circ\,42';\quad 2\alpha_1 = 11{\cdot}6\ \text{gauss}$$
$$\Phi_0^2 = -110^\circ;\quad \delta_2 = 30^\circ\,12';\quad 2\alpha_2 = 12{\cdot}0\ \text{gauss}$$
$$\Phi_0^3 = -97^\circ;\quad \delta_3 = 23^\circ\,20';\quad 2\alpha_3 = 10{\cdot}8\ \text{gauss}$$

Average $2\alpha = 11{\cdot}5$ gauss.

In Fig. 2, the dots, squares and triangles are the experimental points and the smooth line is the theoretical curve obtained by using these α, Φ_0 and δ values.

In the conventional notation in which anticlockwise rotations are reckoned +ve, the Φ_0 values become

$$\Phi_0^1 = 20^\circ,\quad \Phi_0^2 = 110^\circ,\quad \text{and}\quad \Phi_0^3 = 97^\circ\ \text{respectively.}$$

The direction angles of the three *P–P* vectors with respect to the positive direction of the crystallographic axes are:

	$\bar{\alpha}$	$\bar{\beta}$	$\bar{\gamma}$
$(P\text{–}P)_{\rm I}$	28° 20′	71° 15′	69° 18′
$(P\text{–}P)_{\rm II}$	72° 48′	35° 31′	59° 48′
$(P\text{–}P)_{\rm III}$	83° 23′	24° 15′	66° 40′

Discussion

With the $2\alpha = 3\mu/r^3$ value of 11·5 gauss, we get the *P–P* distance as 1·54 Å. Using this value of *r* and an O–H distance of 0·97 Å (as has been assumed by Silvidi, McGrath & Carroll (1959) in the study of $Li_2SO_4.H_2O$)—the vibration frequencies in ice correspond to 0·99 Å when the O–H–O bonds are formed— the angle H–O–H is calculated to be 105° 4′. This is less than the tetrahedral angle of 109° 28′ found in ice. This may mean that the H-bonds are slightly bent, *i.e.* H is off the O · · · O axis in the bond. This implies, as Pimentel & McClellan (1960) have already concluded, that the rehybridization required to open the H–O–H angle a few degrees (in order to make the H-bond linear) is energetically less favourable by an amount comparable to the energy required to bend the H-bond a few degrees. Once the molecular positions are fixed, the protons of the water molecules select the H–O–H angle that represents the best compromise between the strain energy required to move the protons off the H-bond line. This best compromise is reached here at 105° 4′, 4° 24′ below the tetrahedral angle.

Again, using these bond lengths we find that the H-bonds which the water oxygens may form with the sufficiently near (usually when the O · · · O distance is 3 Å, though from infrared data, the limit is 3·2 Å) electronegative atom are asymmetric.

This is in agreement with the conclusions regarding the symmetry or otherwise of the O–H–O bond reached by earlier workers. For example, Rundle & Parasol (1952) feel that only the H-bond lengths near 2·45 Å are symmetric, and Pimentel & McClellan (1960) have collected the H-bond data from various methods and come to the conclusion that O–H–O bond lengths <2·30 Å are symmetric. Since in the case of $MgS_2O_3.6H_2O$ it is found from the X-ray data of Nardelli *et al.* (1962) that the O · · · O distances are larger than 2·6 Å, it can be surmised that the H-location is asymmetric in the chelated H-bond formed between the water oxygen and an oxygen of the nearby $S_2O_3^{2-}$ group.

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References

BRUNT, N. A. (1946). Dissertation, Leiden. *Structure Reports*, **10**, 148.

DEBUS, H. (1882). *Trans. Roy. Soc.* **173**, 540. *Encyclopaedia of Chemical Reactions*, Vol. VI, p. 366. C. A. JACOBSON & C. A. HAMPELL. New York: Reinhold. London: Chapman & Hall.

MELLOR, J. W. (1937). *Comprehensive Treatise on Inorganic Chemistry*, Vol. 10, p. 545. London, New York, Toronto: Longman's Green and Co.

NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 227.

PAKE, G. E. (1948). *J. Chem. Phys.* **16**, 327.

PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond.* San Francisco and London: Freeman.

RAMMELSBERG (1855). *Kristallogr. Chemie, Berlin*, **63**.

RUNDLE, R. E. & PARASOL, M. (1952). *J. Chem. Phys.* **20**, 1487.

SILVIDI, A. A. & MCGRATH, J. W. (1961). *J. Chem. Phys.* **34**, 322.

SILVIDI, A. A., MCGRATH, J. W. & CARROLL, J. C. (1959). *J. Chem. Phys.* **31**, 1444.

VISWESWARAMURTHY, S. (1961). *Proc. Low Energy Nuclear Physics Symposium, Bombay*, p. 384.