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Covalence in $CuCl_2 \cdot 2D_2O$ from neutron diffraction

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The magnetic neutron-diffraction data on $CuCl_2 \cdot 2D_2O$ have been reanalyzed using a model which incorporates covalence in the Cu—Cl and Cu—O bonding interactions, and local-density-approximation calculations have been performed on the molecule and its dimer to examine the validity of the model. It was found that the model leads to distinctly different conclusions about the ground-state wave function than do earlier treatments which assume an entirely ionic model perturbed by spin-orbit coupling. The degree of covalence in the bonding deduced is considerable, with only 80% of the spin remaining on the copper center. The calculations support the degree of covalence. In addition, by assuming the canting angles on the copper atom and on the ligands differ, we were able to model adequately the canting of the magnetic moment away from the *a* crystal-axis direction.

We are currently investigating the spin and charge densities in $M(\mathrm{II})(H_2O)_6$ and $M(\mathrm{II,III})Cl_4$ ions by means of polarized neutron diffraction (PND) and x-ray-diffraction experiments. In order to provide additional information in this area we reanalyze the neutron-diffraction data of Umebayashi *et al.*[1] on $CuCl_2 \cdot 2D_2O$.

The $CuCl_2 \cdot 2D_2O$ crystal is orthorhombic, *Pbmn*, with copper(II) ions at 0,0,0 and $\frac{1}{2},\frac{1}{2}$,0. The nuclear structure has been defined by neutron diffraction.[2] Each copper site is octahedrally coordinated by two water molecules and four chloride ions. The site symmetry is close to *mmm* with two chloride ions at 2.91 Å, two at 2.27, and water oxygen atoms at 1.93 Å. The chloride ions bridge copper atoms at 0,0,0 and 0,0,1, and each chloride ion has one long and one short bond to copper. In that way a chain structure along *c* is formed.

Below 4.33 K the crystal is antiferromagnetic. The Néel temperature,[3] the spin-flop transition,[4] and the antiferromagnetic resonance experiment[5] initially defined the phase. Neutron diffraction[1] confirmed the four sublattice canted antiferromagnet magnetic structure deduced earlier by Moriya.[6] Subsequent theoretical[7] and Cu NMR (Ref. 8) studies are in accord with that structure.

The magnetic moment at 0,0,0 is canted 6(1) deg (Ref. 8) away from *a* in the *a*-*c* plane, the 0,0,1 site moment is antiparallel, and the moment at $\frac{1}{2},\frac{1}{2}$,0 is canted at $-6(1)$ deg to *a* in the *a*-*c* plane. The fourth sublattice is centered at $\frac{1}{2},\frac{1}{2}$,1 and is antiparallel to that at $\frac{1}{2},\frac{1}{2}$,0. This arrangement completely separates the nuclear and the magnetic neutron-diffraction Bragg peaks into two sets. Magnetic reflections $(h,k,l+\frac{1}{2})$ with $(h+k)$ even sample the component of the moment parallel to *a* in the cell, and those with $(h+k)$ odd sample the component parallel to *c*. Thus the small canting moment component is also entirely separated from the dominant antiferromagnetic component along *a*. Umebayashi *et al.* also showed that the moment is dominated by spin in the Cu $3d_{x^2-y^2}$ orbital (*z* parallel to the long Cu—Cl bond). The canted moment had a more complex distribution. A contraction of 7% in the 3*d* radial distribution function for Cu was also noted.

Kirtane and Khan[9] reanalyzed the data on the compound. Their ionic model assumes no covalence in the bonding between copper and chlorine. The ground-state wave function contains four adjustable parameters, three of them related to the spin-orbit coupling. The latter set has been evaluated from the electron-spin-resonance (ESR) *g* tensor. They produce good agreement with the neutron data for small and reasonable values of the fourth parameter, which is the mixing coefficient for $3d_{z^2}$. However, the agreement may be misleading, given the large effects even small covalence can have on the ESR data,[10] and the consideration of our analysis and calculations below.

No previous attempt has been made to analyze the magnetic neutron-diffraction (MND) data for $CuCl_2 \cdot 2D_2O$ with the inclusion of covalent effects, notably spin transfers to ligands. We present the results of such an analysis, and they show significant covalence. In addition, we present the results of *ab initio* discrete variational $X\alpha$ calculations of spin and charge density in the compound and a related dimer. They show good agreement with the experimental covalence and the 3*d* spin distributions.

The data are not all on an absolute scale, so we have normalized the spin population in the compound to unity in the refinements discussed below.

Only 25 MND reflections were measured for $CuCl_2 \cdot 2D_2O$, so our choice of model for the magnetization density cannot be as flexible as it has been in other cases such as $CoCl_4^{2-}$,[11] where an extensive data set is available. For the 20 $(h+k)$-even data, we refined populations of the moment along *a*. These correspond to spherical functions on the three independent atoms of the ligands, Cl, O, and D, with, respectively, 3*p*, 2*p*, and 1*s* radial function dependence. On the copper center we refined $3d_{x^2-y^2}$ and $3d_{z^2}$ orbital occupation coefficients in a wave function. This implies that there are $3d_{x^2-y^2}$, $3d_{z^2}$, and $3d_{x^2-y^2}$-$3d_{z^2}$ mixing densities there. We also refined a parameter which defines the 3*d* radial extent. A correction for the orbital moment scattering based on the dipole approximation[12] with $g=2.19$ was used. Spin-orbit coupling also mixes the $3d_{xy,xz,yz}$ orbitals into the ground state with small coefficients (<0.1). Since the coefficients are small and there are no mixing cross terms there is negligible relativistic correction to the spin density from this source. This six-parameter model gave a fit to the data with $R=0.039$. Since the $(h+k)$-even data were presented without error estimates, a goodness of fit cannot be evaluated. The results of the refinement are listed in Table I. Refinement of this same $(h+k)$-even data without allowing for covalence (viz. the model of Umebayashi *et al.*) gave $R=0.070$, showing the importance of its effects.

For the five $(h+k)$-odd data, we refined populations of the moment along c. A contribution from a population on the D atoms was not included since the $(h+k)$-even refinement gave no significant population there. We obtained $R=0.12$ with a goodness of fit of 1.9. The value of R is higher than for the $(h+k)$-even data, reflecting the weakness of the data, and consequently relatively higher errors. The results of this refinement also are listed in Table I.

A variety of other test refinements were carried out, including varying the $3d$ configuration on the copper atom and using sp hybrid orbitals on the ligand atoms, but none were a significant improvement on the results given in Table I.

The discrete variational $X\alpha$ (DV-$X\alpha$) scheme has been described elsewhere in detail.[13–17] It employs numerical basis functions in the solution of an unconstrained Hartree-Fock-Slater (UHFS) local-density formalism. The Coulomb potential is approximated here by a monopole on each atom, viz. the self-consistent-charge method.

We employed basis functions $1s$-$4p$ on copper, $1s$-$3p$ on chlorine, $1s$-$2p$ on oxygen, and $1s$ on hydrogen, derived from numerical solutions of atomic calculations on Cu^{2+}, Cl^-, O, and H. This is a small set, but because of the numerical nature it is of about double-zeta quality in conventional parlance. It has produced semiquantitative results in a number of transition-metal complexes and crystals, such as FeF_2, NiF_2, $Cs_3Mo(NCS)_6$, $M(II)(H_2O)_6{}^{2-}$ ions, and $CuCl_4{}^{2-}$ complexes.[14,18–21] Here we calculated on a $CuCl_4(OH_2)_2{}^{2-}$ complex unit idealized to mmm symmetry, and also the triplet state of the dimer $Cu_2Cl_4(OH_2)_4$, with symmetry $2/m$, in the geometry of that fragment observed in the neutron-diffraction experiment on $CuCl_2\cdot 2D_2O$. The coordinates of the atoms are listed in Table II. 6000 and 9000 integration points were used, respectively, and frozen cores were employed, leaving active the $3d$, $4s$, and $4p$ orbitals on Cu, $3s$ and $3p$ on Cl, $2s$ and $2p$ on O, and $1s$ on H. Selected spin and charge populations from the calculation are given in Table III. Eigenvalues (with notes on the eigenvectors) are given in Table IV.

We discuss the $X\alpha$ calculation results first, since our purpose in performing them was to provide some justification for the model used for analyzing the experimental data. With the limited basis sets employed, although we should see all the major features, agreement with experiment can at best be semiquantitative.

The wave function of $CuCl_4(OH_2)_2{}^{2-}$ shows just the features expected from the bond lengths present in the structure. The long Cu—Cl bond has little effect, while the short Cu—Cl and Cu—O bonds are of roughly comparable importance. The net effect is to give an energy ordering for the $3d$-dominated molecular orbitals of $3d_{x^2-y^2} > 3d_{z^2} > 3d_{xz,xy,yz}$. The copper dimer shows the same ordering of the $3d$ orbitals, and approximate energy separations. In each case the positive-spin manifold is about 0.7–1.0 eV more stable than negative-spin, an effect expected given the spin hole which is equivalent to the $3d^9$ configuration.

Covalence is, however, marked in each case. Only 75–80% of the spin remains on the copper center. 6% of the spin is delocalized to each chlorine atom, and 4% to each water molecule, mainly onto the oxygen atom. Charge transfers between atoms show a similar pattern, with copper gaining $\sim 1e$, 0.33 from each chlorine atom and 0.17 from each water molecule. The covalent transfers from chlorine are evidently more than from water. The difference between the terminal chlorine atoms in the monomer and the bridging chlorine atoms in the dimer is significant, but does not alter these qualitative conclusions. We might expect similar results from a calculation which simulates the complete crystal.

TABLE I. Population and other parameters from refinements of the magnetic neutron-diffraction data on $CuCl_2\cdot 2D_2O$. Units of population: spins. r_{3d} is the effective radius of the $3d$ orbitals relative to a free Cu^{2+} ion.

Population	a moment		c moment
Cu $3d$	$3d_{x^2-y^2}$	0.81(2)	0.10(1)
	$3d_{z^2}$(constrained)	0.01	
	$3d_{z^2}$-$3d_{x^2-y^2}$ mixing	−0.24(7)	
	r_{3d}	0.79(3)	
Cl		0.054(32)	−0.085(24)
O		0.034(16)	−0.003(35)
D		0.001(12)	

TABLE II. Atomic coordinates used in the calculations (Å).

	x	y	z
	$CuCl_4(OD_2)_2{}^{2-}$		
Cu	0	0	0
Cl	2.279	0	0
Cl	0	0	2.922
O	0	1.931	0
H	0	2.476	0.778
	$Cu_2Cl_4(OD_2)_4$		
Cu	0	0	1.870
Cl	1.780	0	3.293
Cl	−1.780	0	0.477
O	0	1.931	0
H	0.609	2.476	2.354
H	−0.609	2.476	1.386

TABLE III. Selected spin and charge Mulliken populations from the calculations. Asterisk denotes net charge.

	Spin	Charge
$CuCl_4(OH_2)_2^{2-}$		
Cu $3d_{z^2}$	0.005	1.967
$3d_{x^2-y^2}$	0.763	1.203
$3d_{xy}$	0.000	2.000
$3d_{xz}$	0.000	2.000
$3d_{yz}$	−0.003	1.993
$3d_{z^2}$-$3d_{x^2-y^2}$ mixing	−0.150	0.030
Total $3d$ population	0.765	9.163
$4s$	0.005	0.373
$4p$	0.009	0.407
Total Cu	0.779	1.057*
Ligand		
Cl (long)	0.002	−0.892*
Cl (short)	0.068	−0.758*
O	0.022	−0.660*
H	0.007	0.390*
Total H_2O	0.037	0.120*
$Cu_2Cl_4(OH_2)_4$		
Cu $3d$ population	0.753	9.169
$4s$	0.003	0.416
$4p$	0.007	0.436
Total Cu	0.763	0.980*
Ligand		
Cl (bridging)	0.061	−0.662*
Cl (terminal)	0.088	−0.659*
O	0.030	−0.683*
H	0.006	0.424*
H	0.008	0.430*
Total H_2O	0.044	0.171*

TABLE IV. Calculated eigenvalues. For $CuCl_4(OH_2)_2^{2-}$ all values are between 3.3 and 9.6 eV. For $Cu_2Cl_4(OH_2)_4$ only the 10 eigenvalues with the highest Cu $3d$ participation are listed.

Symmetry label	Spin	Eigenvalue	Eigenvector
		$CuCl_4(OH_2)_2^{2-}$	
$2B_{3g}$	+	3.694	0.81 $3d_{yz}$
$4B_{1u}$	+	3.843	ligand
$4B_{1u}$	−	3.863	ligand
$4B_{2u}$	+	3.867	ligand
$4B_{2u}$	−	3.871	ligand
$2B_{3g}$	−	3.882	ligand
$3B_{3g}$	+	4.015	−0.59 $3d_{yz}$
$4B_{3u}$	+	4.100	ligand
$4B_{3u}$	−	4.103	ligand
$3B_{1g}$	+	4.150	0.94 $3d_{xy}$
$2B_{2g}$	+	4.156	0.83 $3d_{xz}$
$2B_{2g}$	−	4.221	ligand
$3B_{2g}$	+	4.228	0.39 $3d_{xz}$
$3B_{3g}$	−	4.719	0.98 $3d_{yz}$
$7A_{1g}$	+	4.764	0.76 $3d_{z^2}$, 0.21 $3d_{x^2-y^2}$
$3B_{2g}$	−	4.955	0.96 $3d_{xz}$
$3B_{1g}$	−	4.961	0.97 $3d_{xy}$
$8A_{1g}$	+	5.356	0.11 $3d_{z^2}$, −0.86 $3d_{x^2-y^2}$
$7A_{1g}$[a]	−	5.373	0.87 $3d_{z^2}$, 0.11 $3d_{x^2-y^2}$
$8A_{1g}$	−	6.050	0.06 $3d_{z^2}$, −0.90 $3d_{x^2-y^2}$

Symmetry label	Spin	Eigenvalue
	$Cu_2Cl_4(OH_2)_4$	
$11A_g$	+	−4.935
$7B_g$	+	−4.856
$8B_g$	+	−4.701
$12A_g$	+	−4.507
$11A_g$	−	−4.140
$7B_g$	−	−4.030
$8B_g$	−	−3.964
$12A_g$	−	−3.842
$13A_g$[a]	+	−3.333
$13A_g$	−	−2.663

[a] The highest occupied molecular orbital (HOMO).

The copper atom configuration shows large charge gains in the $4s$ and $4p$ orbital occupations, but these remain spin paired, giving little spin in these diffuse orbitals. The orbitals of approximately π symmetry ($3d_{xy,xz,yz}$) are almost ionic in composition. Apart from any necessary orthogonalization, the ligand-copper π interactions are not large. The orbitals with approximate σ symmetry interactions are more strongly perturbed by the covalence. The major effect is donation of charge into the empty $3d_{x^2-y^2}$ orbital from chlorine and water oxygen atoms. There is some mixing of the $3d_{z^2}$ orbital into the mainly $3d_{x^2-y^2}$ spin hole, resulting in an observable amount of $3d_{z^2}$-$3d_{x^2-y^2}$ mixing. This latter effect shows the rhombic distortion from tetragonal symmetry.

Spin-polarization effects associated with the covalence are thus small. This is a result of the relatively ionic bonding combined with the small energy difference between corresponding positive- and negative-spin orbitals, because the system is one with S only $\frac{1}{2}$. In other systems of higher spin or covalence, for example, $Cr(CN)_6^{3-}$ (Ref. 22) and cobalt(II) phthalocyanine,[23] spin polarization and differential covalence are much more marked.

Last, the $t_{2g} \rightarrow e_g$- lowest unoccupied molecular-orbital (LUMO) separations of 9500 (monomer) and mer) cm^{-1} agree as well as can be expected with the observed peak in the optical absorption spectrum at ~12 500 cm^{-1} (Ref. 24).

Given these $X\alpha$ results, in spite of the low local symmetry, we might expect a rather simple model, invoking only σ donation and $3d_{z^2}$-$3d_{x^2-y^2}$ mixing, to provide a relatively good model for the experimental spin density. The good fit to the $(h+k)$-even results confirms this. We see significant covalence, and a copper-atom spin population of 0.81(2) units. The spin does not appear as far out as the deuterium atoms, and, although at a low level of significance, the chlorine atom population is greater than that of oxygen. Such large covalence must render ionic models and theories of very limited validity.

The spin on the copper atom is in the $3d_{x^2-y^2}$ orbital, but we also find a $3d_{z^2}$-$3d_{x^2-y^2}$ mixing coefficient at a good level of significance. It is of negative sign, and of similar magnitude to that predicted in the $X\alpha$ calculation, demonstrating the greater covalence in the short Cu—Cl bond compared to the Cu—O bonds. The greater covalence reduces the density in the x lobe of the $3d_{x^2-y^2}$ orbital more than in the y lobe by transfer of spin to the ligand.

There are experimental features that the $X\alpha$ calculation does not predict. The effective radius of the $3d$ orbitals of the copper atom is 0.79(3) times that of a free Cu^{2+} ion. This difference may be due to the effects of ligation and covalence, to spin polarization of the ion, or to our neglect of orbital angular momentum. The latter phenomenon should contract the apparent $3d$ radius, as observed. We are not able to decide between the possibilities on the basis of our model calculation. If our $X\alpha$ basis functions were sufficiently flexible we might be able to see a theoretical contraction due to ligation and spin polarization, thus distinguishing covalency from orbital moment effects, as we noted above.

Another observed effect is in the $(h+k)$-odd data. The small c moment, positive on Cu, negative on Cl, and essentially zero on the water molecule, is sufficient to explain the data. A theoretical account of such a moment would require a relativistic calculation, since the canting is known to be due to spin-orbit coupling. It is, however, very interesting that the canting angle on Cl is much larger than, and of opposite sign to, that on Cu. The relative sizes of the moment bear no relation to the amount of covalence. If they did we would expect negligible c moment on all ligand atoms.

The canting angle on Cu has been deduced to be 6(1) deg by the Cu NMR experiment. Our present value of 7.0(8) deg agrees well with that.

Since complications such as π bonding and electron-electron correlation in the covalence appear to be unimportant here, an analysis of the ESR data should give reasonably reliable estimates of the covalence and mixing in the wave function. Moriya and Yoshida[25] analyzed the ESR data neglecting covalence. Buluggiu *et al.* included covalence in their analyses. They obtained five coefficients in a system of wave functions. If we transform these to our parameter set, we find their results predict a copper spin population of 0.69 in the $3d_{x^2-y^2}$ orbital, a $3d_{z^2}$-$3d_{x^2-y^2}$ mixing coefficient of -0.11, populations of 0.10 spin on the chlorine atoms and of 0.05 spin on the oxygen atoms, according to a Mulliken population analysis. The $3d_{xz}$ π-bonded population is predicted to be $1.88e$. These results agree well, in relative magnitudes, with both the *ab initio* calculation and our analysis of the MND data.

The small differences between the ESR and MND results probably reflect use of oversimplified modeling in both experiments. We believe that we have shown here that one should first explicitly consider covalence, and that spin-orbit effects are a further perturbation. The converse assumption of Kirtane and Khan[9] is based on the earlier ionic ESR analysis[25] and is contradicted by both the MND results, and by the present *ab initio* calculation.

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[1] H. Umebayashi, B. C. Frazer, D. E. Cox, and G. Shirane, Phys. Rev. **167**, 519 (1968).

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

[3] N. J. Poulis and G. E. G. Hardeman, Physica (Utrecht) **18**, 315 (1952).

[4] C. J. Gorter and J. Haantjes, Physica (Utrecht) **18**, 285 (1952).

[5] J. Ubbink, J. A. Poulis, H. J. Gerritsen, and C. J. Gorter, Physica (Utrecht) **18**, 361 (1952); **19**, 928 (1953).

[6] T. Moriya, Phys. Rev. **120**, 91 (1960).

[7] S. J. Joshua, Phys. Status Solidi **38**, 643 (1970).

[8] T. Kubo and H. Yamahaku, Phys. Rev. B **32**, 1831 (1985).

[9] S. M. Kirtane and D. C. Khan, J. Chem. Phys. **67**, 4711 (1977).

[10] E. Buluggiu, G. Dascola, D. C. Giori, and A. Vera, J. Chem. Phys. **54**, 2191 (1971).

[11] G. S. Chandler, B. N. Figgis, R. A. Phillips, P. A. Reynolds, and R. Mason, Proc. R. Soc. London, Ser. A **384**, 31 (1982).

[12] W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, Oxford, 1971).

[13] R. J. Deeth, B. N. Figgis, and M. I. Ogden, Chem. Phys. **121**, 115 (1988).

[14] D. E. Ellis and G. S. Painter, Phys. Rev. B **2**, 2887 (1970).

[15] A. Rosen, D. E. Ellis, H. Adachi, and F. W. Averil, J. Chem. Phys. **65**, 3629 (1976).

[16] J. C. Slater, in *Advances in Quantum Chemistry,* edited by P. O. Lowdin (Academic, New York, 1972).

[17] B. Delley and D. E. Ellis, J. Chem. Phys. **76**, 1949 (1982).

[18] R. J. Deeth, J. Chem. Soc. Dalton Trans. **1990**, 355.

[19] P. J. Brown, B. N. Figgis, and P. A. Reynolds, J. Phys. Condens. Matter (to be published).

[20] P. A. Reynolds and B. N. Figgis, Aust. J. Chem. **43**, 1097 (1990).

[21] G. S. Chandler, G. A. Christos, B. N. Figgis, and P. A. Reynolds (unpublished).

[22] B. N. Figgis, J. B. Forsyth, and P. A. Reynolds, Inorg. Chem. **26**, 101 (1987).

[23] P. A. Reynolds and B. N. Figgis, J. Am. Chem. Soc. (unpublished).

[24] M. A. Hitchman, J. Chem. Soc. **1970**, 4.

[25] T. Moriya and K. Yoshida, Prog. Theor. Phys. **9**, 663 (1953).