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Determination of hydrogen positions in some crystalline hydrates with use of nuclear magnetic resonance results.*

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Nuclear magnetic resonance data have been studied in crystalline hydrates whose X-ray structures are available with a view to establishing the positions of the hydrogen atoms in the unit cell. The method of calculation of the hydrogen positions has been previously described by the author and shown to give satisfactory results. The method has been applied here to determine a total of 52 hydrogen positions belonging to 13 hydrates.

Applications of the nuclear magnetic resonance (n.m.r.) technique in hydrate crystals (Pake, 1948) provide the magnitudes and directions of the proton–proton ($p-p$) vectors in the unit cell but give no indication as to the location of these protons. Nevertheless, the n.m.r. results coupled with some assumptions about the atomic structure can be used to establish the H-bonding scheme and determine the approximate positions of the H atoms. In a previous publication, the author (El Saffar, 1966*a*) presented a method which may be used to determine the H positions in hydrates from n.m.r. and X-ray results. This method was then applied to 12 hydrates whose neutron-diffraction structures were available. It was found that on the average, the discrepancy between the positions determined from the n.m.r. data and those obtained by neutron diffraction was ~0·06 Å. This small discrepancy makes it appear that the method is a valuable one and renders pertinent the calculation of the H positions in other hydrates.

In calculating the positions of the H atoms belonging to the molecules of water of hydration, the H-bonding scheme must first be established. Each $p-p$ vector determined by n.m.r. must then be assigned to one of the nonequivalent water molecules in the unit cell. Computation of the positions H(I) and H(J) belonging to any water molecule is then made under the following assumptions: (1) the O–H distance is 0·987 Å; and (2) the sum of the squares of the two distances H(I)...X(I) and H(J)...X(J) satisfies a minimum condition, where X(I) and X(J) are the H-bond acceptor atoms. These assumptions were examined and discussed in detail in the light of available neutron diffraction measurements (El Saffar, 1966*a*). It was shown that while assumption (1) introduces only a small error, assumption (2) introduces an average error ~0·04 Å in the calculated H position. This is within the experimental error estimated for the n.m.r. experimental measurements.

The H positions calculated by the method outlined above are given in Table 1 for 13 hydrates involving 52 hydrogen atoms. The n.m.r. and X-ray references employed to make the calculations are also given in Table 1. In cases where the compound has been investigated more than once by n.m.r. the reference employed is the one considered more reliable. The heavy atom coordinates used in the case of $K_2HgCl_4.H_2O$ were those given by X-ray except for z(oxygen) where a value of 0·23 (instead of the X-ray 0·25) was used as suggested by the n.m.r. work of Itoh, Kusaka, Yamagata, Kiriyama & Ibamoto (1953*a*; Itoh, Kusaka, Yamagata, Kiriyama, Ibamoto, Kanda & Masuda, 1953). These authors also investigated $K_2SnCl_4.H_2O$ and suggested a set of atomic coordinates for this compound. However, no calculation of the H positions is made here since there exists no X-ray verification of these coordinates.

Positions of the H atoms were given by the n.m.r. investigators for $CaHPO_4.2H_2O$, $Na_2Al_2Si_3O_{10}.2H_2O$, $Na_2CO_3.H_2O$ and $Na_2S_2O_6.2H_2O$. Examination of these positions shows that they are somewhat inconsistent with the experimental $p-p$ vectors from which they were derived, and with the respective O–H distances assumed by these investigators. Such inconsistencies were previously discovered by the author in $(COOH)_2.2H_2O$ and $Na_2CO_3NaHCO_3.2H_2O$ (El Saffar, 1966*a*), $CoCl_2.6H_2O$ (El Saffar, 1966*b*) and $Cu(HCO_2)_2.4H_2O$ (El Saffar, 1967). The results given in Table 1 have been made to agree exactly with the experimental $p-p$ vectors found by the n.m.r. authors and with the O–H distance assumed.

The neutron-diffraction structure of $Na_2Al_2Si_3O_{10}.2H_2O$ has been determined by Torrie, Brown & Petch (1964). The discrepancy between the positions given in Table 1 and the corresponding positions obtained by neutron diffraction are found to be 0·09 Å for both H(1) and H(2). This is considered to be reasonable since (*a*) the experimental $p-p$ direction deviates by 4° from the neutron-diffraction H–H direction, thus contributing 0·05 Å to the discrepancy, and (*b*) the H positions given by neutron diffraction are not 'corrected' for the influence of thermal motion, thus resulting in low values of the 'apparent' O–H distance. It must be mentioned here that the positions H(1) and H(2) predicted by the n.m.r. investigator (Gabuda, 1962) deviate by 0·26 Å and 0·11 Å respectively from the corresponding positions obtained by neutron diffraction.

The H positions given for the ferroelectric compound $C(NH_2)_3Al(SO_4)_2.6H_2O$ were also determined by the X-ray workers using difference syntheses. The deviations of the X-ray positions from those given in Table 1 range from 0·06 Å [H(7)] to 0·24 Å [H(5)], and have a mean of 0·15 Å. When compared with neutron-diffraction results, the shifts in the H positions obtained from X-rays are found to be ~0·24 Å (Baur, 1965; El Saffar & Brown, 1968). This, and the fact that the O–H distances obtained from the X-ray data are rather low (average ~0·83 Å) favor the results given in Table 1 for $C(NH_2)_3Al(SO_4)_2.6H_2O$.

The H positions given for $FeCl_2.4H_2O$ and $Cu_6Si_6O_{18}.6H_2O$ should be useful in studying the antiferromagnetic states of these compounds. In the case of $FeCl_2.4H_2O$, Spence, Au & Van Dalen (1964) used the n.m.r. 'local' field directions at the proton sites and symmetry arguments to infer the Shubnikov group of this compound in its magnetically ordered state below 0·7°K. However, according to these authors, it is uncertain whether the sublattice magnetization is exactly parallel to the b axis. The H positions given in Table 1 should be useful in confirming the Shubnikov group and establishing the exact direction of sublattice magnetization. Here a dipolar sum may be used to predict the magnitudes of the local fields at the proton sites and adjust the sublattice magnetization accordingly. This technique has been applied successfully

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in studying the antiferromagnetic state of $MnCl_2.4H_2O$ (Spence & Nagarajan, 1966) whose H positions have been determined by neutron diffraction (El Saffar & Brown, 1968).

The $p-p$ vectors used to calculate the H positions for $NiSO_4.7H_2O$ were originally obtained from n.m.r. measurements on the isostructural diamagnetic compounds $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$. In this particular series of compounds there are 4 molecules per unit cell all occupying general positions in the orthorhombic space group $P2_12_12_1$. Although one expects only 7 unique $p-p$ vectors, there are in fact 28 nonparallel vectors which occur in 4 sets related by reflections in the *ab*, *ac* and *bc* planes. Thus the resonance spectrum will have at least 28 resonance components (corresponding to 14 $p-p$ vectors) that overlap and result in poor resolution. If the uncertainty in determining the $p-p$ direction is assumed to be as much as 10°, the resulting error in the determination of the H positions of $NiSO_4.7H_2O$ given in Table 1 is estimated to be 0·15 Å.

The n.m.r. results obtained for $MnSO_4.4H_2O$ (Rao, 1964) and $MgS_2O_3.6H_2O$ (Visweswaramurthy, 1963) were also examined with a view to calculating the H positions.

Table 1. *Positional parameters of the* H *atoms as determined from the X-ray structure for non-hydrogen atoms, the n.m.r. proton–proton vectors, and the assumptions discussed in the text*

The starred n.m.r. reference is the one from which the values of the proton–proton vectors were acquired to carry out the calculations. The designation of the H atoms follows closely wherever possible that of the X-ray reference.

Compound	X-ray reference	n.m.r. reference	H atom	*x*	*y*	*z*
$Ba(ClO_3)_2.H_2O$	Kartha (1952)	Spence (1955)	H(1)	0·075	−0·012	0·202
		McGrath & Silvidi (1961)*	H(2)	−0·075	−0·012	0·298
$K_2HgCl_4.H_2O$	McGillavry *et al.* (1938)	Itoh *et al.* (1952, 1953*a*), Itoh *et al.* (1953)	H(1)	0·090	0·525	0·289
		McGrath & Silvidi (1961)*	H(2)	−0·090	0·475	0·289
$Na_2Co_3.H_2O$	Harper (1936)	Van Meerssche *et al.* (1962)*	H(1)	0·445	0·128	0·783
			H(2)	0·422	−0·104	0·855
$CaHPO_4.2H_2O$	Beevers (1958)	Jones & Smith (1960)*	H(1)	0·190	0·996	0·310
			H(2)	−0·006	0·916	0·244
$K(H_4B_5O_{10}).2H_2O$	Zachariasen & Plettinger (1963)	Smith & Richards (1952)	H(I)	−0·035	0·208	0·682
		McGrath & Silvidi (1961)*	H(II)	−0·035	0·125	0·828
$K_2CuCl_4.2H_2O$	Chrobak (1934)	Itoh *et al.* (1953*b*), Itoh *et al.* (1957)	H(1)	0·076	0·076	0·178
		McGrath & Silvidi (1961)*	H(2)	−0·076	−0·076	0·178
$Na_2Al_2Si_3O_{10}.2H_2O$	Meier (1960)	Gabuda (1962)*	H(1)	0·054	0·142	0·039
			H(2)	0·103	0·191	0·184
$Na_2S_2O_6.2H_2O$	Martinez *et al.* (1956)	Van Meersche *et al.* (1963)*	H(1)	0·360	0·072	0·108
			H(2)	0·202	0·119	0·234
$Na_2S_2O_3.5H_2O$	Taylor & Beevers (1952)	Itoh *et al.* (1957)	H(41)	0·715	0·207	0·198
		Murty & El Saffar (1962)*	H(42)	0·446	0·220	0·135
			H(51)	0·114	0·310	0·416
			H(52)	0·148	0·271	0·247
			H(61)	0·592	0·333	0·432
			H(62)	0·746	0·392	0·421
			H(71)	0·848	0·482	0·194
			H(72)	0·771	0·463	0·995
			H(81)	0·752	0·019	0·203
			H(82)	0·480	0·019	0·195
$FeCl_2.4H_2O$	Penfold & Grigor (1959)	El Saffar & Murty (1962)*	H(1*a*)	0·135	0·076	0·352
			H(1*b*)	−0·091	−0·064	0·292
			H(2*a*)	0·378	−0·283	0·196
			H(2*b*)	0·372	−0·283	0·002
$C(NH_2)_3Al(SO_4)_2.6H_2O$	Schein, Lingafelter & Stewart (1967)	Spence & Muller (1957)*	H(4)	0·869	0·080	0·848
			H(5)	0·920	0·140	0·116
			H(6)	0·753	0·210	0·900
			H(7)	0·592	0·129	0·900
			H(8)	0·801	0·260	0·214
			H(9)	0·881	0·420	0·214
$Cu_6Si_6O_{18}.6H_2O$	Heide & Boll-Dornberger (1955)	Spence (1958)*	H(1)	0·102	0·702	0·163
			H(2)	0·149	0·564	0·117
$NiSO_4.7H_2O$	Beevers & Schwartz (1935)	Van Meerssche *et al.* (1962)*	H(5*a*)	0·00	0·23	0·11
			H(5*b*)	−0·04	0·19	−0·10
			H(6*a*)	0·15	0·29	0·27
			H(6*b*)	0·28	0·25	0·27
			H(7*a*)	0·18	0·23	−0·32
			H(7*b*)	0·29	0·18	−0·23
			H(8*a*)	0·37	0·07	0·16
			H(8*b*)	0·34	−0·04	0·04
			H(9*a*)	0·17	−0·05	−0·18
			H(9*b*)	0·09	−0·12	−0·05
			H(10*a*)	0·15	0·00	0·40
			H(10*b*)	0·03	0·03	0·33
			H(11*a*)	0·22	0·38	0·03
			H(11*b*)	0·17	0·49	−0·04

The H positions calculated for $MnSO_4.4H_2O$ deviate on the average by as much as 0·2 Å from the corresponding neutron-diffraction values given by Bauer (1964) for $MgSO_4.4H_2O$, which is isostructural with $MnSO_4.4H_2O$. The n.m.r. vectors given for $MgS_2O_3.6H_2O$ appear to disagree with the hydrogen-bonding scheme suggested by the X-ray investigators (Nardelli, Fava & Giraldi, 1962). Both these compounds have been reexamined in this laboratory. The resonance component lines for $MnSO_4.4H_2O$ appear to be rather wide providing no room for improvement over the measurements made by Rao. However, the n.m.r. results for $MgS_2O_3.6H_2O$ appear to be in excellent agreement with the predictions of Nardelli *et al.* (1962).

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Refinement of the structure of diaquobisglycinatonickel(II), $Ni(NH_2CH_2COO)_2(OH_2)_2$.

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The structure of diaquobisglycinatonickel(II), determined by Stosick (*J. Amer. Chem. Soc.* (1945) **67**, 365) from three projections, has been refined with use of three-dimensional data. The metal–donor bond-lengths are Ni–N(amino) 2·08 Å, Ni–O(carboxyl) 2·06 Å, Ni–O(water) 2·10 Å, and the angle N(amino)–Ni–O(carboxyl) is 81·1°.

The structure of diaquobisglycinatonickel(II) was determined by Stosick (1945) from three incompletely resolved projections. In order to obtain accurate values of bond lengths and angles for subsequent comparison with the dimensions of nickel–peptide complexes, the structure has been reinvestigated with three-dimensional data.

The cell data are shown in Table 1. The unit-cell dimensions were determined from 104 values of θ between 58° and 81°, measured on $h0l$ and $hk0$ Weissenberg photographs calibrated with aluminum powder lines. The cell parameters were refined in ten cycles of non-linear least-squares as functions of $\sin^2\theta$. The density was determined by flotation.

Table 1. *Crystal data*

$C_4H_{12}O_6N_2Ni$ F.W. 242·7

Monoclinic. $a=7{\cdot}625(5)$, $b=6{\cdot}596(5)$, $c=9{\cdot}670(5)$ Å, $\beta=116{\cdot}57(1)°$, $U=435{\cdot}0$ Å^3. $D_m=1{\cdot}86$, $D_x=1{\cdot}85$ g.cm^{-3}, $Z=2$. $\lambda(\text{Cu } K\alpha_1)=1{\cdot}5405$ Å, $\lambda(\text{Cu } K\alpha_2)=1{\cdot}5443$ Å, $a(\text{Al})=4{\cdot}04925$ Å, $\mu=34$ cm^{-1}. Space group $P2_1/c$ from systematic absences ($0k0$ absent for $k=2n+1$, $h0l$ absent for $l=2n+1$).