

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

Antiferromagnetic Ordering and Electronic Structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as Determined from Nuclear Magnetic Resonance¹

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The nuclear magnetic resonance study of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by Poulis and Hardeman is coupled with neutron diffraction data on proton positions to obtain the type of antiferromagnetic ordering in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and the distribution of the odd-electron in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ "molecule." It is found that the odd-electron must be about 25% on each chlorine, 50% on copper. This distribution is consistent with a molecular orbital treatment of the complex, but not with crystal field theory or with Pauling's theory of directed valence in square copper complexes. The use of nuclear magnetic resonance in crystals as a probe for determining the distribution of magnetic electrons appears to be sensitive and deserving of further use.

Introduction

Recently Poulis and Hardeman (P and H) have examined proton magnetic resonance in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ down to very low temperatures, finding that below 4.3°K. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is antiferromagnetic.² By studying the proton resonance in single crystals both above and below the Néel point they have attempted to determine both the magnetic structure and the proton positions in this compound.² These problems are related since, in a paramagnetic or antiferromagnetic crystal, the magnetic field at the proton is a function of the crystal field as well as the external field.

The conclusions of P and H on the magnetic structure are shown in Fig. 1. The positions of copper, oxygen and chlorine were determined by Harker, using X-ray diffraction,³ which, of course, did not yield proton positions. In Fig. 1 the arrows give the spin arrangement inferred by P and H.

The proton positions of P and H are quite unsatisfactory, leading to O-H distances of 1.7 Å. within the water molecules, whereas positions determined by neutron diffraction yield O-H distances and HOH angles which are nearly the same as in free water molecules⁴ (0.97 Å. and 104.5°, respectively).⁵ Since, as noted above, the proton positions and antiferromagnetic ordering are related, it seems likely that the erroneous proton positions resulted from an erroneous magnetic structure.

In the subsequent sections of this paper using proton positions as obtained by Peterson and Levy,⁴ it is shown that the magnetic ordering suggested by P and H is unable to account for the field at the proton. A different magnetic ordering is next shown to be more consistent with the structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and, finally, taking the proton position and the magnetic ordering to be known, it is shown that the odd-electron in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is not localized on copper but is distributed over copper and chlorine sites. In an independent paper it is shown that

this electron distribution arises naturally from a molecular orbital treatment of square, planar copper complexes.⁶

Proton Magnetic Resonance and the Proton Position.—In a proton magnetic resonance experiment the energy difference between parallel and antiparallel arrangements of the proton magnetic moment in the field at the proton is measured. Under these circumstances the energy difference is proportional to the magnitude of the field at the proton, or

$$\Delta E = K |H| \quad (1)$$

In a magnetic substance, such as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, the local field at the proton is the vector sum of the external field, H_0 , and the crystal field, H_c , and since H_c depends upon the location of the electrons giving rise to the magnetic properties of the compound, proton resonance may yield information concerning electronic structure by serving as a measure of H_c .

In the antiferromagnetic region at low fields, $H_0 < 2000$ oersteds P and H have shown that the moments in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ point parallel and antiparallel to a , and this result seems certain although their exact arrangement of spins may be in error. Let the moment on the j th atom be μ_j . Then

$$H_0 = \sum_j -\text{grad} \frac{\mu_j \cdot r_j}{r_j^3} \quad (2)$$

where r_j is the vector from the j th atom to the proton in question. It follows that

$$H_{cx} = \sum_j \pm \mu_j \frac{[2(X - x_j)^2 - (Y - y_j)^2 - (Z - z_j)^2]}{r_j^5} \quad (3)$$

$$H_{cy} = 3 \sum_j \pm \mu_j \frac{(X - x_j)(Y - y_j)}{r_j^5} \quad (4)$$

$$H_{cz} = 3 \sum_j \pm \mu_j \frac{(X - x_j)(Z - z_j)}{r_j^5} \quad (5)$$

where H_{cx} , H_{cy} , H_{cz} are the components of H_c , and the sign of μ_j is positive or negative depending upon whether the moment on the j th atom is parallel or antiparallel to a . X , Y , Z are coordinates of the proton under consideration, and x_j , y_j , z_j are the coordinates of the j th atom. In the crystal there are many hydrogen positions, all related by symmetry, so that only one is unique.

For H_0 in the ab plane, $H_{0x} = H_0 \sin \alpha$ and $H_{0y} = H_0 \cos \alpha$ where α is the angle between b of the crys-

(6) R. E. Rundle and J. W. Richardson, presented at the Dallas Meeting of the A.C.S., April, 1955.

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(2) N. J. Poulis and G. E. G. Hardeman, *Physica*, **18**, 201 (1952); *J. chim. phys.*, **50**, C110 (1953).

(3) D. Harker, *Z. Krist.*, **93**, 136 (1936).

(4) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **26**, 220 (1957).

(5) Originally positions were inferred from infrared data and hydrogen bonding and were accurate enough to support the conclusions reported in Dallas.¹ Due, presumably, to large thermal vibration certain aspects of the polarized infrared data were misinterpreted [Rundle, Nakamoto and Richardson, *ibid.*, **23**, 2450 (1955)] and more accurate H positions are used in this revised paper.

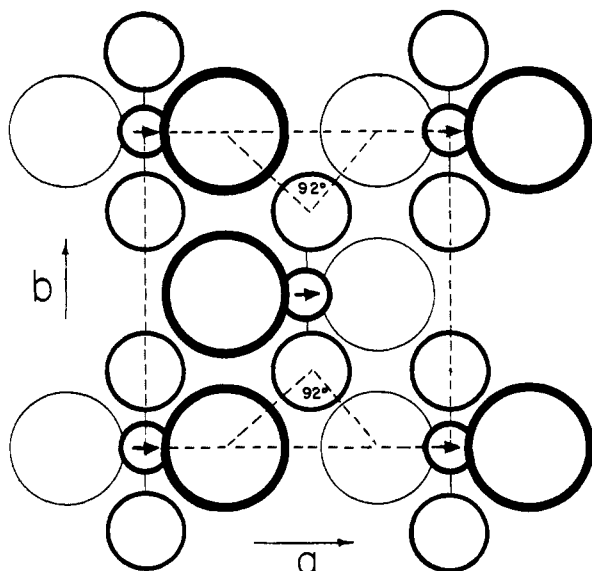


Fig. 1.—Structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Large circles are chlorine atoms, medium are oxygen atoms, small are copper atoms. Arrows show magnetic ordering on (001) as proposed by Poullis and Hardeman. Copper atoms in alternate planes have antiparallel moments.

tal and the external magnetic field vector \mathbf{H}_0 . Then $|H| = [(H_0 \sin \alpha + H_{c_x})^2 + (H_0 \cos \alpha + H_{c_y})^2 + H_{c_z}^2]^{1/2}$ (6)

The maximum energy difference between the parallel and antiparallel proton alignments will then occur at H_{\max} , and setting $\partial |H| / \partial \alpha = 0$

$$\tan \alpha_{ab_{\max}} = H_{c_x} / H_{c_y} \quad (7)'$$

where $\alpha_{ab_{\max}}$ is the direction of \mathbf{H}_0 which maximizes the proton resonance energy for \mathbf{H}_0 in the ab -plane. P and H have examined resonance in the ab plane, and find $\alpha_{ab_{\max}} = 56^\circ$.

To find H_{c_y} and H_{c_x} at the proton it is necessary to sum over the copper atoms. P and H summed over the nearest nine coppers which form a trigonal prism with the proton in question off-center within the prism. Convergence is not excellent, and we have summed over the nearest thirty copper atoms. This results in a correction of several per cent. It was found that for the known proton position the calculated $\alpha_{ab_{\max}}$ was $\sim 12^\circ$, far from that observed by P and H. In this stage of the calculation the magnetic ordering suggested by P and H, Fig. 1, was used, and it was assumed that the magnetic moment was localized on copper.

In another paper we show that localizing the odd-electron, responsible for the moment, upon copper cannot be justified⁶; consequently, the calculations were repeated with part of the moment on chlorine. Taking the moment on chlorine to be $\lambda \mu_{\text{Cu}}$, the magnetic ordering suggested by P and H produced negative values for λ . This is physically unacceptable since the moment of an electron shared between copper and chlorine should surely have the same orientation on both. A similar negative value

(7) These equations are equivalent to those of P and H except for some typographical errors.³

arose when the moment was delocalized onto oxygen and chlorine.

The Antiferromagnetic Ordering.—Having been satisfied that the suggested magnetic ordering is incorrect we have considered what to expect for magnetic ordering from the structure. Here it is to be noted that $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is unusual among known antiferromagnetic materials, in that the metal ions are not bridged together into a three-dimensional network. Along the C -axis of the crystal run chains, Fig. 2, with short (3.73 Å) copper-copper distances. Two oxygen and/or chlorine atoms separate each chain from its neighbors, and the Cu-Cu distance between chains is 5.5 Å. Hence, it seems unreasonable to expect super-exchange to cause the ordering except within the chains, where the spin arrangement along the chains should be alternate.

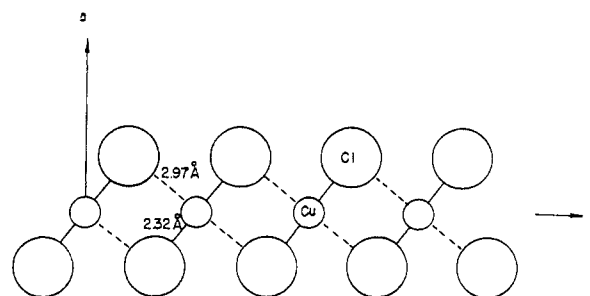


Fig. 2.— CuCl_2 chain in the hydrate. Water molecules lie above and below each chain, so that copper atoms in neighboring chains are well shielded from each other.

If it is correct that super-exchange is important only along the chains, it then seems likely that direct magnetic interaction among the chains is responsible for the rest of the ordering. Looking at the (001) face, the copper arrangement within the face is face-centered (Fig. 3). It is, then, easily seen that spin arrangement (A) (Fig. 3) is favored

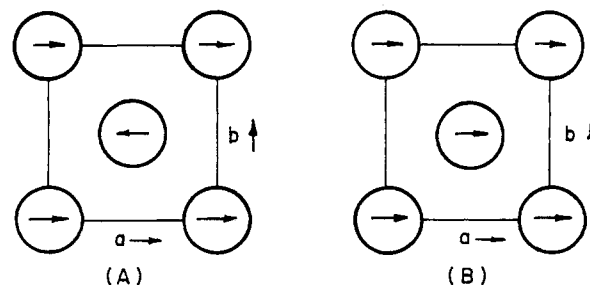


Fig. 3.—(A) is magnetic ordering proposed in this paper; (B) is the magnetic ordering of P and H. In both cases, alternate planes are antiparallel.

by magnetic interactions if an appreciable part of the moment is on chlorine, as seems likely, while B is the arrangement suggested by P and H. It is to be noted that the chains with alternating spins run normal to (001) , and in proposing arrangement (A) we are proposing not that direct magnetic interactions of spins cause antiferromagnetic ordering, but that whole chains of already ordered spin-moments interact magnetically to cause the three-dimensional magnetic ordering.

Electron Distribution in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.—The proton position and magnetic arrangement (A), Fig. 3, still will not explain the proton resonance data of P and H if all the magnetic moment is centered on copper. (A calculation of α_{max} for this case yielded $\sim 80^\circ$ vs. 56° observed.) It is necessary, therefore, to again consider whether the odd-electron is also distributed over chlorine positions. To do this we have considered that the moment on copper is μ , while that on chlorine is $\lambda\mu$, and have carried out the sums in equations 3 and 4 over the nearest thirty coppers and the nearest forty-four chlorine atoms, assuming the magnetic ordering (A) above. For this model, equation 7, above, yields $\lambda = 0.55$, whence the odd-electron distribution is approximately 26% on each chlorine, 48% on copper.

The magnetic electron might well be distributed over oxygens and chlorines, but unfortunately the data do not allow determination of the amounts on each separately. One can, however, check what the distribution would have to be to satisfy α_{max} (antiferromagnetic) if the odd-electron were distributed *equally* on oxygen and chlorine. The result, 2.5% on *each* oxygen and chlorine, 90% on copper, is strikingly different and shows how sensitive the field at the proton is to any magnetic moment on the very near oxygen.

The two distributions, above, might be taken as extremes, and the real distribution might well be intermediate. However, it can be demonstrated from the data of P and H in the paramagnetic range² that the former is more nearly correct than the latter.

Neutron Resonance in the Paramagnetic Region.—In the paramagnetic case, proceeding as before, but assuming that on the average field and proton moment are parallel, it is found that

$$\tan 2\alpha_{\text{max}} = \frac{-2\sum_j (X - x_j)(Y - y_j)/r^5}{\sum_j (X - x_j)^2 - (Y - y_j)^2/r^5} \quad (8)$$

In this case the calculated value of α_{max} is almost independent of the amount of the magnetic electron on chlorine; α_{max} is $26^\circ 45'$ for the moment localized on copper, $27^\circ 17'$ if it is distributed 26% on each chlorine, 48% on copper. Both values are probably within the limits of error of the value of about 25° observed by P and H.²

The value for α_{max} (paramagnetic) is, however, very sensitive to any moment on oxygen. A 2.5% contribution on oxygens and chlorines raises the calculated value of α_{max} to $32^\circ 35'$. Hence, agreement with the observed value of α_{max} (paramagnetic) is lowered by putting any amount of the odd-electron onto oxygen.

It seems reasonable to assume that the observed value of α_{max} may be in error by several degrees. (P and H gave no estimate of their error in mounting the crystals, etc.). Setting an upper limit upon α_{max} (paramagnetic) of 29° , the maximum allowable part of the magnetic electron on each oxygen is 0.008. Using this value, and solving for λ_{Cl} in the antiferromagnetic case, it is found that $\lambda = 0.63$

and the magnetic electron distribution is 0.44 on Cu, 0.27 on each Cl, almost identical with that found by ignoring the oxygen contribution. (The influence of the moment on the oxygens changes sign and becomes exceedingly important in the antiferromagnetic case only for somewhat higher distributions onto the oxygens.) Hence, it appears that to fit both the antiferromagnetic and the paramagnetic data the magnetic electron must be about 25% on each chlorine, 50% on copper, and less than 1% on each oxygen.

Discussion

The result above requires that the odd-electron in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ be in a molecular rather than a copper orbital, and almost certainly in an antibonding orbital. For the case of a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ molecule with D_{2h} symmetry, $3d_{x^2-y^2}$, $3d_{z^2}$, and $4s$ of the metal, and $(\sigma_{\text{Cl}_I} + \sigma_{\text{Cl}_{II}})$ and $(\sigma_{\text{O}_I} + \sigma_{\text{O}_{II}})$ all belong to a_{1g} . However, by analogy with the square planar case the antibonding level occupied by the odd-electron probably consists largely of an admixture of the $3d_{x^2-y^2}$ of copper and the σ -ligand levels. The strong mixing in the antibonding level suggests a similar strong mixing in the corresponding bonding level.

These results are clearly incompatible with crystal field theory, where the odd-electron is assumed to be localized in a $3d$ -orbital of copper, or with Pauling's theory of directed valence, where the odd-electron is localized in a $4p$ -orbital of copper. They are, however, in keeping with other recent work where quite generally magnetic electrons of transition metal complexes are found to occupy antibonding molecular orbitals rather than localized metal orbitals.⁸

It is to be noted that the conclusions reached here relative to magnetic ordering and odd-electron distribution are, in principle, and probably in fact, subject to check by neutron diffraction. It is hoped that studies along these lines will be possible in spite of the very low temperature required for the neutron diffraction work.

Finally, the method employed, of using a nucleus with spin as a probe for the magnetic field within a magnetic crystal, appears to give a sensitive method for discovering the magnetic electron distribution within the crystal. The interpretation of the experimental results appears to be straightforward when the crystal structure is known, and the method appears to deserve wide use.

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(8) J. H. E. Griffiths and J. Owens, *Proc. Roy. Soc. (London)*, **A226**, 6 (1954); K. W. H. Stevens, *ibid.*, **A129**, 542 (1953); J. Owens and K. Stevens, *Nature*, **171**, 836 (1953); M. Tinkham, *Proc. Roy. Soc. (London)*, **A236**, 535, 549 (1956). For other work on copper compounds see R. B. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956), and J. E. Bennett and D. J. E. Ingram, *Phil. Mag.*, [8] **1**, 970 (1956).