

HYPERFINE AND SUPER-EXCHANGE INTERACTIONS IN $M_2CuX_4 \cdot 2H_2O$ COMPOUNDS

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The ground state of the magnetic copper ion and the transfer of unpaired spin to the ligands is described taking into account the influence of the crystalline field and the partly covalent bonding with three inequivalent pairs of ligands. Experimentally determined (super) hyperfine interactions of all nuclei, electronic g tensor and crystal field parameters form the data on which the analysis of the covalency is based. A discussion of the super-exchange mechanisms and exchange paths in these compounds is given. From this analysis the nearest-neighbour exchange interactions are estimated in close agreement with experimental values.

1. Introduction

It is well known that in isolating compounds the forces that hold the ions together are not purely ionic. Convincing experimental evidence has been found for the presence of covalent bonding, even in the most "ionic" type of compounds. For the description of the effects of this—usually small—covalency two different approaches are commonly used. The first is the so-called molecular orbital (MO) method, in which the atomic orbitals of two (or more) ions are admixed to obtain one-electron orbitals for the whole molecule. The second method is the configuration interaction (CI) approach in which a combination is formed of the original ionic configuration with excited configurations in which one or more electrons are transferred. Both methods, MO and CI, are equivalent as long as no approximations are made.

The obvious reason for the occurrence of covalent bonding is the possibility to lower the electrostatic energy of the molecule as a whole by the redistribution of the electronic charges. A microscopic quantity sensitive for charge distribution is the nuclear electric quadrupolar interaction. For instance, the deuterium quadrupolar interaction can be used to determine the charge transfer over a hydrogen bridge. In fact in that case the CI description has been applied successfully.

In the present paper we deal with the impact of

covalent bonding on the magnetic properties of the $M_2CuX_4 \cdot 2H_2O$ compounds where MX stands for KCl, NH_4Cl , RbCl, CsCl, NH_4Br and RbBr. These include copper and ligand magnetic hyperfine interactions and the superexchange coupling between neighbouring copper ions. The general arrangement of this paper is as follows. We start with the presentation of all experimental data that will be used in this paper. In section 4 the molecular orbital approach is shortly outlined in order to introduce a number of useful quantities. Next the magnetic ground state of the copper ion is described for a tetragonal crystal field with rhombic distortion and expressions that include the covalency effects are derived for the electronic g tensor and nuclear hyperfine tensor. These are fitted to the experimental data. In section 6 the ligand hyperfine interactions are analysed to calculate the strength of the covalent bondings and thus the amount of electron transfer. Finally, the information then gathered concerning the electronic structure of the copper octahedron is used to discuss the super-exchange interaction between nearest-neighbour copper ions.

2. Crystallographic structure, g values and crystal field splitting

The crystals with the $K_2CuCl_4 \cdot 2H_2O$ structure have tetragonal symmetry with space group $P4_2/mnm$.

In fig. 1 the unit cell of $K_2CuCl_4 \cdot 2H_2O$ as determined by neutron diffraction [1] is shown. The unit cell contains two formula units, related to each other by a 4_2 axis parallel to the c axis. The copper ion at $(0,0,0)$ has a six coordination (D_{2h} -symmetry). The distorted octahedral surrounding consists of two strongly

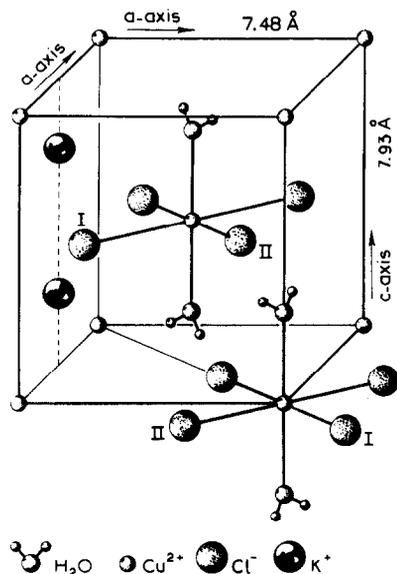


Fig. 1. Crystal structure of $K_2CuCl_4 \cdot 2H_2O$.

bonded halide X(II) ions at $\pm(0.21, 0.21, 0)$, two weakly bonded halide X(I) ions at $\pm(0.27, -0.27, 0)$ and two water molecules with the oxygen ions situated at $\pm(0, 0, 0.25)$. The protons at $\pm(0.07, 0.07, \pm 0.31)$ form hydrogen bridges with the X(I) ions belonging to the nearest-neighbour copper octahedra. A convenient definition of the direction of principal axes of interaction tensors of the nuclei belonging to an octahedron is obtained by denoting the Cu–X(I) direction by γ and the Cu–X(II) direction by γ' (see fig. 3).

The g tensors of two copper neighbours are related to each other through a rotation over 90° about the c axis. So in general in an ESR experiment one expects to observe two electron resonance lines when the external field rotates in the a – a plane. However, due to the exchange interaction J_1 between nearest-neighbour ions the two resonance lines coalesce if $2J_1 \gtrsim |\Delta g| \mu_B H_0$, where Δg is the difference in g value between the two copper ions for the given direction of the external field H_0 .

Only on $K_2CuCl_4 \cdot 2H_2O$ a number of high-frequency ESR experiments at different temperatures has been reported. The most important are those reported by Okuda et al. [2], Kennedy et al. [3] and Henderson et al. [4]. At high temperatures ($T > 250$ K) for frequencies above 30 GHz they observe two resonance lines for the magnetic field along the $[110]$ direction. To lower temperatures and/or lower frequencies these two lines coalesce. The results on the g values at high temperature and high frequency are $g_\gamma = 2.34$, $g_{\gamma'} = 2.11$ and $g_c = 2.06$. The amalgamated g value in the a – a plane is found to be $g_a = \frac{1}{2}(g_\gamma + g_{\gamma'})$, independent of temperature and frequency. On the contrary, a small frequency dependence of the value of g_c is reported by Henderson et al. [4]. This effect is related to the well known “10/3 effect” in the linewidth and can be described well with the formalism of Kubo and Tomita [5].

Onderwaater et al. [6] have measured the value of g_c and of the amalgamated g_a at a frequency of 9.5 GHz for all six compounds at liquid-nitrogen temperatures. We have corrected the apparent g_c value for the above mentioned frequency dependence. On the basis of the results given in refs. 5 and 6 we estimate that in these compounds at $\nu = 9.5$ GHz and $T = 77$ K this correction is given by $g_c^{\text{exp}} - g_c^{\text{true}} = \delta(a^2 c J_1)^{-1}$ with $\delta = 1.3 \text{ \AA}^3 \text{ K}$, a and c the unit cell dimensions and J_1 the nearest-neighbour exchange interaction constant. The corrected g values are given in table I.

In table I also the data on the crystal field splittings are given as determined by Haeck of our laboratory [7]. The E values have been obtained from single crystal near-infrared spectra at $T = 5$ K using polarized light. Only in the two ammonium compounds all three E values could be determined separately. In the other four compounds two lines coalesce. The difference $|E_{yz} - E_{zx}|$ is estimated to be less than $0.1 \times 10^3 \text{ cm}^{-1}$ in these four compounds.

3. (Super)hyperfine interaction parameters

An extensive description of the NMR spectra observed in the $M_2CuX_4 \cdot 2H_2O$ has been given in previous papers [8–18]. In the mentioned references also a number of methods has been reviewed which are needed to derive the various interaction parameters from the observed spectra. The here presented values

Table I
Electronic g values, crystal field splittings and critical temperatures T_c

MX	KCl	NH ₄ Cl	RbCl	CsCl	NH ₄ Br	RbBr
g_c	2.047	2.043	2.046	2.043	2.039	2.041
g_a	2.223	2.219	2.217	2.210	2.193	2.193
E_{xy} (10^3 cm ⁻¹)	11.04	11.24	11.43	10.96	11.26	11.39
E_{yz} (10^3 cm ⁻¹)	13.14	12.85	13.07	13.07	12.74	13.16
E_{zx} (10^3 cm ⁻¹)	13.14	13.22	13.07	13.07	13.11	13.16
T_c (K)	0.877	0.701	1.017	0.752	1.836	1.874

Table II
Interaction parameters of the ⁶³Cu, ³⁵Cl, ⁷⁹Br, ¹⁷O, ³⁹K, ⁸⁷Rb, ¹³³Cs and ¹H, ²H nuclei in the $M_2CuX_4 \cdot 2H_2O$ compounds. The values for ν_Q and F_{ij} are in MHz. The indices x, y, z refer to the principal directions of the electric field gradient, indicated in the third column (see also fig. 3). The indices a, b, c refer to the principal axes of the H magnetic interaction viz. $a \parallel \gamma, b$ and c in (110), the angle between c and $[001]$ being roughly 29° (see ref. 12).

MX		KCl	NH ₄ Cl ^a	RbCl	CsCl	NH ₄ Br ^a	RbBr	KCl	RbCl	RbBr
		H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	D ₂ O	D ₂ O	D ₂ O
X(I)	ν_Q	1.730	1.239	2.101	2.294	7.335	13.456	1.727	2.106	13.406
	η	0.898	0.996	0.706	0.427	0.940	0.639	0.887	0.701	0.624
	F_{xx} c	-0.064	0.002	0.136	0.424	0.781	1.414	-0.077	0.116	1.325
	F_{yy} γ	0.707	0.688	0.854	1.035	4.405	5.126	0.693	0.831	5.035
	F_{zz} γ'	-0.145	-0.094	0.027	0.240	0.487	1.200	-0.162	0.022	1.174
X(II)	ν_Q	9.432	9.411	10.30	11.15	75.88	81.80	9.454	10.31	
	η	0.190	0.251	0.156	0.168	0.31	0.22	0.188	0.155	
	F_{xx} γ	3.370	3.40	2.938	2.437	6.98	6.02	3.359	2.994	
	F_{yy} c	4.191	4.19	3.804	3.345	10.48	8.22	4.222	3.775	
	F_{zz} γ'	27.42	27.74	27.31	27.35	129.3	126.2	27.8	27.7	
O	ν_Q	1.38	1.20	1.24	1.25	1.26	1.28	1.36	1.24	1.28
	η	0.45	0.40	0.43	0.46	0.46	0.46	0.45	0.43	0.46
	F_{xx} c	43.24	43.7	44.44	45.64	45.1	46.23	43.25	44.64	46.35
	F_{yy} γ'	31.81	32.0	32.70	33.94	33.3	34.44	32.05	32.91	34.62
	F_{zz} γ	32.27	32.4	32.95	34.32	33.8	34.79	32.53	33.26	35.04
Cu	ν_Q	46.25	43.6	43.71	38.65	41.29	40.8			
	η	0.20	0.20	0.16	0.20	0.189	0.16			
	F_{xx} c	-25.2	-26.8	-19.3	-17.91	-48.9	-42.5			
	F_{yy} γ'	-8.99	-10.8	-13.5	-15.80	-33.8	-37.1			
	F_{zz} γ	-229	-237	-229	-231	-272	-274			
M	ν_Q	0.057		0.802	0.0132		0.808		0.799	0.805
	η	0	(*)	0	0	(*)	0		0	0
	F_{zz} c	-0.075		-1.450	-0.957		-1.702		-1.418	-1.691
	F_{\perp} $\perp c$	-0.108		-1.148	-0.812		-1.370		-1.142	-1.345
H	F_a	-0.94	-0.99	-0.84	-0.78	-0.69	-0.57	-0.165	-0.135	-0.101
	F_b	1.04	1.02	1.12	1.34	1.08	1.15	0.157	0.165	0.185
	F_c	6.52	6.62	6.51	6.98	6.42	6.38	1.02	0.98	1.00

^a For the ammonium compounds averaged values of the ¹⁷O parameters are given (see ref. 15).

differ from those in previous publications mainly because now under all experimental conditions an accurate magnetization scale could be used. Moreover, it has now been argued that the y axis of the X(I) EFG tensor rather than its z axis corresponds with the X(I)—Cu direction (see section 6).

In table II the values of the electric quadrupolar interaction (ν_Q and η) and of the principal components of the magnetic frequency shift tensor F are summarized for all compounds. The tensor F describes the total magnetic shift at saturated magnetization; it is defined in section 6.1, eq. (10). All measurements of F were performed in the paramagnetic state at $T = 1.2$ K and $H_0 = 10$ kOe on spherical samples. The crystal orientation and the magnetization were well known, which enabled us to determine the parameters in table II within 1%, although at least ± 1 kHz. If necessary, the quadrupolar interaction parameters have been corrected for the pseudo quadrupolar interaction as discussed in ref. 16.

The frequency shift observed in the ferromagnetic state in zero field differs from that in the paramagnetic state only by an amount $F_{ii}(\text{ferro}) - F_{ii}(\text{para}) = (\gamma/2\pi) \times (4/3) \pi M$ due to the cancelling of the demagnetizing field by the domain structure in the ferromagnetic state. This has been verified for all nuclei, as far as their spectra could be observed in the ferromagnetic state, viz. Cu, ^{17}O , Cl(I), Cl(II), Br(I), Br(II), Rb and Cs.

About the ammonium compounds a few remarks have to be made. The principal axes of the halide EFG and magnetic interaction tensors are not perfectly parallel (see section 6.3) due to the fact that in these compounds the site symmetries are lower than in the "isomorphous" alkali compounds. As mentioned in ref. 15, two sets of oxygen interaction parameters are found in the ammonium compounds. The differences are, however, small, so in this paper we will use only the averaged values. Also for N in the NH_4 ions two sets of interaction parameters are found [8, 10]. Since the values of these parameters are mainly determined by the strength of the hydrogen bridges $\text{N}-\text{H}\cdots\text{X}(\text{I})$ and $\text{N}-\text{H}\cdots\text{X}(\text{II})$, respectively, they cannot be compared with the corresponding values for the alkali nuclei and are therefore left out of consideration here.

4. Molecular orbital theory

For the description of the molecular orbitals of the copper octahedron we use the approach of Owen and

Thornley [19]. A short outline is given here to define the basic ideas concerning electron transfer and the magnetic properties resulting therefrom.

Consider a $\text{Cu}^{2+}(3d^9)$ ion with the 3d shell filled except the $3d(x^2 - y^2)$ orbital which is singly occupied and one ligand X with all shells filled up to and including 3p. The atomic orbitals of interest are, in shorthand notation:

$$\frac{\text{Cu}(3d^9)}{\text{half-filled}} \quad d(x^2 - y^2) \quad (\sigma)$$

$$\text{filled} \quad \begin{cases} d(3z^2 - r^2), & (\sigma) \\ d(xy), d(yz), d(zx) & (\pi) \end{cases}$$

$$\frac{\text{X}(3s^2 3p^6)}{\text{filled}} \quad \begin{cases} s & (\sigma) \\ p_x, p_y, p_z & (\sigma, \pi) \end{cases}$$

In this simplified picture all higher—empty—orbitals are neglected. The symbols σ and π designate zero or unit angular momentum about the Cu—X bonding axis, respectively. The principal bonds between Cu and X are formed using those d orbits on Cu which have non-zero overlap with p or s orbits on X. Thus for the Cu—X(II) system, with the coordinates given in fig. 3, s and p_z can form σ bonds with $d(x^2 - y^2)$ and $d(3z^2 - r^2)$ whereas p_x and p_y can form only π bonds with $d(zx)$ and $d(xy)$, respectively. We now define molecular orbitals constructed from the atomic p and d orbitals

$$\Psi_A = N_A(d - Ap) \quad (\text{antibonding}),$$

$$\Psi_B = N_B(p + Bd) \quad (\text{bonding}),$$

A and B are small admixture coefficients. The normalization constants N_A and N_B can be deduced from the orthonormality relation $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ yielding

$$N_A^{-2} = 1 - 2AS + A^2,$$

$$N_B^{-2} = 1 + 2BS + B^2,$$

$$0 = B - A + S - ABS,$$

where $S = \langle p | d \rangle$ is the overlap integral. If the small term ABS is neglected we have $A \approx B + S$.

Formally, the admixture occurs because the one-electron hamiltonian \hat{h} for the system has a non-zero

matrix element $\langle p|h|d\rangle = a_{pd}$. Neglecting small terms in the overlap, the simple perturbation theory expression for the admixture is then

$$A \approx B \approx a_{dp}(E_d - E_p),$$

where E_d and E_p are the energies of the original d and p orbitals.

The effect of the formation of a covalent bond is thus that the copper d orbital becomes the molecular orbital Ψ_A and the ligand p orbital the molecular orbital Ψ_B . The probability of finding the electron in the original d orbital is then N_A^2 whereas there is now also a probability $A^2N_A^2$ to find it in the p orbital. Consequently a fraction $A^2N_A^2$ of the electron is transferred from X towards M. The same holds for the bonding orbital in reversed sense. It is easy to see that an electron in the bonding orbital Ψ_B has a larger probability inbetween the Cu and the X ion than in the original atomic p orbital. The bonding orbital is thus stabilized because of the attractive force between the negative electron and the two positive nuclei. On the contrary, Ψ_A has a node in the region between M and X. An antibonding electron will be mainly confined to the space outside the overlap region and is therefore less stable than a bonding electron. The perturbation theory expression for the energy shift of the molecular orbitals with respect to the energy of the pure d and p orbitals is

$$\Delta E = |a_{dp}|^2(E_d - E_p) = B^2(E_d - E_p).$$

The bonding orbital is thus stabilized by ΔE per electron whereas the antibonding orbital is destabilized by the same energy per electron. In fact, when the overlap integral is taken into account it can be shown that Ψ_A is somewhat more raised in energy than Ψ_B is lowered.

When before bonding there were two electrons in p and one in d, then after bonding the bonding orbital is filled and the antibonding orbital is singly occupied. The net stabilizing energy is thus ΔE . Consequently a fraction $f = N_A^2 A^2$ of unpaired spin is found in the original ligand p orbital. In fact a net electron transfer has taken place from the ligand towards the copper ion. It can be argued [19] that the fraction of unpaired spin has to be associated with the bonding electron with spin down, or alternatively with the anti-

bonding "hole" with spin up. Nevertheless it is conventional to talk about the distribution of the unpaired electron rather than of the unpaired hole.

As a result of this spin transfer to the ligand, there is an interaction between the ligand nuclear spin, if any of course, and the unpaired electron spin of the magnetic ion; the so-called transferred hyperfine or super-hyperfine interaction. In so far as the magnetic part of this interaction is concerned, the interaction can be written as

$$\mathcal{H}_{sh} = f S \cdot A_p^0 \cdot I,$$

where f is the fraction of unpaired spin in the ligand p orbital, A_p^0 is the hyperfine-structure constant of this p electron. I is the ligand nuclear spin and S the unpaired electron spin. The fraction f can thus be determined directly from a measurement of the ligand hyperfine interaction. However, in practice the situation becomes more complicated since usually there is a number of similar contributions to the observed hyperfine interaction. These complications will be discussed in detail when analysing the experimental data on the ligand hyperfine interactions.

Before doing this we need to know the bonding scheme of the copper d orbital in which the unpaired electron is present. To that purpose in the next section expressions are presented for the copper hyperfine interaction tensor and the electronic g tensor, including the effects of the crystal field and covalent bonding. Since we are mainly interested in the ligand hyperfine interactions and the super-exchange interaction the description of the groundstate of the copper ion has been kept as simple as possible. That means that the covalent bonding between the copper ion and the six ligands is described in a first-order approximation. Thus among others we neglect mutual overlap of the ligand orbitals and electron transfer to copper 4s or 4p orbitals. Because of these approximations it cannot be expected that the description of g and A , given below, is perfect. Nevertheless, to obtain reliable information on the ligand covalent bonding from the observed hyperfine interactions it has to be verified that the description of the copper ground state is realistic.

5. Copper ground state

The ground state of the free copper Cu^{2+} ion is $3d^9, ^2D$. In a crystal the ion is subject to a crystalline field that causes an energy splitting of the orbital levels. The eigen functions corresponding to these energy levels are linear combinations of the free-ion 3d orbitals.

In the $M_2CuX_4 \cdot 2H_2O$ compounds the crystal field is cubic with small tetragonal and rhombic components. In fig. 2 the successive splittings of the orbital energy levels are shown. Via the spin-orbit coupling the excited t_{2g} orbitals are admixed into the ground state. Because the orbital magnetic moment in the t_{2g} orbitals is not quenched, the admixture of these orbitals into the ground state gives contributions to the g tensor and the copper hyperfine tensor \mathbf{A} . Moreover the rhombic component of the crystal field gives rise to an admixture of the $d(3z^2 - r^2)$ orbital into the $d(x^2 - y^2)$ orbital, leading to extra contributions to g and \mathbf{A} .

Following Bleaney et al. [20] the wave functions of the two components of the ground state Kramers doublet are given by

$$\begin{aligned}\Psi^+ &= \frac{1}{2}\sqrt{5N}f(r) \{ [\sqrt{3} \cos \phi (x^2 - y^2) + \sin \phi (3z^2 - r^2) + i\gamma xy] \chi^+ + [i\alpha yz - \beta zx] \chi^- \}, \\ \Psi^- &= \frac{1}{2}\sqrt{5N}f(r) \{ [\sqrt{3} \cos \phi (x^2 - y^2) + \sin \phi (3z^2 - r^2) - i\gamma xy] \chi^- + [i\alpha yz + \beta zx] \chi^+ \},\end{aligned}\quad (1)$$

χ^+ and χ^- are the two spin functions for the spin-up and spin-down states; $f(r)$ is the radial part of the wave functions. N is a normalizing factor given by $N^{-2} = 1 + (\alpha^2 + \beta^2 + \gamma^2)/12$. The angle ϕ is a measure of the rhombic distortion of the octahedron. If no rhombic distortion is present, $\phi = 0$. The admixture coefficients α , β and γ are given by

$$\alpha = -\lambda \frac{b - c}{E_{yz}} + \frac{1}{2}\lambda^2 \left(\frac{c - a}{E_{yz}E_{zx}} + \frac{a - b}{E_{xy}E_{yz}} \right) \quad (2)$$

with

$$a = \sqrt{3} \cos \phi - \sin \phi, \quad b = -\sqrt{3} \cos \phi - \sin \phi, \quad c = 2 \sin \phi.$$

β and γ are obtained from (2) by cyclic permutation of $\{a, b, c\}$ and $\{x, y, z\}$.

To account for spin transfer effects in the copper complex, molecular orbitals (MO) have to be used instead of the pure 3d orbitals. For the ligand orbitals the directions of x, y and z are chosen corresponding to the x, y and z

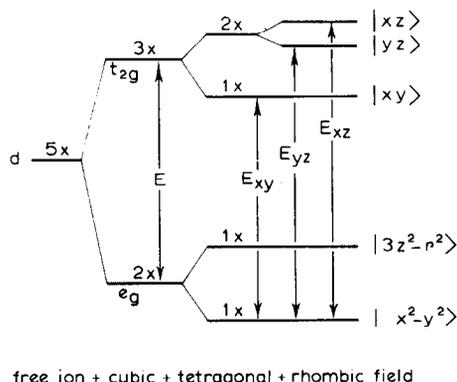


Fig. 2. Orbital energy levels for a Cu^{2+} ion in a crystal field.

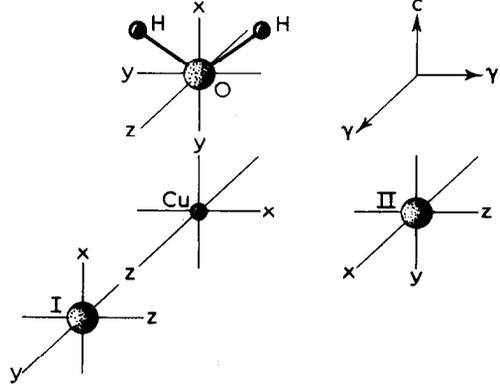


Fig. 3. The principal axes of the EFG tensors of copper and its ligands.

axes of the EFG tensors which are indicated in fig. 3. The ligands 1 and 4 stand for X(II), 2 and 5 for oxygen and 3 and 6 for X(I). We assume that the ligands participate in bonding with s , p_x , p_y and p_z orbitals only. Then the antibonding molecular orbitals with the shorthand notation x_i for the p_x orbital of the i th ligand etc., are given by

$$\begin{aligned} \Psi(x^2 - y^2) &= N_\sigma \left\{ d(x^2 - y^2) - \frac{1}{\sqrt{2}} \alpha_{\sigma 1} (-z_1 + z_4) - \frac{1}{\sqrt{2}} \alpha_{\sigma 2} (-x_2 + x_5) - \frac{1}{\sqrt{2}} \alpha_{s1} (s_1 + s_4) \right. \\ &\quad \left. - \frac{1}{\sqrt{2}} \alpha_{s2} (-s_2 - s_5) \right\}, \\ \Psi(3z^2 - r^2) &= N'_\sigma \left\{ d(3z^2 - r^2) - \frac{1}{\sqrt{12}} \alpha_{\sigma 1} (z_1 - z_4) - \frac{1}{\sqrt{12}} \alpha_{\sigma 2} (-x_2 + x_5) - \frac{1}{\sqrt{3}} \alpha_{\sigma 3} (-y_3 + y_6) \right. \\ &\quad \left. - \frac{1}{\sqrt{12}} \alpha_{s1} (-s_1 - s_4) - \frac{1}{\sqrt{12}} \alpha_{s2} (-s_2 - s_5) - \frac{1}{\sqrt{3}} \alpha_{s3} (s_3 + s_6) \right\}, \\ \Psi(xy) &= N_{\pi 3} \left\{ d(xy) - \frac{1}{\sqrt{2}} \alpha_{\pi 1} (y_1 - y_4) - \frac{1}{\sqrt{2}} \alpha'_{\pi 2} (y_2 - y_5) \right\}, \\ \Psi(yz) &= N_{\pi 1} \left\{ d(yz) - \frac{1}{\sqrt{2}} \alpha_{\pi 2} (z_2 - z_5) - \frac{1}{\sqrt{2}} \alpha'_{\pi 3} (x_3 - x_6) \right\}, \\ \Psi(zx) &= N_{\pi 2} \left\{ d(zx) - \frac{1}{\sqrt{2}} \alpha_{\pi 3} (z_3 - z_6) - \frac{1}{\sqrt{2}} \alpha'_{\pi 1} (-x_1 + x_4) \right\}. \end{aligned} \quad (3)$$

The normalization factors N_i are obtained from the orthonormality condition for the MO's. For instance, $N_{\pi 1}^{-2} = 1 - 2\sqrt{2}\alpha_{\pi 2}S_{\pi 2} - 2\sqrt{2}\alpha'_{\pi 3}S'_{\pi 3} + \alpha_{\pi 2}^2 + \alpha'_{\pi 3}^2$ where the overlap integrals are defined as $S_{\pi 2} = \langle d(yz)|z_2 \rangle$ etc. The experimental results are usually expressed in terms of the fraction f of unpaired electron spin transferred from the copper ion towards the ligand orbitals as discussed in section 4. For the singly occupied ground state (eq. (1)) the s and σ fractions are

$$f_{si} = \frac{1}{2} N_{\sigma}^2 \alpha_{si}^2, \quad f_{oi} = \frac{1}{2} N_{\sigma}^2 \alpha_{oi}^2. \quad (4)$$

In the expressions for the π fractions the coefficients α , β , γ arise; for instance

$$f_{\pi 1} = \frac{1}{2} \gamma^2 N_{\pi 3}^2 \alpha_{\pi 1}^2. \quad (5)$$

Because $\Psi(yz)$ and $\Psi(zx)$ admix in the ground state (eq. (1)) with spin down, the corresponding transferred spin density has also spin down. Experimentally this is equivalent to a negative spin density with spin up.

It is well known [19] that the formation of a covalent bond causes a reduction of the effect of the spin-orbit coupling on \mathbf{g} and \mathbf{A} as a consequence of the reduction of the orbital magnetic moment and of the virtual expansion of the copper 3d orbitals. Therefore in the calculation of the contribution of the admixed t_{2g} states to the \mathbf{g} and \mathbf{A} tensors a reduced effective value λ^* has to be used for the spin-orbit coupling constant. Similarly in the calculation of the copper hyperfine interaction a reduced value $P^* = 2g_n \beta \beta_n \langle r^{-3} \rangle^*$ needs to be used for the 3d hyperfine constant.

5.1. Principal values of \mathbf{g} and \mathbf{A}

From the wave function (eq. (1)) and the molecular orbitals (eq. (3)) the components of the tensors \mathbf{g} and \mathbf{A} can be calculated with the usual perturbative procedure [21, 22]. For rhombic symmetry \mathbf{g} and \mathbf{A} are symmetric tensors. The directions of their respective principal axes coincide with the x , y and z axes of the copper orbitals. The tensors are thus fully described by their diagonal components.

Correct to second order in λ^*/E the following expressions for g are found:

$$\begin{aligned} g_{xx} &= 2.0023 - \frac{2\lambda^*}{E_{yz}} N_{\pi 1}^2 \frac{b-c}{\sqrt{3}} \left[\frac{b-c}{\sqrt{3}} + 2\alpha_{s2} S_{s2} + 2\alpha_{\sigma 2} S_{\sigma 2} + \alpha_{\sigma 2} \alpha_{\pi 2} T_2 \right] - \left(\frac{\lambda^*}{E} \right)^2 \frac{(b-c)^2 + 9}{3}, \\ g_{yy} &= 2.0023 - \frac{2\lambda^*}{E_{zx}} N_{\pi 2}^2 \frac{c-a}{\sqrt{3}} \left[\frac{c-a}{\sqrt{3}} + 2\alpha_{s1} S_{s1} + 2\alpha_{\sigma 1} S_{\sigma 1} + \alpha_{\sigma 1} \alpha_{\pi 1} T_1 \right] - \left(\frac{\lambda^*}{E} \right)^2 \frac{(c-a)^2 + 9}{3}, \\ g_{zz} &= 2.0023 - \frac{8\lambda^*}{E_{xy}} N_{\pi 3}^2 \frac{a-b}{2\sqrt{3}} \left[\frac{a-b}{2\sqrt{3}} - \alpha_{s1} S_{s1} - \alpha_{s2} S_{s2} - \alpha_{\sigma 1} S_{\sigma 1} - \alpha_{\sigma 2} S_{\sigma 2} \right. \\ &\quad \left. - \frac{1}{2} \alpha_{\sigma 1} \alpha_{\pi 1} T_1 - \frac{1}{2} \alpha_{\sigma 2} \alpha_{\pi 2} T_2 \right] - \left(\frac{\lambda^*}{E} \right)^2 \frac{(a-b)^2 + 9}{3}. \end{aligned} \quad (6)$$

In these expressions is $E = (E_{xy} + E_{yz} + E_{zx})/3$ and

$$T_i = n + \frac{(1-n^2)^{\frac{1}{2}}}{\sqrt{3}} R_i \int r^2 \mathcal{R}_{pi} \frac{d}{dr} \mathcal{R}_{si} dr,$$

where \mathcal{R}_{pi} and \mathcal{R}_{si} are the normalized radial p and s functions of the i th ligand and R_i is the metal-ligand distance. The number n is the hybridization coefficient given by $n^2 = \alpha_{\sigma}^2 / (\alpha_{\sigma}^2 + \alpha_s^2)$. The values for the overlap integrals S_i have been taken from the calculations by Smith [23].

For the copper hyperfine interaction the following expressions can be derived:

$$A_{xx} = P^* \left[N_{\sigma}^2 \left\{ -\kappa + \frac{2}{7} (a^2 - 2) \right\} + \frac{1}{7} \frac{\lambda^*}{E_{xy}} N_{\pi 3}^2 (a^2 - b^2) - \frac{2}{3} \frac{\lambda^*}{E_{yz}} N_{\pi 1}^2 (b-c)^2 - \frac{1}{7} \frac{\lambda^*}{E_{zx}} N_{\pi 2}^2 (a-c)b \right],$$

$$A_{yy} = P^* \left[N_{\sigma}^2 \left\{ -\kappa + \frac{2}{7}(b^2 - 2) \right\} - \frac{1}{7} \frac{\lambda^*}{E_{xy}} N_{\pi 3}^2 (a^2 - b^2) - \frac{1}{7} \frac{\lambda^*}{E_{yz}} N_{\pi 1}^2 (b - c)a - \frac{2}{3} \frac{\lambda^*}{E_{zx}} N_{\pi 2}^2 (a - c)^2 \right],$$

$$A_{zz} = P^* \left[N_{\sigma}^2 \left\{ -\kappa + \frac{1}{7}(4 - c^2) \right\} - \frac{2}{3} \frac{\lambda^*}{E_{xy}} N_{\pi 3}^2 (a - b)^2 + \frac{1}{7} \frac{\lambda^*}{E_{yz}} N_{\pi 1}^2 (b - c)a + \frac{1}{7} \frac{\lambda^*}{E_{zx}} N_{\pi 2}^2 (a - c)b \right], \quad (7)$$

where κ is the core polarization factor.

As can be seen, the unknown (or better: not exactly known) parameters in the six expressions for the components of \mathbf{g} and \mathbf{A} are κ , ϕ , λ^* and P^* . In fact g_{xx} and g_{zz} are not known separately, but only the amalgamated value $g_a = \frac{1}{2}(g_{xx} + g_{zz})$ so that we have five relations and only four parameters to be determined. This yields the possibility to verify the validity of the approximations made in the given description (see section 4).

The evaluation of the unknown parameters is basically an iterative process. To start, all ligand admixture coefficients α_{σ} , α_{π} are set to zero. Then with eqs. (6) and (7) the copper ground state is calculated. With the so derived values for the admixture coefficients α , β and γ the ligand super-hyperfine interactions are analysed to obtain a first estimate of the ligand admixture coefficients. The copper ground state is then recalculated, and so on.

For the calculation of κ , ϕ , λ^* and P^* we have chosen to proceed as follows. Using expressions (6) for the g tensor, λ^* and ϕ are calculated from the experimental values g_c and g_a . P^* and κ are obtained most easily from combinations of the A_{ii} , i.e. κ from $A_{iso} = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$ and P^* from $\Delta A = A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})$. The deviation from axially of the hyperfine tensor, $\delta A = A_{xx} - A_{yy}$, has been used to compare the experimental values δA^{exp} with the values δA^{cal} calculated from expression (7) using the obtained values for κ , ϕ , λ^* and P^* . When \mathbf{g} and \mathbf{A} are correctly described by the given expressions, we expect to find $\delta A^{\text{exp}} = \delta A^{\text{cal}}$. So, the relative deviation between experiment and theory, expressed as

$$\epsilon = (\delta A^{\text{exp}} - \delta A^{\text{cal}})/P^* \quad (8)$$

is a measure of the correctness of the description.

In table III the results of our analysis are shown. As can be seen, there is no strong variation in the values for κ , ϕ , λ^* and P^* over the series. This is not surprising since there is no strong variation in the experimental parameters used in the analysis (see tables I and II). From the expressions (6) for the g tensor the two components g_{xx} and

Table III
Parameters of the copper ground state, copper hyperfine interaction and electronic g values

MX	KCl	NH ₄ Cl	RbCl	CsCl	NH ₄ Br	RbBr
ϕ (deg)	3.9	4.4	3.9	3.8	4.1	4.1
κ	0.408	0.412	0.408	0.405	0.453	0.448
λ^* (cm ⁻¹)	-681	-669	-665	-647	-621	-590
λ^{\dagger} (cm ⁻¹)	-685	-685	-662	-664	-595	-616
P^* (MHz)	998	999	966	972	1004	1002
ϵ	0.04	0.05	0.06	0.07	0.04	0.06
α^2	0.013	0.014	0.013	0.012	0.013	0.012
β^2	0.007	0.007	0.007	0.007	0.007	0.006
γ^2	0.055	0.052	0.049	0.052	0.049	0.042
g_{xx} ($\parallel \gamma'$)	2.107	2.111	2.107	2.101	2.099	2.096
g_{yy} ($\parallel c$)	2.047	2.043	2.046	2.043	2.039	2.041
g_{zz} ($\parallel \gamma$)	2.339	2.327	2.327	2.319	2.287	2.290

g_{zz} of the amalgamated g_a can now be separated. The g_{xx} and g_{zz} values listed in table III, are in full agreement with the already mentioned high-frequency ESR results of Okuda [2] and Kennedy [3] on $K_2CuCl_4 \cdot 2H_2O$. This result supports strongly the applicability of the expressions used for the g tensor. The value for P^* is smaller than the free-ion value $P = 1164$ MHz [24] as a consequence of the expansion of the 3d wave function. The value of the spin-orbit coupling constant is reduced by the same factor. Moreover an extra reduction arises due to the formation of molecular orbitals by which the unpaired electron spends a fraction f_i of its time on the ligand i . It can be shown [19] that the resulting spin-orbit coupling constant can be approximated by

$$\lambda^\dagger = (\lambda - \frac{1}{4}\alpha_{\sigma 1}\alpha_{\pi 1}\lambda_1 - \frac{1}{4}\alpha_{\sigma 2}\alpha_{\pi 2}\lambda_2)P^*/P. \quad (9)$$

The parameters λ_1 and λ_2 are the spin-orbit coupling constants for electrons in the ligand p orbitals. In table III the values for λ^* , which have been determined from expression (6), are compared with those calculated from expression (9), denoted by λ^\dagger , using the values of the parameters given in table III.

From the analysis of the ligand super-hyperfine interactions (section 6) we find for the admixture coefficients the values $\alpha_{\sigma 1} = 0.51$ and $\alpha_{\pi 1} = 0.38$ for Cl(II) and $\alpha_{\sigma 1} = 0.55$ and $\alpha_{\pi 1} = 0.46$ for Br(II) and $\alpha_{\sigma 2} = 0.33$ and $\alpha_{\pi 2} = 0.20$ for oxygen. The values of the (atomic) spin-orbit coupling constants are $\lambda(\text{Cu}) = -828 \text{ cm}^{-1}$, $\lambda(\text{Cl}) = -587 \text{ cm}^{-1}$, $\lambda(\text{Br}) = -2456 \text{ cm}^{-1}$ and $\lambda(0) = -75 \text{ cm}^{-1}$ [25, 26]. It can be seen from table III that also for λ^* the description is satisfactory.

The values for the empirical core polarization factor κ compare rather well with those obtained in other copper compounds [27]. The magnitude of the systematic error ϵ (see eq. (8) and table III) is satisfactory in view of the fact that our description of the copper hyperfine interaction contains the effects of orbital admixture up to first order only. As mentioned already the theory does not account for a number of effects like the deformation of the angular extension of the 3d wave function (but only for the reduction of the $\langle r^{-3} \rangle_{3d}$ value), ligand-ligand overlap and transfer to empty orbitals. We feel that when these more sophisticated corrections are also taken into account the agreement between theory and experiment can be improved, however without significant change in the values for the parameters κ , ϕ , λ^* and P^* .

6. Ligand hyperfine interaction

In this section we give an analysis of the observed magnetic interactions of the ligand nuclei and discuss the covalent bonding of the ligands with the copper ion. It should be noted that apart from these magnetic effects, charge transfer has also a strong impact on the electric quadrupolar interaction. This has been discussed in a previous paper [11] and will not be considered here.

6.1. Halide (II)

The analysis of the X(II) super-hyperfine interaction is the most simple of all. A strong bonding is expected with the half-filled copper $\Psi(x^2 - y^2)$ orbital. Therefore the direction for which the largest hyperfine field is observed has to correspond to the Cu-X(II) bond. This direction also proves to be the z axis of the electric field gradient tensor, see fig. 3.

As can be seen in table II the magnetic interaction of the X(II) nuclei is rather large and will thus mainly be due to super-hyperfine interactions. Therefore no serious errors will be introduced when for the much smaller dipolar interaction with all other magnetic moments a value is used calculated with a point dipole model. The principal components of the hyperfine interaction tensor \mathbf{A} are then obtained from the observed frequency shifts (table I) using the relation

$$A_{ii} = 2 \left(F_{ii} - \frac{\gamma}{2\pi} D_{ii} \right), \quad (10)$$

where D_{ii} is the calculated dipolar field tensor and γ the nuclear gyromagnetic ratio. Using x , y and z for the principal axes of the X(II) interaction tensor as given in fig. 3 the contributions of the various electron orbitals to the observed hyperfine interaction can be written as [19]

$$\begin{aligned}
 A_{xx} &= A_s + 2A_{\pi x} - A_{\pi y} - A_\sigma, \\
 A_{yy} &= A_s - A_{\pi x} + 2A_{\pi y} - A_\sigma, \\
 A_{zz} &= A_s - A_{\pi x} - A_{\pi y} + 2A_\sigma.
 \end{aligned} \tag{11}$$

A_σ is the contribution from the p_z orbital; $A_{\pi x}$ and $A_{\pi y}$ are the contributions from the p_x and p_y orbitals, respectively. A_s is the isotropic contribution from the s orbital and can be found from (eq. (11)) directly from the summation of the three A_{ii} values. It can be seen that from these expressions the three p contributions cannot be obtained separately. Therefore we derive an extra relation between them as follows. The unpaired spin in the p orbitals can only be due to the covalent bonding of these orbitals with the copper $\Psi(x^2 - y^2)$ orbital. From the expressions (3) for the molecular orbitals and the expression (1) for the copper ground state it can be concluded that the fraction of unpaired spin in the p_x orbital of X(II) is proportional to $\frac{1}{2}(N_{\pi 2} \alpha'_{\pi 1} \beta)^2$ with the spin down, and that the fraction in the p_y orbital is proportional to $\frac{1}{2}(N_{\pi 3} \alpha_{\pi 1} \gamma)^2$ with the spin up. We feel that it is not too bad an approximation to assume $N_{\pi 2} \alpha'_{\pi 1} = N_{\pi 3} \alpha_{\pi 1}$ which means that both π bonds $\Psi(zx) - p_x$ and $\Psi(xy) - p_y$ are taken equal. Then the ratio of $A_{\pi x}$ and $A_{\pi y}$ can be written as

$$A_{\pi x}/A_{\pi y} = -\beta^2/\gamma^2. \tag{12}$$

Combining (11) and (12) now the contributions from the three p orbitals to the hyperfine interaction can be determined. The fraction f_i of unpaired spin in orbital i is given by the relation $f_i = A_i/A_i^0$, where A_i^0 is the hyperfine constant for an electron in the orbital i . The values used for these constants A_i^0 are $A_{3s}^0 = 4520$ MHz [28] and $A_{3p}^0 = 129$ MHz [29] for ^{35}Cl and $A_{4s}^0 = 21010$ MHz [28] and $A_{4p}^0 = 588$ MHz [29] for ^{79}Br . These hyperfine constants are valid for the valence state $-\frac{1}{2}$, which is about the actual situation for these ligand ions.

In table IV the resulting values for $f_s, f_\sigma, f_{\pi x}$ and $f_{\pi z}$ are listed. A negative value for $f_{\pi x}$ corresponds with an unpaired spin density $|f_{\pi x}|$ with spin down in the πx orbital.

From the spin densities in table IV it can be seen that f_σ is much larger than f_s . It can thus be concluded that the halide (II) orbitals are not or very weakly hybridized (compare with oxygen, section 6.2).

6.2. Oxygen and hydrogen

In ref. 15 the oxygen hyperfine interaction has been analysed only approximately. Now using a scheme similar to (11) the analysis yields values for A_{2s} and for the differences in $A_\sigma - A_{\pi y}$ and $A_\sigma - A_{\pi z}$ (the oxygen reference frame is given in fig. 3). When we use similar arguments as for X(II) to obtain an expression for the ratio $A_{\pi y}/A_{\pi z}$ we find $A_{\pi y}/A_{\pi z} = -\gamma^2/\alpha^2$ with $A_{\pi z}$ negative. Then for all values of α^2 and γ^2 one expects $A_{zz} < A_{yy}$. However, experimentally we observe that $A_{zz} = 2F_{zz} - (\gamma/\pi)D_{zz}$ is larger than $A_{yy} = 2F_{yy} - (\gamma/\pi)D_{yy}$. The magnitude of this discrepancy is much too large to be explained by errors in the calculation of the—relatively small—dipolar interaction tensor D .

So we have to conclude that although the spin densities in the oxygen orbitals are mainly due to the covalent bonding with the copper ion, they must also be influenced by the hydrogen bonds to the nearby X(I) ions. Fortunately, the admixture coefficients α and γ are small (table III) so that also $A_{\pi y}$ and $A_{\pi z}$ can be expected to be small compared to A_σ (like we found already for X(II)). Consequently, no strong errors will be introduced when we neglect these π contributions in the hyperfine interaction and put $f_{\pi y} = f_{\pi z} = 0$. The resulting values for the spin densities in the $2s$ orbital (f_s) and in the p_x orbital (f_σ) are listed in table IV for the six compounds.

In ref. 12 we have discussed the proton magnetic interaction. The anisotropy in F is completely due to dipolar interactions and only the isotropic shift is caused by spin transfer to the hydrogen $1s$ orbital. The results are listed in table IV.

From an inspection of table IV it is striking that the s spin density is relatively much larger for oxygen than for X(II). We will show here that this is caused by the fact that in a water molecule the oxygen s and p orbitals form hybridized orbitals, which in turn form molecular orbitals with the hydrogen $1s$ orbitals. It will appear that the σ bonding orbital is not only responsible for the relatively large oxygen s spin density but also for the spin density in the hydrogen s orbitals.

According to Ellison and Shull [30] the simplest molecular orbitals for the H_2O molecule are linear combinations of the five oxygen orbitals denoted here by $1s, 2s, 2p_x, 2p_y$ and $2p_z$ and the two hydrogen $1s$ orbitals denoted by h and h' . The coordinates of the oxygen orbitals are taken from fig. 3 again. For a

Table IV
Ligand spin densities

MX			KCl	NH ₄ Cl	RbCl	CsCl	NH ₄ Br	RbBr
X(II)	f_s	(%)	0.52	0.52	0.50	0.49	0.47	0.45
	f_σ	(%)	12.0	12.1	12.1	12.5	13.6	13.5
	$f_{\pi x}$	(%)	-0.05	-0.05	-0.05	-0.05	-0.05	-0.03
	$f_{\pi y}$	(%)	0.34	0.33	0.36	0.38	0.34	0.20
O	f_s	(%)	1.47	1.48	1.51	1.56	1.54	1.59
	f_σ	(%)	4.89	5.16	5.23	5.26	5.24	5.27
H	f_s	(%)	0.33	0.33	0.34	0.37	0.34	0.34
X(I)	f_s	(10 ⁻⁵)	7.14	8.47	14.8	25.1	17.9	24.5
	$f_\sigma - f_{\pi z}$	(%)	0.29	0.27	0.28	0.28	0.38	0.38
	$f_{\pi x} - f_{\pi z}$	(%)	0.01	0.02	0.02	0.06	0.02	0.01

water molecule with an H–O–H bond angle of 110° Ellison and Shull derived the following normalized MO's, arranged according to increasing orbital energy E :

$$\Psi(1a_1) = -0.002(h + h') + 1.00(1s) + 0.02(2s) + 0.002(2p_x) \\ \{E = -557 \text{ eV}\},$$

$$\Psi(2a_1) = 0.12(h + h') - 0.03(1s) + 0.85(2s) + 0.01(2p_x) \\ \{E = -36 \text{ eV}\},$$

$$\Psi(1b_2) = 0.55(h - h') + 0.53(2p_y) \\ \{E = -19 \text{ eV}\},$$

$$\Psi(3a_1) = 0.23(h + h') - 0.03(1s) - 0.44(2s) + 0.84(2p_x) \\ \{E = -13 \text{ eV}\},$$

$$\Psi(1b_1) = 1.00(2p_z) \\ \{E = -12 \text{ eV}\},$$

$$\Psi(4a_1) = 0.76(h + h') - 0.09(1s) - 0.84(2s) - 0.61(2p_x) \\ \{E = +14 \text{ eV}\},$$

$$\Psi(2b_1) = 0.86(h - h') - 1.03(2p_y) \\ \{E = +16 \text{ eV}\}.$$

(13)

In the ground state the first five orbitals are occupied each by two electrons and $\Psi(4a_1)$ and $\Psi(2b_2)$ are

empty. Inspecting the occupied orbitals it can be seen that $\Psi(1a_1)$ is nearly the pure oxygen 1s orbital and that $\Psi(2a_1)$ is largely the oxygen 2s orbital. These orbitals are thus not strongly bonding to the copper orbitals. The ligand bonding between the water molecule and the copper ion is thus mainly due to the $\Psi(3a_1)$ orbital (σ bond) and the $\Psi(1b_1)$ and $\Psi(1b_2)$ orbitals (π bonds). When we consider the admixture coefficients of the original oxygen and hydrogen orbitals in the σ bonding orbital $\Psi(3a_1)$, we expect that, due to this bond only, the ratios of spin densities in the 2s, 2p_x and h orbitals are given by

$$f_s : f_{p_x} : f_h = (0.44)^2 : (0.84)^2 : (0.23)^2 \approx 1.5 : 5.5 : 0.4. \quad (14)$$

As can be seen from table IV these ratios compare very well with the ratios of the observed spin densities in these orbitals. These molecular orbitals of the free water molecule are thus a good approximation for the orbitals of the water of hydration in these compounds. This proves that the original ligand orbitals are not strongly deformed in the crystal and can thus safely be used in a simple molecular orbital description to determine the distribution of the unpaired spin.

6.3. Halide (I)

The X(I) ligand has no strong σ bond with the half filled copper 3d orbital. Therefore no a priori argu-

ments are present to identify the Z axis of the EFG tensor with the copper-halide (I) direction like we did for X(II). For oxygen we used the observation that the resonance lines of the Z axis spectrum show a fine structure due to the nuclear copper–ligand interaction, which has been discussed in ref. 17, to determine the direction of the Z axis. In the X(I) spectra, however, this effect cannot be observed because the X(I) hyperfine interaction is much too small to make this splitting larger than the linewidth.

Fortunately the problem to correlate the EFG Y and Z axes to the crystallographic directions is solved in the two ammonium compounds since there the X(I) site symmetry is lower (see ref. 14). In these compounds we observed from the angular dependences of the X(I) resonance lines that only the Z axis of the EFG tensor coincides with the crystallographic $[110]$ axis. The X and Y axes were found to lie in the (110) plane, making an angle α with the c and $[110]$ directions, respectively. In the chlorine compound $\alpha = 1.5^\circ$ and in the bromine compound $\alpha = 5^\circ$. (Similarly we observed that in the two ammonium compounds also the EFG tensor of the X(II) nuclei is rotated about its X axis over a small angle with respect to the crystallographic axes.) In the ammonium compounds the X(I) site symmetry is m , with the mirror plane perpendicular to the γ' direction. It can thus be concluded unambiguously that in the two ammonium compounds the EFG Z axis points along γ' and consequently the Y axis about along γ and the X axis about along c .

For all compounds the largest X(I) hyperfine interaction component is observed along the EFG Y axis. The assumption is thus justified that also in the “non-ammonium” compounds the Y axis points along the γ direction and consequently the X and Z axes point along the c and γ' directions, respectively.

The analysis of the X(I) super hyperfine interaction is much more complicated than that of the ligands whose spin densities are mainly due to covalent bonding with the half-filled copper $\Psi(x^2 - y^2)$ orbital. The X(I) orbitals cannot admix into $\Psi(x^2 - y^2)$ so the spin densities from the nearby copper ion can arise only indirectly via the admixture of the other copper orbitals into the ground state Ψ^+ (eq. (1)) and will consequently be small. A second and even more important contribution to the X(I) spin density arises via the transfer of fractional unpaired electron over the hydrogen bridges $O-H \cdots X(I)$ as discussed in

ref. 14. Moreover, the dipolar contribution to the internal field is relatively large (about 0.1 MHz) so that systematic errors in the calculation of this contribution can influence markedly the results of the analysis.

In the same way as was done before the observed magnetic interaction tensor \mathbf{F} is corrected for the dipolar interaction \mathbf{D} . Next, following the scheme of eq. (11) the values of f_s , $f_\sigma - f_{\pi z}$ and $f_{\pi x} - f_{\pi y}$ can be calculated. These values are listed in table IV for the various compounds. The same values have been used for the halide hyperfine constants A_s^0 and A_p^0 as we did for X(II).

To separate the various contributions to the X(I) hyperfine interaction, and thus to the spin densities, we assume that the total spin density in the p_i orbital can be written as:

$$f_i = f_i' + f_i'' \quad (i = \sigma, \pi x \text{ or } \pi z), \quad (15)$$

where f_i' originates from a covalent bond with the nearby copper, and f_i'' is due to the electron transfer over the (two) hydrogen bridges.

To obtain an estimate of the spin-transfer coefficients f_i' we proceed as follows. According to Smith [23] the ligand orbital admixture coefficients in the antibonding orbital are approximately proportional to the overlap integrals of the orbitals involved. For instance the ratio of the admixture coefficients of the X(I) and X(II) ions is about equal to the ratio of the overlap integrals in question i.e. proportional to

$$\langle y_3 | \Psi(3z^2 - r^2) \rangle / \langle z_1 | \Psi(x^2 - y^2) \rangle, \quad \text{etc.}$$

Using the expression for the copper ground state (eq. (1)), the expressions for the copper ligand MO's (eq. (3)) and the definitions of the overlap integrals we arrive at the following estimate of the X(I) spin densities due to the bonding with the nearest copper ion:

$$\begin{aligned} f_\sigma' &\approx f_\sigma(\text{II}) t g^2 \phi S_{\sigma 3}^2 / S_{\sigma 1}^2, \\ f_{\pi x}' &\approx -f_{\pi y}(\text{II}) \alpha^2 S_{\pi 3}^2 / \gamma^2 S_{\pi 1}^2, \\ f_{\pi z}' &\approx -f_{\pi y}(\text{II}) \beta^2 S_{\pi 3}^2 / \gamma^2 S_{\pi 1}^2. \end{aligned} \quad (16)$$

Using our values for the copper parameters (table III) and for the X(II) spin densities (table IV) combined

with $S_{\sigma 1}/S_{\sigma 3} = 2.4$ and $S_{\pi 1}/S_{\pi 3} = 3.0$ [23] we obtain for $K_2CuCl_4 \cdot 2H_2O$

$$f'_\sigma = 0.010\%, f'_{\pi x} = -0.009\% \text{ and } f'_{\pi z} = -0.005\%.$$

Approximately the same values are found for the other five compounds. Because of the approximation involved, these values should not be considered as very accurate but merely as an order of magnitude.

When we consider the contribution f_i'' from the hydrogen bridges we can safely put $f_{\pi z}'' = 0$ because the chlorine p_z orbital can only admix in the oxygen p_z orbital in which the fraction of unpaired spin, if any, is very small. Moreover this admixture will be rather small because of the large distance between the orbitals. Finally f_σ'' and $f_{\pi x}''$ can now be calculated from $f_\sigma - f_{\pi z}$ and $f_{\pi x} - f_{\pi z}$. For the chlorine compounds we find

$$f_\sigma'' = 0.26\% \text{ and } f_{\pi x}'' = 0.04\%, \quad (17a)$$

whereas for the bromine compounds

$$f_\sigma'' = 0.36\% \text{ and } f_{\pi x}'' = 0.04\%. \quad (17b)$$

It should be noted that $f_{\pi x}''$ is positive whereas $f'_{\pi x}$ is negative.

In ref. 14 it has been shown that over the hydrogen bridge $O-H \cdots X(I)$ a small amount of charge is transferred from oxygen to halide (I). To be more precise, a fraction W_3 of an electron is transferred from filled X(I) orbitals to half filled or empty water molecule orbitals. The H_2O orbitals that can accommodate such a transferred electron are therefore the empty orbitals $\Psi(4a_1)$ and $\Psi(2b_2)$ which both are directed towards the halide (I) ion, and the half filled antibonding molecular orbital formed by the copper Ψ^+ and the H_2O $\Psi(3a_1)$ orbitals. Consequently, the upper limit for the fraction of unpaired spin transferred to the halide ion is $f(3a_1)W_3$ where $f(3a_1)$ is the total spin density in $\Psi(3a_1)$. The lower limit occurs when the electron is transferred only to empty H_2O orbitals. In that case the transferred fraction of unpaired spin is zero. Since f_σ'' is due to two equal hydrogen bridges we have as boundary conditions $0 \leq f_\sigma'' \leq 2f(3a_1)W_3$. From table II and $W_3 \approx 0.04$ (see ref. 14) it is calculated that $2f(3a_1)W_3 \approx +0.6\%$. The f_σ'' values in (17) are about one half of the upper

limit $2f(3a_1)W_3$, which means that in the electron transfer over the hydrogen bridge also empty—and thus non-magnetic—water orbitals are involved.

Summarizing this section we conclude that because f_σ'' is much larger than all other spin densities, the obtained value for f_σ'' certainly is a good estimate of the fraction of unpaired spin in the X(I) p_σ orbital, not much influenced by the rough approximations that are used in the derivation. It should be emphasized that about the total spin density on the X(I) ion originates from next-nearest copper ions rather than—what should be expected—from the nearby copper.

7. Super-exchange interaction and covalency

The super-exchange interaction between neighbouring magnetic ions in transition metal salts is closely related to covalency. Since the early work of Kramers [31] and Anderson [32] there have been many theoretical contributions to this subject which have been reviewed by Anderson [33]. In general this is a complicated subject because there are many mechanisms contributing to the total exchange interaction in any particular case. Some of them are ferromagnetic and some antiferromagnetic, so that without detailed knowledge about the electronic structure, it is even hard to estimate the sign of the resulting exchange interaction.

In the present case, we have determined the covalent bonding parameters of all ions that are involved in the dominant super-exchange paths in the series of six $M_2CuX_4 \cdot 2H_2O$ compounds. Our main interest is now to inspect whether it is possible to predict on the basis of this knowledge not only the correct sign of the exchange interaction, but also its order of magnitude. As already mentioned, the number of contributions to the exchange interaction is rather large. Therefore, we restrict ourselves to a discussion of the dominant contributions only.

7.1. The super-exchange mechanisms

For the description of the various super-exchange mechanisms we use a configuration interaction approach. This means that a purely ionic ground state is considered in which (also ionic) excited configurations are admixed in which an electron has hopped from one ion to another. To start with, we simplify the

picture such that all diamagnetic ions in an exchange path are taken together and are represented by L. Of course, when discussing an actual situation, the various configurations concerning these ions have to be considered separately. The magnetic ions are denoted by M_1 and M_2 . The ground state is then simply given by

$$M_1^{2+} - L^- - M_2^{2+}. \quad (18)$$

Both M^{2+} ions have one unpaired electron spin, denoted by S_1 and S_2 , respectively. When we neglect direct exchange, the spin configurations of the complex, $\uparrow\uparrow$ and $\uparrow\downarrow$, have both the same energy.

A) An excited configuration of interest is

$$M_1^+ - L^- - M_2^{3+}. \quad (19)$$

The exchange interaction due to this configuration is sometimes referred to as *delocalization exchange*. Here, one electron is transferred from M_2 to M_1 . Since the Cu^{2+} ions have a $3d^9$ configuration it is more convenient to talk about the hole with spin S_1 (simply denoted by S_1) that is transferred, in the reversed sense, from M_1 to M_2 . Now there are two possibilities for the two holes S_1 and S_2 on M_2 .

a) S_1 and S_2 are found in *different* orbitals of M_2 . According to Hund's rule, the parallel spin configuration is now favoured with respect to the antiparallel one by an energy J^{intra} , the intra-atomic exchange. For the free copper ion $J^{intra} \approx 1.5 \times 10^4 \text{ cm}^{-1}$. In a crystalline surrounding J^{intra} will not be very different. Denoting $p_1(Aa)$ the probability of finding S_1 in an orbital of M_2 and $p_2(Aa)$ the probability of finding S_2 in another orbital on M_2 , the contribution $J(Aa)$ of configuration Aa to the exchange interaction J between S_1 and S_2 is then

$$J(Aa) = +p_1(Aa)p_2(Aa)J^{intra}(M) \quad (\text{ferromagnetic})$$

b) S_1 and S_2 are found in the *same* orbital on M_2 . According to Pauli's principle only the antiparallel spin configuration is allowed. The contribution to the total exchange is therefore always antiferromagnetic. The magnitude is determined by the probabilities of finding S_1 and S_2 in the appropriate orbital and the energy decrease ΔE that is obtained by the admixture of this configuration into the antiparallel ground state

with respect to the parallel one. According to Anderson [33] this energy decrease ΔE is approximately given by

$$\Delta E = 4[E_d(1) - E_p(L)][E_d(2) - E_p(L)]/U,$$

where E_i are the atomic orbital energies of the copper d and ligand p electrons and U is the energy that is required to form the excited configuration. From the ionization potentials for the different ions involved [34] U is estimated to be about 2 eV. The value of $(E_d - E_p)$ can be estimated from the transfer bands in the near-ultraviolet spectra [7] to be of the order of magnitude of $25 \times 10^3 \text{ cm}^{-1}$. Consequently the magnitude of ΔE is about $1.5 \times 10^5 \text{ cm}^{-1}$. The contribution $J(Ab)$ of this configuration to the exchange interaction is thus

$$J(Ab) = -p_1(Ab)p_2(Ab)\Delta E \quad (\text{antiferromagnetic}).$$

B) Another excited configuration that contributes to the exchange interaction is

$$M_1^+ - L^+ - M_2^+, \quad (20)$$

sometimes referred to as *correlation exchange*. In this situation (the holes) S_1 and S_2 are hopped simultaneously from M_1 and M_2 respectively towards the ligand. Again there are two possibilities.

a) S_1 and S_2 are found in different orbitals on L. Again, when $p_1(Ba)$ and $p_2(Ba)$ are the appropriate probabilities for this arrangement, the contribution to the exchange interaction is

$$J(Ba) = +p_1(Ba)p_2(Ba)J^{intra}(L) \quad (\text{ferromagnetic}).$$

For Cl, Br and O the intra-atomic exchange equals about $J^{intra}(L) \approx 1.5 \times 10^4 \text{ cm}^{-1}$.

Recently Gill and Cox used this type of configuration to obtain an estimate of the exchange interaction in cesium copper sulphate in correct order of magnitude [35].

b) S_1 and S_2 are found in the same orbital on L. Analogously to case Ab, we find for the contribution to the exchange interaction

$$J(Bb) = -p_1(Bb)p_2(Bb)\Delta E' \quad (\text{antiferromagnetic}).$$

From the ionization potentials [34] of the ions in question it can be calculated that the energy U required to form this configuration is somewhat higher than to form configuration Ab, resulting in $\Delta E' \approx 1.0 \times 10^5 \text{ cm}^{-1}$.

Apart from the mentioned ones there are some other configurations, such as configurations that involve the empty 4s and 4p orbitals at the metal ions. These contributions to the total exchange interaction are much smaller and will therefore not be considered here.

7.2. Nearest-neighbour super-exchange

Now we apply the above given scheme to the actual situation. The strongest covalent bond between nearest-neighbour copper ions is formed by the chain



For configuration Aa we want to know the probability p_1 of finding S_1 in any orbital of Cu_2 with exception of the half-filled orbital $\Psi_2(x^2 - y^2)$. Using the information that we obtained from the analysis of the X(I) magnetic interaction, the fraction of S_1 that is found in the X(I) p_σ orbital is given by $\frac{1}{2}f''_\sigma$, and is rather accurately known (see formula (17)). This p_σ orbital is admixed into the (filled) Cu_2 orbital $\Psi(3z^2 - r^2)$ by an amount $(N'_\sigma \alpha_{\sigma 3} / \sqrt{3})^2$, see eq. (3). The value of $\alpha_{\sigma 3}$ can be estimated from the measured X(II) spin densities and calculated overlap integrals $S_{\sigma 3}$ and $S_{\sigma 1}$, as argued in section 6.2. Consequently, p_1 is given by $p_1 = \frac{1}{2}f''_\sigma f'_\sigma(\text{II}) S_{\sigma 3}^2 / S_{\sigma 1}^2$ which yields for the chlorine compounds $p_1 \approx 2.8 \times 10^{-5}$ and for the bromine compounds $p_1 \approx 3.9 \times 10^{-5}$. The probability that S_2 is present in the Cu_2 orbital $d(x^2 - y^2)$ is $p_2 = 1 - \sum f_i$, where the summation runs over all ligand orbitals, leading to $p_2 = 0.60$ for the chlorine compounds and $p_2 = 0.57$ for the bromine ones. Combining these values we obtain

$$J(\text{Aa})/k = +0.34 \text{ K} \quad (\text{chlorine compounds})$$

$$J(\text{Aa})/k = +0.45 \text{ K} \quad (\text{bromine compounds}).$$

Another contribution of type Aa runs via the X(I) p_x orbital, but since $f''_{\pi x} \ll f''_\sigma$ and $\alpha_{\pi 3} < \alpha_{\sigma 3}$, this

interaction is negligibly small.

For configuration Ab now the transfer f'_σ from the X(I) p_σ orbital into the half-filled Cu_2 orbital is of importance. In section 6.3 we estimated this quantity to be about $f' = 0.0001$. Consequently for this configuration we have $p_1 = \frac{1}{2}f''_\sigma f'_\sigma$. p_2 is the same as in the former case, thus

$$J(\text{Ab})/k \approx -0.02 \text{ K}$$

which is much smaller than the ferromagnetic contribution $J(\text{Aa})$.

Configurations of type B have to be considered both on oxygen, as well as on X(I). For case Ba on X(I) p_1 is given by $p_1 = \frac{1}{2}f''_\sigma$ and $p_2 = f'_{\pi x} + f'_{\pi z}$, resulting in

$$J(\text{Ba})/k \approx -0.004 \text{ K}.$$

Although contributions of the Ba type are ferromagnetic, yet a minus sign arises because $f'_{\pi x}$ and $f'_{\pi z}$ are negative (eq. (16)). For the corresponding configuration on oxygen, p_2 can be found by considering the unpaired electron transfer from $\Psi_2(x^2 - y^2)$ via X(I) p_σ into the water molecular orbital $\Psi(3a_1)$. This results in $p_2 = f'_\sigma (\frac{1}{2}W_3)$, see section 6.3. The probability p_1 is for this configuration $p_1 = f'_\pi(0)$. Since especially f'_σ but also $f'_\pi(0)$ are very small, this contribution is negligible.

For the Bb case on X(I) again $p_1 = \frac{1}{2}f''_\sigma$ and $p_2 = f'_\sigma$, leading to $J(\text{Bb})/k \approx -0.02 \text{ K}$. For the corresponding situation on oxygen we have again $p_2 = f'_\sigma (\frac{1}{2}W_3)$, but now p_1 is given by $p_1 = f'_\sigma(0)$, resulting in $J(\text{Bb})/k \approx -0.02 \text{ K}$. Together the Bb-type configurations give a contribution to the nearest-neighbour exchange interaction of $J(\text{Bb})/k \approx -0.04 \text{ K}$.

A second possible path between Cu_1 and Cu_2 is formed by the chain



About the strength of the X(II)– H_2O bonding we have no experimental information like we have about the X(I)– H_2O link. However, since none of the H_2O orbitals is directed towards the X(II) orbitals, the admixture between H_2O and X(II) orbitals has to be extremely small. Consequently no contributions of any importance to the exchange interaction over chain (22) can be expected.

The enumeration of nearest-neighbour exchange paths is completed with the chain



In this case, the covalency in all links can be appreciable. Even the link X(II)–X(I) will be somewhat covalent, since the $p_y(II)$ and $p_x(I)$ orbitals are directed approximately along the same line (parallel to the c axis). Inspecting the various exchange mechanisms for this chain it turns out that the probability p_1p_2 is nevertheless always small, since either the rather small transfer coefficient $f_{\pi y}(II)$ is involved, either one of the still smaller coefficients $f'_i(I)$, either both. Consequently also this third path is of no importance to the super-exchange interaction in these compounds. Summing all contributions to the nearest-neighbour exchange interaction we arrive at

$J_1/k = 0.28$ K in the chlorine compounds and

$J_1/k = 0.39$ K in the bromine compounds.

7.3. Further-neighbour super-exchange

Besides the super-exchange interaction J_1 between nearest neighbours the covalent bonds bring about also a super-exchange interaction between further neighbours. Whereas J_1 is equal for all eight nearest neighbours, J_2 for next-nearest neighbours along the c axis (for instance at (0,0,0) and (0,0,1)) differs from the interaction J'_2 between n.n. neighbours in the a – a plane (e.g. at (0,0,0) and (1,0,0)), because J_2 and J'_2 are established via quite different paths. The analysis of the contributions to these interactions is much more involved than those to J_1 because the number of intermediate ions in the exchange path is larger. Moreover, unlike to the nearest-neighbour exchange interaction, to the n.n.n. interactions no dominant contribution is present. In principle it is possible to trace all n.n.n. paths in the same way we did above but since there are both ferromagnetic as well as antiferromagnetic contributions of about equal strength the final result will be rather meaningless.

8. Discussion and conclusion

Summarizing we have found that by far the strongest contribution to the super-exchange interaction J_1 between nearest-neighbour copper ions is

established over the path $\Psi_1(x^2 - y^2) - \Psi(3a_1) - p_y(X(I)) - \Psi_2(3z^2 - y^2)$. It has been argued that this configuration gives a ferromagnetic contribution because it involves the interaction between the half-filled orbital $\Psi_1(x^2 - y^2)$ and the filled $\Psi_2(3z^2 - y^2)$ orbital. In the isostructural manganese compound $(NH_4)_2MnBr_4 \cdot 2H_2O$ all 3d orbitals are half-filled and consequently the exchange interaction is found to be antiferromagnetic. By the same reasons in this compound also the contributions arising from the Mn–Br(II)–Br(I)–Mn path are rather strong. The calculated J_1 values ($J_1/k = 0.28$ K and 0.39 K respectively for the chlorine and the bromine compounds) can be compared with experimental ones. From the T_c values, (table I) assuming $J_2/J_1 \approx 0.5$ [36], for the chlorine compounds on the average the value $J_1/k = 0.3$ K is found and for the bromine compounds $J_1/k = 0.5$ K. In view of the approximations made in our description of the covalency effects the agreement is more than satisfactory.

The small variation of T_c over the four chlorides cannot be explained simply. We have found that the transfer of unpaired spin S_1 from Cu_1 towards X(I), expressed in f''_{σ} is a constant within a few percent. The copper halide (I) distance is not expected to be equal in the four chlorine compounds, so the admixture of the p_y orbital in the copper $\Psi(3z^2 - r^2)$ orbital can be different. Unfortunately, detailed information about the Cu–X(I) distance over the series of compounds is not at hand. An extra complication arises from the influence of the alkali ions on the bonding scheme of X(I). This can be concluded from the fact that the variation of the quadrupolar interaction of the X(I) nuclei (and also of the X(II) nuclei) can only be explained when it is assumed that also a considerable amount of –paired rather than unpaired–charge is transferred over the various bonds [11]. Moreover, it is not unrealistic to suppose that the ratio J_2/J_1 is not the same in the four chlorine compounds because of the probably important role of the alkali ion in the next-nearest-neighbour exchange path. Consequently as long as no accurate measurement of J_1 and J_2 separately is possible the small variation of the Curie temperature remains hard to explain.

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