Ligand Hyperfine Interaction in the Complex $[Mn(H_2O)_6]^{++}$ in $La_2(Mg, Mn)_3(NO_3)_{12} \cdot 24\,H_2O$

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The elements of the hyperfine interaction (h.f.i.) between the manganese ion and the protons in the complex $[Mn(H_2O)_6]^{++}$ in one of the two possible sites in $La_2(Mg, Mn)_3(NO_3)_{12} \cdot 24\,H_2O$ have been measured with ENDOR at 15 to 20 K. The six water molecules in the complex at the chosen site are equivalent for reasons of symmetry.

One principal direction of the h.f.i. tensor of each proton is found to be perpendicular to the Mn, O line. With the assumption that each proton is located in the plane of the other two principal directions of its interaction tensor the positions of the protons are evaluated from the anisotropic parts of the h.f.i. tensors. In this calculation the effect of covalency on the anisotropic h.f.i. is accounted for with the aid of a simple model.

The isotropic h.f.i.'s with the two protons of a water molecule appear to be very nearly equal (+0.890 MHz for both). This latter result is remarkable in view of the fact that one proton is distinctly nearer to the manganese ion than the other.

The covalent character of the bonds between the manganese ion and the surrounding water molecules in the complex $[Mn(H_2O)_6]^{++}$ has been studied by various authors with optical methods[1, 2]. By considering the energy of the $^4A_{1g}$ and the ^4E_g levels of the manganese ion with respect to its ground level an intermixing of the manganese and water orbitals by an amount of 5 to 10% could be estimated. Additional evidence for the existence of covalency in a complex can be obtained from the magnetic hyperfine interaction (h.f.i.) between the paramagnetic ion and the nuclei of the ligands[3]. If the metal to ligand bond in the complex $[Mn(H_2O)_6]^{++}$ would be completely ionic the isotropic part of the h.f.i. would be weak (of the order of 1 kHz, see section III). Furthermore the manganese ion would behave as a magnetic point dipole located at the position of its nucleus as far as the anisotropic h.f.i. with the protons is concerned[4] (point dipole model). However, if covalency is present the unpaired manganese electrons are spread over the complex which results in an enhancement of the isotropic h.f.i. and also makes the point dipole model just mentioned invalid. Thus the fact that the isotropic h.f.i. between the manganese ion and the protons in the complex $[Mn(H_2O)_6]^{++}$ — in an aqueous solution — is as high as 0.79 ± 0.03 MHz[5] supports the conclusion drawn from the optical data. The figure just mentioned has been determined by Sprinz[5] from proton relaxation measurements with protons in water contaminated with manganese ions. Details about the anisotropic h.f.i. and the sign of the isotropic h.f.i. could not be obtained with this method.

The present paper concerns the determination and the discussion of the complete tensors of the h.f.i. between the manganese ion and the protons in the complex $[Mn(H_2O)_6]^{++}$, incorporated in a single crystal of $La_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$. The measurements were carried out with the ENDOR technique in the temperature region of 15 to 20 K. An advantage of using a solid host is that a possible dependence of the covalency effects on the orientation of the water molecules can be determined by choosing various types of crystals. So far we have investigated one complex having six equivalent water molecules so that only the difference between the isotropic h.f.i.'s with the two protons within a water molecule could be studied. As the coordinates of the protons in our crystal were not known precisely, they had to be evaluated from the ENDOR data. For this purpose we introduced a simple model that enabled us to correct the anisotropic part for the invalidity of the point dipole model.

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In the next sections the following subjects are treated. Details about the mounting of the sample and the accuracy of the orientation of the crystal axes with respect to the magnetic field are given in section I. In section II various aspects of the evaluation of the ENDOR data are dealt with. The principal values of the tensors are given, along with the direction cosines of the principal axes. The isotropic h.f.i. constants of the two protons in a water molecule appear to be equal within experimental accuracy, while the principle values of the anisotropic part of the h.f.i. indicate that the point dipole model is not quite correct. In section III the coordinates of the protons are calculated and the result is used for a discussion of the isotropic h.f.i.

I. Experimental

The measurements were carried out with the aid of a home made X-band ENDOR spectrometer. The frequency range of the RF oscillator and power amplifier is 4 to 28 MHz; ENDOR lines outside this range were ignored. The temperature of the sample was adjusted to the region of 15 to 20 K, by passing cold helium gas through the cavity. Details about the method of producing the ENDOR signals have been published elsewhere [6, 7] and are therefore not treated here. As host crystal for the complex $[\mathrm{Mn(H_2O)_6}]^{++}$ we used $\mathrm{La_2Mg_3(NO_3)_{12} \cdot 24\, H_2O}$. In this substance the manganese ions can occupy the magnesium sites. There are two different sites denoted by I and II, each one being surrounded by six water molecules that form a complex with the metal ion. Site I possesses trigonal as well as inversion symmetry, site II has only trigonal symmetry; the trigonal symmetry axes of the sites coincide with that of the crystal. In this paper we consider only site I which has but two inequivalent protons, H1W1 and H2W1 [8]. The ratio of the numbers of manganese and magnesium ions in the solution from which the crystals were grown was 1 : 3000.

The samples were glued to a quartz rod that could be rotated during the measurements. In all measurements the trigonal (c) axis was either parallel or perpendicular to the applied static magnetic field $\boldsymbol{H}$. The appropriate orientation of the sample with respect to the quartz rod could be adjusted to within $\pm 0.3^\circ$ with the aid of a polarization microscope.

In the cases where the c axis was parallel to $\boldsymbol{H}$ the remaining misorientation could be eliminated by fine adjustment of the direction of the axis of the quartz rod. A criterion for the right orientation was the coincidence of three ENDOR peaks because of the trigonal symmetry. In the perpendicular cases ($c \perp \boldsymbol{H}$) the effect of a misorientation was eliminated by averaging the ENDOR frequencies measured at the six equivalent (due to trigonal and inversion symmetry) positions of the sample with respect to $\boldsymbol{H}$. This procedure also enabled us to determine the actual misorientation of the sample with respect to the rotation axis and the angle between this axis and a plane perpendicular to $\boldsymbol{H}$. A typical value of the latter angle is 0.10 to 0.15 degrees.

For each proton the measurements with $c \perp \boldsymbol{H}$ were carried out at two different values of the angle between the a axis of the crystal and $\boldsymbol{H}$. These positions were 15° and 105° away from the angle where the ENDOR frequency was maximal for the electronic spin ($S = 5/2$) in the state $M = -3/2$. As mentioned earlier the ENDOR frequencies at angles which follow from the above ones by adding multiples of 60° were also measured. Overlapping ENDOR lines were not used as a rule.

II. Evaluation of the h.f.i. Tensors

The Hamiltonian used for the interpretation of the ENDOR data is:

$$\mathcal{H} = g\,\beta\,\boldsymbol{S}\cdot\boldsymbol{H} + \boldsymbol{S}\cdot\widetilde{D}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\widetilde{A}_J\cdot\boldsymbol{J} - g_\mathrm{p}\,\beta_\mathrm{p}\,\boldsymbol{I}\cdot\boldsymbol{H} + \boldsymbol{S}\cdot\widetilde{A}\cdot\boldsymbol{I}\,, \qquad (1)$$

in which the five terms are the electron Zeeman interaction, the interaction with the axial crystal field, the h.f.i. with the manganese nucleus, the proton Zeeman interaction and the h.f.i. with a ligand proton respectively ($S = 5/2$, $J = 5/2$, $I = 1/2$). The principal elements of $\widetilde{D}$ und $\widetilde{A}_J$ expressed in units of $10^{-4}\,\mathrm{cm}^{-1}$ are $(1/3,\ 1/3,\ -2/3) \times 220$ and $(-90.2,\ -90.2,\ -90.4)$ respectively, while $g = 2.001$ [9]. The last two terms are of the same order

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of magnitude if the proton belongs to a nearest neighbour of the manganese ion; they are three orders of magnitude smaller than the electron Zeeman interaction. The proton h.f.i. tensor $\widetilde{A}$ was supposed to be symmetric.

For the three orientations of the crystal mentioned in section I the electron spin $\mathbf{S}$ is quantized along $\mathbf{H}$. In the first step of the calculation all parts of the Hamiltonian containing S_x and S_y, the components of $\mathbf{S}$ perpendicular to $\mathbf{H}$, were ignored. With this simplification the ENDOR frequency is equal to

$$\nu = h^{-1} g_{\mathrm{p}} \beta_{\mathrm{p}} \{H - M H_{\|})^2 + M^2 H_{\perp}^2\}^{1/2}, \qquad (2)$$

where

$$H_{\|} = A_{zz}/g_{\mathrm{p}} \beta_{\mathrm{p}}\,, H_{\perp}^2 = (A_{xz}^2 + A_{yz}^2)/(g_{\mathrm{p}} \beta_{\mathrm{p}})^2,$$

M is the electronic magnetic quantum number and the z axis is directed along $\mathbf{H}$. Conversely, $H_{\|}$ and $H_{\perp}^2$ can be evaluated from the two ENDOR frequencies ν_1 and ν_2, belonging to M_1 and M_2 and measured at $H = H_1$ and $H = H_2$ respectively:

$$H_{\|} = \frac{1}{2 M_1 M_2} \left[M_2 H_1 + M_1 H_2 - \frac{h^2 (M_2^2 \nu_1^2 - M_1^2 \nu_2^2)}{g_{\mathrm{p}}^2 \beta_{\mathrm{p}}^2 (M_2 H_1 - M_1 H_2)} \right] \qquad (3\,\mathrm{a})$$

and

$$H_{\perp}^2 = \frac{-1}{4 M_1^2 M_2^2} \left[(M_1 H_2 - M_2 H_1)^2 + \left(\frac{h^2 (M_2^2 \nu_1^2 - M_1^2 \nu_2^2)}{g_{\mathrm{p}}^2 \beta_{\mathrm{p}}^2 (M_2 H_1 - M_1 H_2)} \right)^2 \right] + \frac{h^2}{g_{\mathrm{p}}^2 \beta_{\mathrm{p}}^2} \left(\frac{\nu_1^2}{2 M_1^2} + \frac{\nu_2^2}{2 M_2^2} \right). \qquad (3\,\mathrm{b})$$

After this the ignored components containing S_x and S_y in the second and third term of $\mathcal{H}$ were considered. These operators mix the eigenstates $|M\rangle$ of the simplified Hamiltonian which results in a small change of the quantities M_1 and M_2 mentioned above. The correct eigenstates were determined by diagonalization of the Hamiltonian consisting of the first three terms (S_x and S_y included) in (1). Then M_1 and M_2 were reevaluated by calculating the expectation values of S_z in the new eigenstates, and the result was substituted again in the Eqs. (3 a) and (3 b). With this procedure the effect of the state of the manganese nucleus appeared to be effectively accounted for.

Subsequently approximate values of the tensor elements were determined from the quantities $H_{\|}$ and $H_{\perp}^2$ thus obtained for the three mutually perpendicular orientations of the crystal mentioned in section I. The signs of the nondiagonal elements followed from a comparison with the tensor calculated on the basis of the point dipole model using approximate proton positions.

Finally the ignored components of the fifth term in $\mathcal{H}$ containing S_x and S_y were accounted for. Using the approximate values obtained in the preceeding stage the shift of the theoretical ENDOR frequency due to these components was evaluated with a second order perturbation calculation (S_x and S_y containing components in the second and third term in $\mathcal{H}$ excluded). This shift amounted to 10 kHz at most, the magnitude being smallest for the maximum value of $|M|$. The measured ENDOR frequency was corrected for this effect and again substituted into (3 a) and (3 b) together with the expectation values mentioned above.

Summarizing, the final values of $H_{\|}$ and $H_{\perp}^2$ were obtained from Eqs. (3 a) and (3 b) after replacing M_1 and M_2 by the proper expectation values of S_z and substracting a second order shift from the measured ENDOR frequencies ν_1 and ν_2.

The final diagonalized h.f.i. tensors for H1W1 and H2W1 are listed in Table 1, along with the direction cosines of the principal axes, expressed in

		$n_{x'}$	$n_{y'}$	$n_{z'}$
	H1 W1			
A_1	-2.716 ± 0.012	$+0.329 \pm 0.014$	-0.782 ± 0.007	-0.530 ± 0.003
A_2	-2.411 ± 0.012	$+0.714 \pm 0.011$	$+0.572 \pm 0.013$	-0.403 ± 0.005
A_3	$+7.796 \pm 0.004$	$+0.618 \pm 0.003$	-0.246 ± 0.006	$+0.746 \pm 0.001$
	H2 W1			
A_1	-2.840 ± 0.013	-0.023 ± 0.046	$+0.998 \pm 0.017$	$+0.064 \pm 0.126$
A_2	-2.580 ± 0.019	-0.298 ± 0.015	-0.068 ± 0.127	$+0.952 \pm 0.013$
A_3	$+8.089 \pm 0.008$	$+0.955 \pm 0.001$	$+0.002 \pm 0.010$	$+0.298 \pm 0.002$

Table 1. Principal values expressed in MHz and direction cosines of the principal axes of the h.f.i. tensors of two protons in the same water molecule in the complex $[\mathrm{Mn(H_2O)_6}]^{++}$ at site I in $\mathrm{La_2(Mg,Mn)_3(NO_3)_{12} \cdot 24\,H_2O}$. The x' and z' axes concide with the a axis and c axis respectively. The y' axis is perpendicular to these axes such that a right-handed reference frame is formed.

a crystal reference frame. The z' and x' axes are parallel to the c axis and a axis respectively; the y' axis is directed such that an orthogonal right-handed reference frame is formed. The isotropic interactions are

$$A_i = +(0.890 \pm 0.002)\,\mathrm{MHz} \quad \text{for H1W1},$$

and $A_i = +(0.890 \pm 0.003)\,\mathrm{MHz}$ for H2W1.

For $c \parallel \boldsymbol{H}$ about sixty different pairs of ENDOR lines were used for each proton; for $c \perp \boldsymbol{H}$ this number was about 25 per direction. The pairs were always chosen such that $|M_2 H_1 - M_1 H_2| > 1$ kOe and the fraction between the parentheses in Eq. (3 a) smaller than about 2 kOe, in order to increase the accuracy of the results. The errors were calculated directly from the standard deviations of $H_{\parallel}$ and $H_{\perp}^2$.

III. Discussion

In this section the positions of the protons in the complex are derived from the h.f.i. tensors and then the isotropic part of the h.f.i. is considered. The positions of the ions in the isomorphic salt $\mathrm{Ce_2Mg_3(NO_3)_{12} \cdot 24\,H_2O}$ have been determined at room temperature by means of X-ray diffraction [8]. Since the coordinates of the protons are not very accurate, they had to be evaluated from the ENDOR data. In this calculation the positions of the protons with respect to the oxygen ion had to be known in order to account for a small covalency effect (see below). However, since the manganese ion is greater than the magnesium ion by about 0.15 Å [10] the oxygen coordinates of the complex at site I could not be taken from ref. [8] without applying a correction. In our model the distance from the centre of the complex to the oxygen ion was increased along the original Mg,O vector as given in ref. [8] to $r_0 = 2.20$ Å (see below).

The angles between the Mn,O vector and the principal axes are listed in Table 2. As a first approximation we assumed each proton to be located on the principal axis belonging to the highest eigenvalue (A_3) of the tensor. It followed then that for each proton two principal axes lie approximately in the corresponding Mn,O,H plane, the third one being nearly perpendicular to it. This is what one would have expected on the basis of an elementary physical consideration. As the acute angle between the two A_1 axes is 35° the manganese ion does not lie in the plane of the water molecule.

	A_1	A_2	A_3
H1 W1	90° ± 1°	72° ± 1°	17.8° ± 0.5°
H2 W1	92° ± 2°	71° ± 2°	18.9° ± 0.4°

Table 2. Angles between the principal axes of the h.f.i. tensors of two protons in the same water molecule in the complex $[\mathrm{Mn(H_2O)_6}]^{++}$ and the Mn, O vector at site I in $\mathrm{La_2(Mg,Mn)_3(NO_3)_{12} \cdot 24\,H_2O}$.

If we ignore momentarily that the difference between the A_1 and A_2 principal values indicates that the point dipole model is not quite correct, the manganese — proton distances r_{H} can be derived with the formula

$$r_{\mathrm{H}}^3 = g\,\beta\,g_{\mathrm{p}}\,\beta_{\mathrm{p}} / (2\,\pi\,\mu_0\,A_3)\,, \tag{1}$$

where g and g_{p} are the electronic and nuclear g factors (proton) and β and β_{p} the Bohr and the nuclear magnetons respectively. This procedure yields $r_{\mathrm{H}} = 2.84$ Å for H1W1 and $r_{\mathrm{H}} = 2.81$ Å for H2W1, which is a reasonable result when compared with $r_{\mathrm{H}} = (2.80 \pm 0.07)$ Å found by PFEIFER [11] from proton relaxation in water contaminated with manganese ions. According to HAUSSER and NOACK r_{H} is equal to 2.90 Å [12] in an aqueous solution.

The proton-proton distance l_{pp} following from the above values of r_{H} and the angle between the A_3 axes is 1.73 Å. When compared with $l_{\mathrm{pp}} = (1.58 \pm 0.02)$ Å found by SERRA et al. [13] for $\mathrm{La_2Mg_3(NO_3)_{12} \cdot 24\,H_2O}$ by means of NMR at room temperature, this value seems to be somewhat high. However, if we introduce a simple model to account for the effect of covalency on the anisotropic h.f.i. a better value is found. The essence of the model is that the magnetic point dipole originally located at the manganese ion (in the point dipole model) is partly transferred to the positions of the six oxygen nuclei. The situation is given in Fig. 1. Only one water molecule is drawn, the Mn, O, $\mathrm{H_1}$ plane coinciding with the y'', z'' plane. We consider now the proton located on the z'' axis. The anisotropic h.f.i. tensor $\widetilde{A}_a$ expressed in the x'', y'', z'' reference frame is

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$$\widetilde{A}_a = \frac{g\,\beta\, g_p\, \beta_p}{4\,\pi\,\mu_0}\left[\frac{1-6\,\delta}{r_H^3}\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{pmatrix} + \frac{\delta}{r_{OH}^3}\begin{pmatrix}-1 & 0 & 0\\ 0 & \frac{1}{2}(1-3\cos 2\,\vartheta) & -\frac{3}{2}\sin 2\,\vartheta\\ 0 & -\frac{3}{2}\sin 2\,\vartheta & \frac{1}{2}(1+3\cos 2\,\vartheta)\end{pmatrix}\right] \quad (2)$$

where δ is the amount of magnetism transferred to the oxygen ion, ϑ the angle between the z'' axis and the O, H_1 vector and r_{OH} the oxygen-proton distance. (The effect of the magnetism transferred to the other five oxygen ions was ignored.)

In the purely ionic model ($\delta = 0$) the A_1, A_2 and A_3 axes coincide with the x'', y'' and z'' axes respectively. If $\delta \neq 0$ and positive the A_3 axis is rotated about the x'' axis, away from the oxygen ion. It follows then that if δ has the proper sign, the proton-proton distance derived from the ENDOR data can be reduced by taking this covalency effect into account. The magnitude and sign of δ can be obtained by diagonalizing Eq. (2) and then equating it to the experimental tensors in Table 1. The manganese to oxygen distance r_O required for this calculation was assumed to be equal to 2.20 Å, as follows from the Pauling radii of the two ions[10]. A consequence of the model is of course that the values of δ obtained via the h.f.i.'s with the two protons in the same water molecule should be equal. This condition did not come true exactly, δ being equal to $+0.27 \times 10^{-2}$ for H1W1 and $+0.21 \times 10^{-2}$ for H2W1. This difference was not considered to be serious since the effect of the experimental errors is of the same order of magnitude and, moreover, the oxygen coordinates used by us may not be quite correct. Using the average value $\delta = +0.24 \times 10^{-2}$ and separating the experimental tensor into two parts according to Eq. (2), the proton coordinates given in Table 3 could finally be evaluated. The total amount of transferred magnetism following from the model is $6\,\delta = +1.4 \times 10^{-2}$, while the angle between the Mn, H vectors is decreased by about 3.6° resulting in a corrected proton-proton distance of 1.58 Å. The original "ionic" values of r_H were hardly affected in this model.

Summarizing the situation, the proton coordinates have been determined with the assumption that two axes of the h.f.i. tensor of each proton lie in the Mn, O, H plane. The effect of a small transfer of magnetism from the manganese ion to the oxygen ions due to covalency was taken into account by means of Eq. (2).

	x'	y'	z'
H1W1	1.82	−0.65	2.08
H2W1	2.65	0.00	0.92

Table 3. Coordinates expressed in Å of the protons H1W1 and H2W1 in the complex $[Mn(H_2O)_6]^{++}$ at site I in $La_2(Mg,Mn)_3(NO_3)_{12} \cdot 24\,H_2O$. See Table 1 for a description of the reference frame.

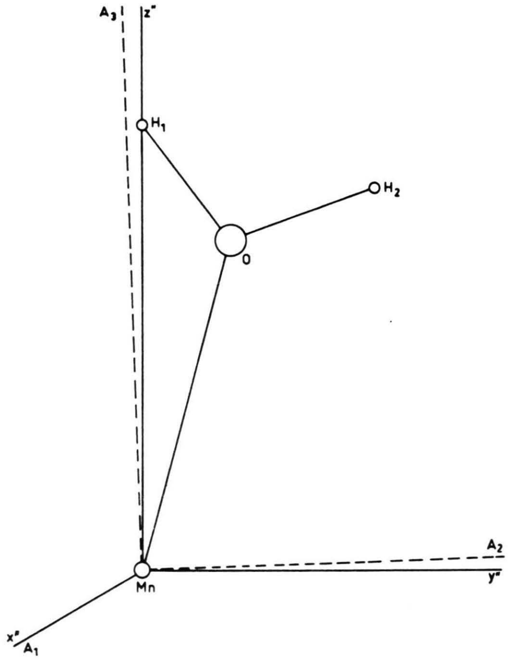

Fig. 1. The A_2 and A_3 principal h.f.i. axes of the proton on the z'' axis do not coincide with the y'' and z'' axes respectively when unpaired electrons are transferred from the manganese ion towards the oxygen ion.

The orientation of one of the water molecules in the complex is illustrated in Fig. 2, the (−1, 1, 1) direction in the chosen reference frame coinciding with the c axis of the crystal.

The positions of the other five water molecules follow from rotation about the c axis over 120° and 240° and inversion. According to ZALKIN et al.[8] H1W1 forms a hydrogen bond with a nearby water oxygen atom (OW4, not belonging to the complex) and H2W1 with a nitrate oxygen atom (ON12). It can be seen that the hydrogen atoms are drawn towards the ligands just mentioned (Fig. 2). In fact, the angle between the planes of OW1, H1W1, H2W1 and OW1, OW4, ON12 is only 13°. As a result of these interactions H2W1 is nearer to the manganese ion than H1W1 by about 0.03 Å, indicating a dis-

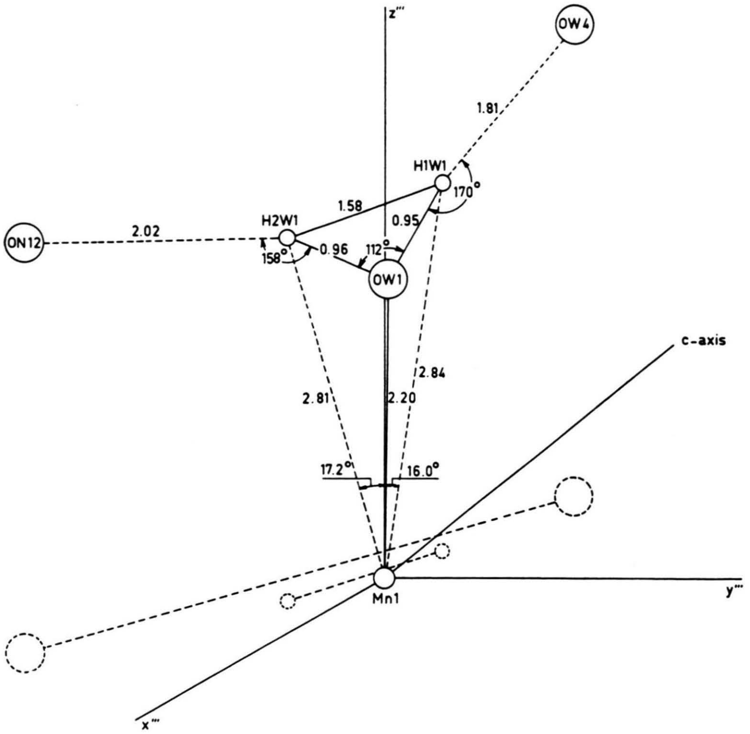

Fig. 2. Detail of the complex $[Mn(H_2O)_6]^{++}$ in $La_2(Mg,Mn)_3(NO_3)_{12} \cdot 24\,H_2O$ and two nearby oxygen ions with which hydrogen bonds are formed. The proton coordinates were determined with ENDOR. The other coordinates were taken from ref. [8] with a correction for OW1 for the greater size of Mn^{++} with respect to Mg^{++}. Also indicated, as dashed lines, are the projections of H1W1, H2W1, OW4 and ON12 on the x''', y''' plane. Distances are expressed in Å.

tinct dissimilarity between the two protons. In the free complex the water molecule would lie in the x''', z''' plane with the proton-proton vector parallel to the x''' axis [14–16].

Next we consider the isotropic h.f.i.. Using WATSON's wave functions [17] for the free manganese ion the theoretical magnitude of A_i for a proton at a distance of 2.80 Å is found to be of the order of 1 kHz. It follows from this that the magnitude of the experimental value of A_i (of the order of 1 MHz) indicates a partly covalent character of the bonds between the manganese ion and the water molecule. If we mix the manganese 3d orbitals with the water orbital that extends most towards the centre of the complex, namely $\Phi(3a_1)$ [18, 19], and set the covalency parameter $N^2 \lambda^2$ equal to 0.09 [2] the theoretical value of A_i is found to be $+0.4$ MHz, which is much nearer to reality.

However it follows from the remaining discrepancy that the situation is more complicated. In fact many more wave functions [18] should be involved in the mixing. Moreover, the difference between our value ($+0.89$ MHz) and that of SPRINZ (0.79 MHz) for the complex in an aqueous solution suggests that the environment of the complex and presumably also the orientation of the water molecule with respect to the axes of the complex influence the strength of the isotropic h.f.i..

It should be noted that although one proton of the water molecule is distinctly nearer to the manganese ion than the other, the isotropic interactions with the two protons are very nearly equal. We might conclude from this fact that in this particular case the water molecule has retained its mirror symmetry so that equal amounts of each hydrogen wave function are mixed with the manganese wave function regardless of the orientation of the water molecule. Unfortunately our determination of the proton coordinates with respect to those of the oxygen nucleus, which are not very precise themselves, is not accurate enough to consider this point any further.

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