Study of Hydrogen Positions in $Cu(NO_3)_2.2.5H_2O$ from PMR and DMR

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Abstract

Proton magnetic resonance (PMR) is used to determine the orientation of the proton–proton vectors of the water molecules in $Cu(NO_3)_2.2.5H_2O$. From a deuteron magnetic resonance (DMR) study of $Cu(NO_3)_2.2.5D_2O$ the orientations of the electric field gradient tensor at the deuterium sites are found. The NMR data are coupled with the hydrogen bonding scheme in the crystal and the crystal structure to determine the hydrogen atom positions.

Introduction

The crystal structure of $Cu(NO_3)_2.2.5H_2O$ was first determined by Dornberger-Schiff & Leciejewicz (1958). Their X-ray study was unable to locate the positions of the hydrogen atoms. A more recent and detailed X-ray study of this crystal by Morosin (1970) gives hydrogen positions also and the hydrogen-bonding scheme. The first proton magnetic resonance (PMR) investigations of this crystal were carried out by Van Tol, Henkens & Poulis (1971). Their interest was to study the high-field magnetic phase transition and the antiferromagnetic exchange interaction between the copper spins through their influence on PMR. In the present work we have made a room-temperature NMR study of paramagnetic $Cu(NO_3)_2.2.5H_2O$ and $Cu(NO_3)_2.2.5D_2O$. The NMR data has been coupled with the hydrogen-bonding scheme and the crystal structure to determine the positions of the hydrogen atoms.

According to Morosin (1970), the crystal of $Cu(NO_3)_2.2.5H_2O$ is monoclinic with space group $I2/a$. The lattice constants are $a = 16.453$, $b = 4.936$ and $c = 15.963$ Å with $\beta = 93.765°$. There are eight molecules in the unit cell. The oxygen atoms of the

water molecules in the crystal are involved in hydrogen bonding. The crystal structure of $Cu(NO_3)_2.2.5H_2O$ in the b-axis projection is shown in Fig. 1.

Experimental

(a) Crystal growth

Single crystals of $Cu(NO_3)_2.2.5H_2O$ were grown at room temperature from an aqueous solution of copper nitrate. The crystals were deep blue in colour and were very hygroscopic. They were elongated along [010] and the prominent face was identified as (001). The crystals used in the present work were given a thin coating of varnish.

$Cu(NO_3)_2.2.5D_2O$ was obtained by repeated crystallization from D_2O. Good single crystals were grown by slow evaporation of a concentrated solution of the above material in D_2O. Special care was taken to prevent the exchange of D_2O with atmospheric H_2O. The crystals have the same morphology and symmetry
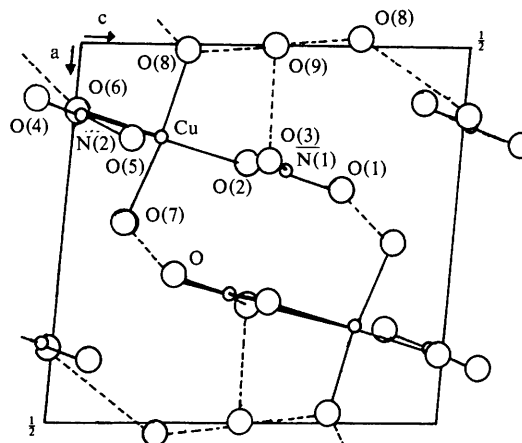

Fig. 1. Crystal structure of $Cu(NO_3)_2.2.5H_2O$ in b axis projection.

as the hydrated crystal. Attempts to detect resonance due to protons in this crystal did not reveal any. The approximate dimensions of the crystals used in the present work are $18 \times 10 \times 8$ mm.

(b) Proton and deuteron spectra

The proton resonance spectra were recorded at $7 \cdot 8$ MHz at room temperature in $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ using a Varian wide-line NMR spectrometer. The angular dependence of the resonance spectrum was studied in planes perpendicular to the $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}' = \mathbf{a} \times \mathbf{b}$ axes of the crystal at $10°$ intervals. Lock-in detection was used to record the first derivatives of the resonance absorption. The magnetic field strength of 183 mT used was considered low enough to diminish any possible anisotropic shifts of the resonance lines due to the crystal paramagnetism.

The deuteron resonance spectra were recorded at $4 \cdot 75$ MHz at room temperature for rotations about the $\mathbf{a}' = \mathbf{b} \times \mathbf{c}$, $\mathbf{b}$ and $\mathbf{c}$ axes of the crystal.

Results and discussion

(a) Proton resonance

In $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$, the unit cell has three nonequivalent water molecules. The space-group symmetry produces six nonparallel proton–proton vectors. The spectrum obtained with the magnetic field in a general direction would lead to twelve resonance lines which reduce to six with the magnetic field in the symmetry plane perpendicular to the $\mathbf{b}$ axis of the crystal. The spectra recorded for $\mathbf{b}$ rotation showed six proton lines for most orientations of the crystal. In the $\mathbf{a}$ and $\mathbf{c}'$ rotations a minimum of four well-resolved lines were observed. The central portion of the spectrum is formed from the overlap of many components which are only partially resolved. The resonance lines are symmetrical about a central free proton line which is due to the trapped water molecules during crystal formation. Fig. 2 shows a typical proton spectrum.

The mean orientation of the proton–proton vectors found from different orientations together with the same directions calculated from the X-ray data (Morosin,

1970) is shown in Table 1. For each direction in this table there is a symmetry-related direction which we have omitted. In designating the hydrogens we have used the same notation as followed by Morosin (1970). The water molecules H(1)H(2)O(7), H(3)H(4)O(8) and H(5)H(5)O(9) are designated as $H_2O(1)$, $H_2O(2)$ and $H_2O(3)$, respectively. The H—O—H angles shown in Table 1 are obtained from the experimental proton–proton distance in the water molecule (r_{pp}) assuming the O—H distance in the water molecule to be $0 \cdot 987$ Å (El Saffar, 1966). The error involved in the determination of the orientations of the proton–proton vectors from the PMR data is estimated to be less than $4°$. The last column of Table 1 lists the angular difference $\Delta\theta$ between the orientation of a given vector found from PMR and from X-rays. According to Morosin (1970) the water molecule $H_2O(3)$ is shared between two copper nitrate groups. The present study also supports this arrangement since the H(5)—H(5) direction determined here is nearly parallel to the O(3)—O(3) direction in Morosin's (1970) notation.
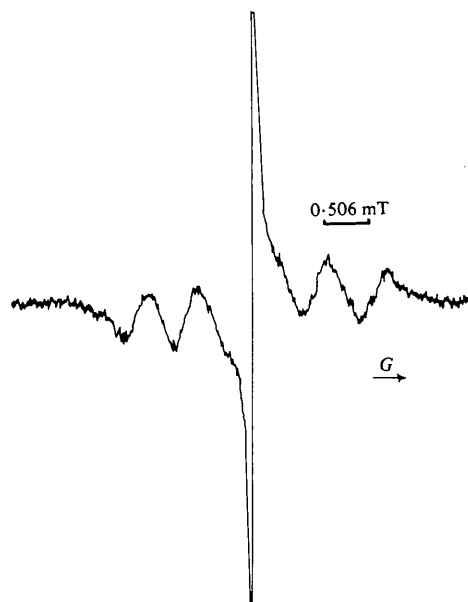
Fig. 2. The observed first derivative of the proton magnetic resonance spectrum from a single crystal of $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ at a certain orientation about the $\mathbf{b}$ axis.

Table 1. *The direction cosines of the p–p vectors of the water molecules as given by PMR and as calculated from the X-ray structure*

	PMR					X-ray			
	a	b	c	r_{pp} (Å)	HOH	a	b	c	$\Delta\theta$
$H_2O(1)$	0·0370	0·9801	0·1923	1·572	106°	0·0077	0·9737	0·2266	2·47
$H_2O(2)$	0·2687	0·4360	0·8394	1·563	105°	0·2068	0·4737	0·8406	4·13
$H_2O(3)$	0·9974	0·0279	0·0002	1·581	106°	0·9982	0·0000	−0·0051	1·72

(b) Deuteron resonance

In the a' and c rotations ten resonance lines were observed; in the b rotation this is reduced to six. The number of lines observed in the different rotations may be accounted for if the structure of $Cu(NO_3)_2.2.5D_2O$ is similar to that of the hydrate in which the water molecules are flipping fast (reorienting about their twofold axis) at room temperature. A typical deuteron spectrum is given in Fig. 3. Because of the larger r.f. power that was applied in this case, stronger resonance lines could be obtained without getting saturation.

Each deuteron in the crystal is in an electric potential V which is due to surrounding charges. The quadrupole splitting of the deuteron magnetic resonance (DMR) line is given by

$$2(\Delta v) = kV_{z'z'}, \tag{1}$$

where Δv is the frequency shift of each line from the unperturbed resonance, $k = \frac{3}{4}(eQ/h)$ for the deuteron and eQ is the electric quadrupole moment of the deuteron. $V_{z'z'}$ is the second derivative of the electrostatic potential at the site of the deuteron under question with respect to the z' direction of the laboratory coordinate system $x'y'z'$ coinciding with that of the constant magnetic field. Let X,Y,Z represent a set of right-handed rectangular axes fixed with respect to the crystal. If now X,Y,Z are in turn oriented perpendicular to the magnetic field, then for the rotation

20·08 kHz

Fig. 3. An example of deuteron magnetic resonance spectrum from a single crystal of $Cu(NO_3)_2.2.5D_2O$ at a certain orientation about the symmetry axis.

of the crystal about X the quadrupole splitting in terms of the electric field gradient tensor components is

$$2(\Delta v) = \frac{1}{2}k(V_{YY} + V_{ZZ}) + \frac{1}{2}k(V_{YY} - V_{ZZ})\cos 2\theta_X$$
$$- kV_{YZ}\sin 2\theta_X \tag{2}$$

$$= A_X + B_X\cos 2\theta_X + C_X\sin 2\theta_X. \tag{3}$$

Here θ_X is measured from the position in which Y coincides with Z. Analogous expressions obtainable by cyclic permutation of (2) hold for rotations about Y and Z. In our experiment we have chosen a', b, c to coincide with X,Y,Z. The curve parameters A_X,B_X,C_X; A_Y,B_Y,C_Y; A_Z,B_Z,C_Z were least-squares fitted using the splittings observed in the experiment. The electric field gradient tensors at the inequivalent deuteron sites in the crystal were constructed from the parameters using a method outlined by Volkoff, Petch & Smellie (1952). In the structure of $Cu(NO_3)_2.2.5D_2O$ there are symmetry-related deuteron sites which are magnetically inequivalent. For a given curve in the b rotation there are two curves in a' and c rotations. The two curves differ only in the sign of C_X,C_Z. The sign of the coefficients C_X,C_Z is indeterminate in our experiments and four different tensors can be constructed from the experimental data depending upon the signs chosen for C_X,C_Z. These four tensors can be split into two sets with the tensors of a given set being symmetry related. To find the tensor which corresponds to the physical situation related in this crystal, we note that for a flipping water molecule the smallest principal component of the electric field gradient tensor is along the bisector of the D—O—D angle while either the medium or the largest principal component is along the D—D vector with the remaining component along the normal to the plane of the water molecule (Soda & Chiba, 1969). We identified the correct set from the above by choosing the tensor whose medium or largest principal component is in good agreement with the p–p direction found from the PMR experiment. The results are shown in Table 2 for one tensor from the correct set, with the data for its symmetry-related tensor being omitted.

Table 2. *Deuteron quadrupole coupling tensors*

	Principal component magnitude (kHz)	Direction cosines			Quadrupole coupling consant (kHz)	Asymmetry parameter
		a	b	c		
$D_2O(1)$	−17·83	0·7562	∓0·1195	0·5921		
	−176·97	−0·0209	∓0·9783	0·2072	129·9	0·82
	194·83	−0·6539	∓0·1695	0·7787		
$D_2O(2)$	−10·16	0·7023	∓0·6802	0·1633		
	−173·52	0·1991	±0·4713	0·8443	122·5	0·89
	183·68	0·6832	±0·5618	−0·5104		
$D_2O(3)$	−10·27	−0·0400	0·9989	0·0276		
	−179·96	0·9956	0·0376	0·0193	126·7	0·89
	190·23	0·0852	0·0278	−0·9994		

Table 3. *Hydrogen atom positions in* $Cu(NO_3)_2.2\cdot5 H_2O$

	PMR			DMR			X-ray		
	x	y	z	x	y	z	x	y	z
H(1)	0·270	0·118	0·124	0·269	0·124	0·123	0·267	0·11	0·120
H(2)	0·269	−0·191	0·100	0·270	−0·187	0·102	0·265	−0·18	0·099
H(3)	−0·033	0·079	0·088	−0·026	0·054	0·089	−0·025	0·05	0·091
H(4)	−0·016	0·209	0·175	−0·002	0·203	0·174	0·000	0·20	0·175
H(5)	0·423	−0·084	0·248	0·453	−0·079	0·245	0·452	−0·05	0·247

(c) *Hydrogen atom positions*

We have determined the hydrogen atom positions in $Cu(NO_3)_2.2\cdot5H_2O$ from the proton–proton vectors determined from the PMR study making use of the hydrogen-bonding scheme in the crystal (Morosin, 1970) and a method due to El Saffar (1966). We have also determined these positions from the orientation of the principal axes of the electric field gradient tensor found from DMR using a method outlined elsewhere (Vizia, Murty, Murty & Nagarajan, 1976). The hydrogen positions determined from PMR and DMR are shown in Table 3 along with those given by X-rays (Morosin, 1970). The agreement can be considered as satisfactory. Neutron diffraction is the technique used to determine accurately the hydrogen atom positions. To our knowledge, for $Cu(NO_3)_2.2\cdot5H_2O$ such a determination of the hydrogen positions has not been made. Hydrogen positions from X-ray studies are relatively less accurate and are not often determined. Positions found from the NMR study, while less accurate compared to those from a neutron diffraction study, are of value, particularly in the absence of the latter in the solution of the magnetic structure of antiferromagnetic crystalline hydrates. A larger number of hydrates appear to have been studied with NMR than with neutron diffraction.

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On the Effect of Thermal Expansion on the Intensity of Diffraction from Molecules

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Abstract

A number of polymers have been discovered recently for which the intensity of some Bragg reflections with $d >$ 10 Å considerably increases with temperature. Thermal expansion may be the reason for this anomalous phenomena. In sufficiently large molecules electron density distribution should change at the molecular boundaries upon thermal expansion. In the middle part of a molecule, owing to the rigidity of interatomic bonds, an increase in temperature will not cause appreciable changes. As a result, thermal expansion may lead to a re-distribution of the electron density and an increase in the intensity of Bragg reflections with temperature. The scattering from model systems of particles was calculated. The calculations show that the rate of the growth of the Bragg reflection intensity with maximum d increases when a relative size of the central part of particle with constant density increases. The larger the molecule, the faster the Bragg reflection intensity increases with temperature rise. Thermal expansion should lead to an increase in the intensity of