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Proton magnetic resonance study of the water molecule in hilgardite, $Ca_2[B_5O_9]Cl \cdot H_2O$

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Abstract

A proton magnetic resonance study, at room temperature, of a single crystal of hilgardite, $Ca_2[B_5O_9]Cl \cdot H_2O$, has been carried out at 270 MHz. The variations of the dipolar splittings in the NMR spectra have been studied as a function of the orientation of the crystal relative to the magnetic field. This provides more accurate information about the orientation of the water molecule than a recently reported X-ray diffraction study of the crystal structure of hilgardite. The proton–proton vector is calculated to be 1.66(1)Å long, and the vector is found to be fairly close to, but significantly out of, the *b–c* plane. The positions of the hydrogen atoms of the water molecule are estimated from the NMR results by making some assumptions about the hydrogen bond arrangement, giving coordinates rather close to those estimated from the X-ray diffraction experiment.

Introduction

The crystal structure of hilgardite, $Ca_2B_5O_9Cl \cdot H_2O$, found in the Choctow Salt Dome, Iberville Parish, Louisiana, has recently been determined by X-ray diffraction by Ghose and Wan (1979). Hilgardite belongs to the monoclinic space group *Aa*, and the structure consists of a three-dimensional pattern of pentaborate polyanions $[B_5O_{12}]^{-9}$. The arrangement of the polyanions is such that open channels parallel to the *a* and *c* axes are formed, with channel diameters of about 5–6Å. Within these channels the water molecules and the chlorine atoms form almost linear hydrogen bonded chains parallel to the *c* axis. As X-ray diffraction gives poor information about the positions of the hydrogen atoms and since we were provided with a single crystal cut from the same crystal used in the X-ray diffraction experiment, we decided to undertake an NMR experiment to obtain more precise information about the orientation of the water molecules.

According to Pake (1948), the dipolar splitting in an NMR spectrum of a single crystal containing an isolated proton pair can be written as

$$\Delta H = \frac{3\mu}{2r^3}(3\cos^2\theta - 1) \qquad (1)$$

where μ is the magnetic moment of the nuclei, r the length of the proton–proton vector, and θ the angle between **r** and the magnetic field.

For the purpose of analyzing proton spectra, a crystal containing water molecules can be considered, in most cases, to contain isolated proton pairs. This is, of course, an approximation, since the water molecules in the structure will couple to each other. Holcomb and Pedersen (1963) have shown, however, that even in such cases, equation 1 can be used if ΔH is taken to be the separation between the centers of gravity of the two peaks rather than between their two maxima. A large number of studies of solid hydrates using Pake's technique have been published and reviews are given by Chidambaram (1962) and El Saffar (1966b).

Experimental

NMR spectra were recorded on a pulsed NMR spectrometer operating at 270 MHz. A solid echo technique was used as described by Boden and Mortimer (1973), and references therein, in order to minimize the deadtime problems usually occurring when

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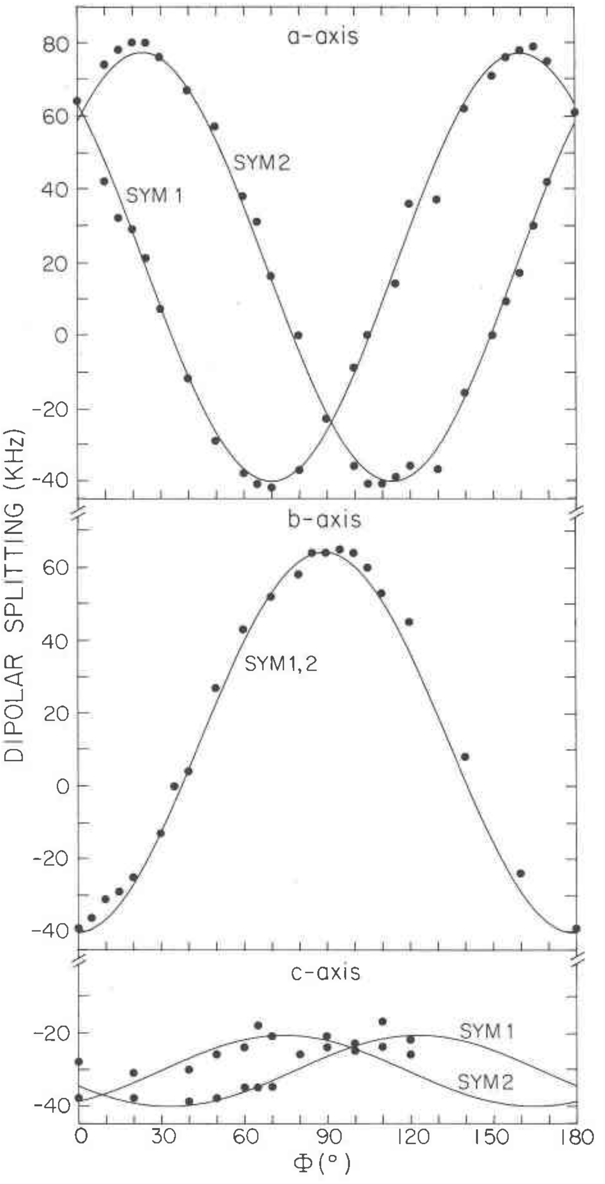

Fig. 1. Experimental dipolar splittings ($\Delta\nu$) for the three axes as a function of the rotation angle Φ together with the calculated splittings (solid lines) after the final cycle. The errors in $\Delta\nu$ and Φ are about 1 KHz and 2°, respectively. Sym 1 and 2 refer to the two symmetry-related proton–proton vectors in the unit cell.

very broad lines are studied by a pulsed NMR spectrometer.

The size of the single crystal of hilgardite used in the experiment was about 4 mm^3, containing 10^{19} protons. The plate-shaped crystal had well-developed faces, which were used in the orientation of the crystal. In order to protect the crystal, it was embedded in a polymer. To eliminate the narrow line from the polymer, a spectrum from the polymer was recorded and subtracted from the crystal spectra.

The NMR spectra were recorded every 5–10 degrees in an 180° rotation of the crystal about an axis perpendicular to the magnetic field. Three mutually orthogonal rotation axes (*a, b, c*, $\beta = 90.06°$) were used to obtain full information about the orientation of the proton–proton vector. Since the crystal belongs to the monoclinic system, two dipolar splittings are expected for each independent proton–proton vector in the unit cell (except when the magnetic field is parallel or perpendicular to the *b* axis, where the two doublets collapse to one, for all angles; see Fig. 1).

The proton–proton vector was refined using a least-squares procedure described by Berglund and Tegenfeldt (1978). The fit between the experimentally observed splittings and the calculated splittings is illustrated in Figure 1.

Results and discussion

The length of the proton–proton vector is 1.66(1)Å and it makes an angle of 24(1)° with the *c* axis and 80(2)° with the *a* axis, *i.e.*, the vector is tilted by 10° from the *b–c* plane. The proton–proton distance is slightly longer than found for other hydrates studied by NMR. El Saffar (1966b) has given a mean value of 1.60Å taken over a number of different hydrates, including lengths up to 1.64Å (Shulman and Wyluda, 1961; El Saffar, 1964a). Therefore the proton–proton distance in hilgardite is considered reasonable. It is known, however, that internuclear distances from an NMR experiment are significantly longer than the equilibrium value, R_e, due to the vibrational averaging. Similarly, the lengths determined from a neutron diffraction experiment are also affected by vibrational motion of the water molecule. In order to obtain a value for R_e from either NMR or neutron diffraction, the vibrational behavior of the molecule has to be known (see Pedersen, 1964; Eriksson *et al.*, 1979).

Table 1. Fractional coordinates of the hydrogen atoms in hilgardite as determined from the NMR data together with those determined from the X-ray data

	NMR	X-ray
	0.006	0.034
H(1)	0.039	0.026
	0.759	0.789
	0.030	0.041
H(2)	-0.015	-0.005
	1.000	1.021

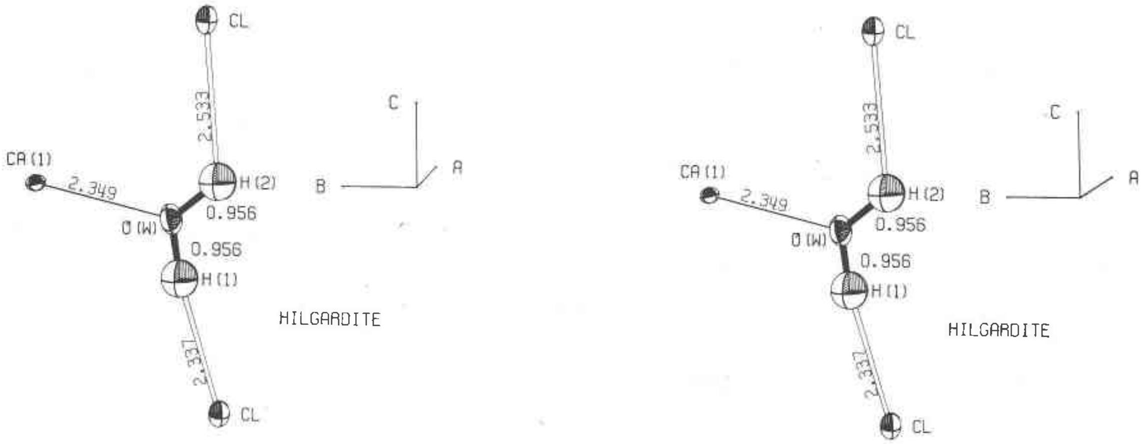

Fig. 2. A stereoscopic view of the water molecule in hilgardite based on parameters from the X-ray and NMR data. The hydrogen bond angles O(W)–H(1)...Cl and O(W)–H(2)...Cl are 170 and 125°, respectively.

From a proton magnetic resonance experiment alone it is impossible to calculate directly the position of the hydrogen atoms. It has been shown, however, by El Saffar (1966b) that estimates of the positions which agree very well with those obtained from neutron diffraction can be obtained from the NMR data if some assumptions about the hydrogen bond arrangement are made. The procedure is as follows: estimate the two O–H distances in the water molecule, and then minimize the sum of the squares of the hydrogen bond distances $H_1 \ldots A_1$ and $H_2 \ldots A_2$, where A_1 and A_2 are the two hydrogen bond acceptors (assuming that for each hydrogen bond there is only one acceptor). In the case of hilgardite only the chlorine atoms in the quasi-linear chain can act as acceptors since all distances from the proton atoms to all oxygen atoms in the borate arrangement are too long to be within the limit for a hydrogen bond (2.4Å). Both O–H distances in the water molecule were put equal to 0.965Å, a mean value calculated by Ferraris and Franchini-Angela (1972) from a review of 41 hydrates studied by neutron diffraction. In this average 90 water molecules were involved.

The fractional coordinates of the hydrogen atoms are given in Table 1 together with those determined from the X-ray diffraction experiment. As can be seen the agreement is fairly good.

The arrangement of the water molecule in hilgardite based on the new hydrogen atom coordinates is illustrated by means of a stereographic plot of the water molecule and its hydrogen bond arrangement (Fig. 2).

Acknowledgments

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