cobalt. The small cobalt–tantalum distance can be attributed to the tantalum valence electrons fitting into a vacant inner $3d$ shell of the cobalt atom.

Table 7. *Nearest neighbor distances in the observed* $\mathrm{Co_2Ta}$ *and* $\mathrm{Co_3Ta}$ *structures*

Structure	Distances		
	Co–Co	Ta–Ta	Co–Ta
Sum of the atomic radii of cobalt of coordination number six and tantalum of coordination number four	2·52 Å	2·86 Å	2·69 Å
α-$\mathrm{Co_2Ta}$, $\mathrm{MgZn_2}$ type	2·40	2·94	2·81
β-$\mathrm{Co_2Ta}$, $\mathrm{MgCu_2}$ type	2·40	2·94	2·81
γ-$\mathrm{Co_2Ta}$, $\mathrm{MgNi_2}$ type	2·35	2·89	2·77
α-$\mathrm{Co_3Ta}$, $\mathrm{Cu_3Au}$ type	2·58	3·65	2·58

In conclusion, the agreement of the determined densities obtained in this work is emphasized. The α and β-$\mathrm{Co_2Ta}$ values are nearly identical while the γ-$\mathrm{Co_2Ta}$ ($\mathrm{Co_{2.2}Ta_{0.8}}$) and $\mathrm{Co_3Ta}$ compounds are less dense in accord with their relative increases in cobalt. The interatomic distances presented in Table 7 agree extremely well for the Laves phases. These distances were calculated from the cell sizes determined in this work and reported in Table 1 and from the 'ideal' atom positions listed in the other tables. It is to be recognized that there are many possible faults in specifying the atom distances to the accuracy indicated in Table 7. However, it is felt that such a calculation, even using the 'ideal' atom positions in each case, helps corroborate the determined cell parameters.

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Nuclear Magnetic Resonance in Sodium Thiosulfate Pentahydrate*

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The proton resonance spectrum of sodium thiosulfate pentahydrate has been studied with a view to establishing orientation of the water molecules. The orientation of the experimentally determined proton–proton vectors is in excellent agreement with those implied by the hydrogen bonding scheme suggested by Taylor & Beevers. One of the proton–proton vectors appears to be much shorter than those reported in other crystalline hydrates.

Introduction

The classic experiment of Pake (1948) established the fact that nuclear magnetic resonance data combined with X-ray information is quite effective in determining the position of hydrogen atoms in a crystal. The technique has been extended by latter workers to a number of simple hydrates i.e. hydrates with only a few pairs of p–p (proton–proton) directions. When one attempts to apply the method to more complicated hydrates one finds that the central portion of the proton resonance line is formed from the overlap of many components which are only partially resolved. Nevertheless at certain orientations some of the components of the resonance pattern are well resolved. The present work was undertaken largely to try to answer the question as to whether the information available from such orientation is sufficient to locate the protons in a relatively complicated hydrate.

The X-ray studies of Taylor & Beevers (1952) give

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the space group of $Na_2S_2O_3.5H_2O$ as $P2_1/c$ with $Z=4$. Their axial ratios $a:b:c=0{\cdot}2745:1:0{\cdot}3508$ and $\beta = 103° 58'$ agree with the morphological results quoted by Groth (1906–19, Vol. 2, p. 670) provided the *a* and *c* axes are interchanged. The choice of axes in the present paper corresponds to that of Taylor & Beevers. The above data implies that there are ten *p–p* directions in the crystal.

Experimental

The crystals of sodium thiosulfate were grown from saturated aqueous solutions. It took considerable time to grow large clear crystals. The samples were cut in cylindrical form and were about 1·5 cm.³ in volume. They were mounted in teflon holders which were in turn attached to a simple indexed head that allowed rotation about the axis of the cylinder.

The proton resonance absorption signals were observed with a conventional marginal oscillator operated at about 10·5 m.c.p.s. The output of the marginal oscillator was passed through a phase-sensitive 'lock-in' amplifier and then to an *X–Y* recorder. The marginal oscillator frequency was slowly swept through the resonance line by a motor drive; the *X*-displacement of the recorder was also geared to this drive. The frequency sweep was calibrated with a Hewlett Packard frequency counter which was accurate to within 1 c.sec.⁻¹. The measurements were made at room temperature since a lower temperature caused the substance to saturate more readily.

In the case of simple hydrates, rotating the crystal about two different axes serves to determine the magnitude and direction of the *p–p* vectors. In the present case however the only resolved resonance components are those arising from *p–p* vectors lying within about 20° from the plane of rotation. Therefore one is forced to use data based on several different axes of rotation. Rotating the crystal about *a*, *b* and *c′* axes served to locate the *p–p* vector approximately. Two additional axes of rotation served to determine the vectors uniquely. The first (*d*-axis) was in the *ab* plane 35° from a towards *b*, while the second (*e*-axis) was in the *ac* plane 6° from *c* towards negative *a*. The choice of such axes became evident when the data from the *a*, *b* and *c′* rotations was available.

Results

The resonance diagram obtained by rotating the crystal about the *b* axis is shown in Fig. 1. Diagrams of comparable complexity were obtained for the other four axes of rotation. The result for orientations of the ten *p–p* vectors are shown in the stereographic projection in Fig. 2. These vectors are labelled *A*, *B*, *C*, *D*, *E*, *A′*, *B′*, *C′*, *D′*, and *E′*. The primed vectors are reflections of the corresponding unprimed ones, the mirror plane being the *ac* plane.

The magnitude and orientation of each vector was determined by at least two different rotations. The three distinct maxima in Fig. 1 outlined the orientations of vectors *E*, *A*, and *D*. The *c′* rotation was employed to determine *E* uniquely, while the orientation of *A* was fixed by the *e*-axis rotation. The *a*, *b* and *d* rotations were used to determine *D*, and so on.

The *p–p* distance was calculated for each vector by using the relation

$$\Delta H = 2\mu(3\cos^2\theta - 1)/r^3$$

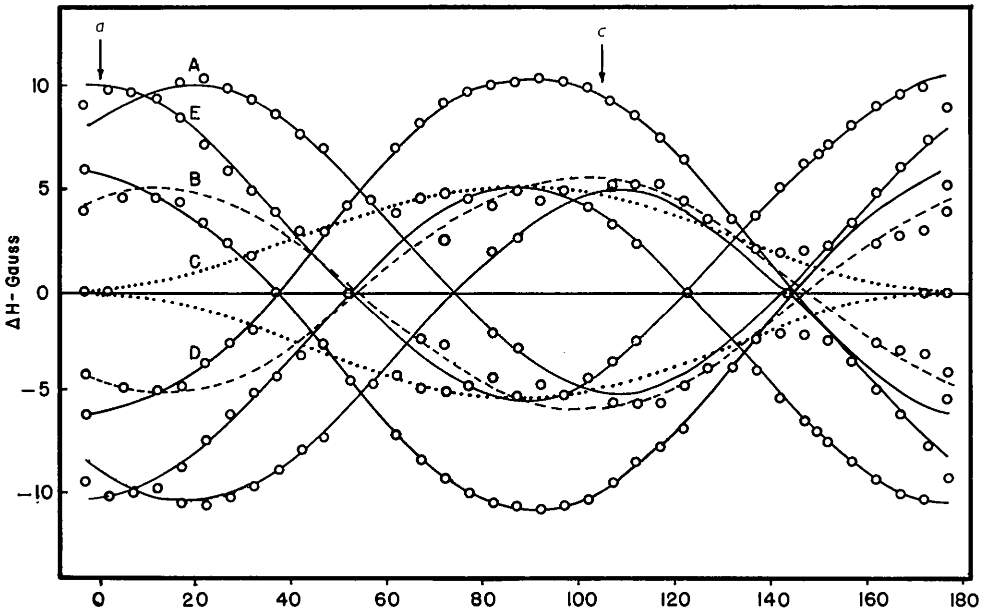

Fig. 1. Angular dependence of the proton resonance spectrum in the *ac* plane. The smooth curves are Pake curves for vectors *A*, *B*, *C*, *D* and *E*, obtained by using the experimental values of α_0, β_0, γ_0 and r given in the table.

Table 1.

	Experimental					Calculated				
Vector	α_0	β_0	γ_0	∠ HOH	r	α_0	β_0	γ_0	∠ XOX'	d
A	20°	80°	87°	108° 2′	1·57 Å	20° 30′	77° 33′	87° 30′	98° 24′	1·04 Å
B	107°	58°	33°	109° 4′	1·58 Å	102° 12′	57° 6′	33°	103° 30′	1·01 Å
C	125°	36°	79°	110° 4′	1·59 Å	128° 48′	39° 12′	77° 30′	94° 30′	1·08 Å
D	87°	74°	24°	103° 12′	1·52 Å	84° 52′	72° 34′	25° 30′	105° 12′	0·95 Å
E	2°	90°	102°	111° 8′	1·60 Å	0° 48′	90° 36′	103° 25′	124° 3′	0·91 Å

where μ is the proton magnetic moment, ΔH is the maximum line pair separation and θ is the smallest angle that the vector makes with the plane of rotation. The discrepancy arising from calculating the same *p–p* distance from different resonance diagrams did not exceed 1%. Values of r for the five vectors are given in the fifth column of Table 1.

Discussion

The orientation of the *p–p* vectors obtained from the hydrogen bonding scheme suggested by Taylor & Beevers are shown in Fig. 2. These *p–p* vectors were calculated from the bonds which they suggest by assuming the vectors to be perpendicular to the bisector of the angle X–O–X' where X and X' are the atoms to which the protons of the water molecules are hydrogen bonded. In the notation of Taylor & Beevers the *p–p* vectors which we designated as *A*, *B*, *C*, *D*, and *E* correspond to the arrangements:

A $O_3 \cdots H \cdots O_4 \cdots H \cdots O_2$
B $O_3 \cdots H \cdots O_5 \cdots H \cdots O_3$
C $O_4 \cdots H \cdots O_6 \cdots H \cdots S_1$
D $O_8 \cdots H \cdots O_7 \cdots H \cdots S_1$
E $S_1 \cdots H \cdots O_8 \cdots H \cdots S_1$

The comparison between our results and those calculated from the Taylor–Beevers scheme is shown in greater detail in Table 1. Here α_0, β_0 and γ_0 are the angles between the positive *a*, *b* and *c* axes and the *p–p* vectors. As can be seen from the table the agreement between the observed and calculated values of α_0, β_0 and γ_0 is quite satisfactory and it appears that the bonds suggested by Taylor & Beevers are correct.

The values of r for vectors *A*, *B*, *C* and *E* lie within the range 1·56–1·61 Å reported by McGrath & Silvidi (1961) for other crystalline hydrates. The value for *D* is considerably shorter and as yet we have been unable to find a satisfactory explanation for this in the environment of the protons.

In column ten of Table 1 we give the O–H distance which would be required to place the protons on the O–X and O–X' lines without changing their experimentally determined r values. The values of d all seem to fall slightly outside the probable range from 0·96 to 1·00 Å and may be considered to indicate that the bonds are bent. To obtain some estimate of this bending we have calculated the H–O–H angle based on the assumption that the O–H distance is 0·97 Å in all cases. These results are given in column four and are to be compared with the angle X–O–X' given in column nine.

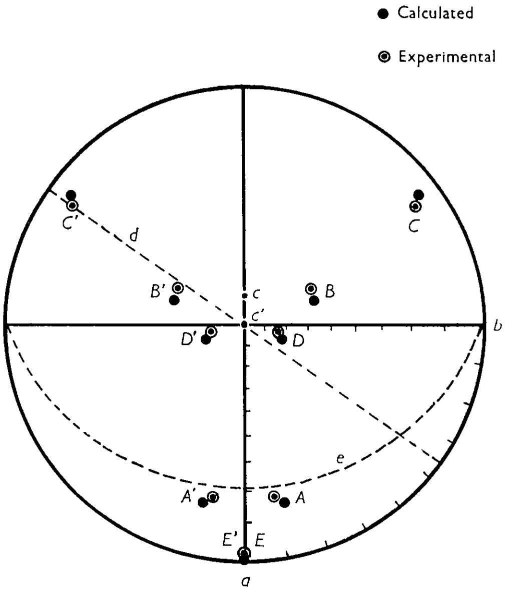

Fig. 2. Stereographic projection showing calculated and experimental *p–p* directions. The solid lines lie in the *a*, *b* and *c′* planes of rotation while the broken lines lie in the *d* and *e* planes.

In conclusion, our results show that nuclear magnetic resonance can be used to investigate crystalline hydrates containing several waters of hydration. The method involves studying resonance diagrams obtained by rotating the crystal about several and sometimes odd axes. It appears that the amount of work could be reduced by using a rotation head which is designed to allow the crystal to rotate in two mutually perpendicular planes.

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