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Evidence for Hydrogen-Bond-Mediated Exchange Coupling in an Aqua-Bridged Cu^{II} Dimer: Synthesis, Magnetic Study and Correlation with Density Functional Calculations

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A rare example of a mono-aqua-bridged copper(II) dimer, namely $[Cu_2(\mu_2\text{-}H_2O)L_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**1**), has been synthesised and its structure determined by single-crystal X-ray diffraction. Each Cu^{II} centre is in a square-pyramidal surrounding formed by a Schiff base and a terminal H_2O ligand; a second H_2O ligand, which acts as a bridge, is common to two metal ions. Hydrogen bonds between the H_2O ligand and the Schiff base of the adjacent centre complete the intra-dimer linkages. This compound exhibits an antiferromagnetic behaviour ($J = -13.2\ \mathrm{cm^{-1}}$, $H = -J\boldsymbol{S}_1\cdot\boldsymbol{S}_2$), and density functional calculations clearly establish that the main exchange does not proceed through the bridging H_2O but is mediated by the intra-dimer H-bonds.

Introduction

Cu^{II} centres coordinated by an O,N,N-tridentate Schiff base derived from 2-hydroxyacetophenone and 2-(dimethylamino)ethylamine can form a variety of chelates by filling out the coordination environment, resulting in a square-planar, square-pyramidal or distorted square-bipyramidal polyhedron. Depending on the proportions and physicochemical properties of the co-ligands, monomeric, dimeric, oligomeric or polymeric crystal structures are formed. Several copper(II) dimeric complexes containing a singly hydroxo-bridged system[1,2] reveal that the hydroxo group acts commonly in the μ_2-O or μ_3-O bridging modes. The aqua ligand almost invariably exhibits the terminal mode in copper(II) complexes, although complexes for which H_2O acts as a bridge have been reported.[3–6]

There are only two Cu^{II} complexes having a single aqua bridge in the CSD (July 2004). Interestingly, it has been shown that such a bridge can induce spin-exchange interactions between the linked Cu^{II} centres.[3]

In our earlier articles, we have reported a mononuclear Cu^{II} complex, its ferrocyanide-bridged pentanuclear complex[7] and a mononuclear Co^{II} complex,[8] all containing the same Schiff base (LH), where the Schiff base acts as a tridentate chelating ligand. Here, the synthesis, structure, spectral properties and the magneto-structural correlation studies of the complex $[Cu_2(\mu_2\text{-}H_2O)L_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**1**) are reported. An exchange interaction between the Cu^{II} ions was found, and density functional calculations clearly establish that the main exchange does not proceed through the bridging H_2O but is mediated by the intra-dimer H-bonds.

Results and Discussion

The complex $[Cu_2(\mu_2\text{-}H_2O)L_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**1**) was synthesised by mixing an aqueous solution of copper(II) perchlorate with a methanolic solution of the Schiff-base ligand LH, which was obtained by the condensation of 2-hydroxyacetophenone and 2-(dimethylamino)ethylamine.

Crystal Structure of Complex 1

Complex **1** contains a cationic dimeric unit consisting of two $\{Cu(L)(H_2O)\}^+$ moieties bridged by one water molecule. The dinuclear cation is positioned on the twofold rotation axis of the unit cell (orthorhombic, *Fdd*2), which is shown in Figure 1. The two perchlorate counterions present in the lattice show threefold disorder. The unique Cu^{II} atom adopts a (4+1) square-pyramidal geometry, formed by an O,N,N-tridentate Schiff base and an O atom of a water

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molecule in the basal plane. The apical position is occupied by the oxygen atom (O3) of the bridging water molecule. The resulting dimer, which contains one bridging water molecule, is reinforced by intra-dimer H-bonds between the H_2O ligand (O2) in an equatorial position and the phenolate O atom (O1) of the adjacent Cu^{II} unit [O1···O2 = 2.627(9) Å; Figure 2 and Table 1]. A number of intermolecular hydrogen bonds are also formed between the dimeric cations, the solvate H_2O molecules and the ClO_4^- ions. The coordination polyhedra of the two central Cu^{II} atoms in **1** are uniformly square-pyramidal. The equatorial Cu1–O2(water) bond length in the basal plane of the pyramid is decreased to 1.980(8) Å (see Table 2) and the apical Cu1–O3 bond length is increased to 2.496(7) Å, resembling a Jahn–Teller effect. The Cu–O(water) lengths are comparable to the average lengths (1.95 and 2.43 Å) of these bonds in related Cu complexes reported in the Cambridge Structural Database (version 5.25.3). The Cu1–N2(imine) bond is shorter [1.959(8) Å] than the Cu1–N1(amine) bond [2.018(9) Å].

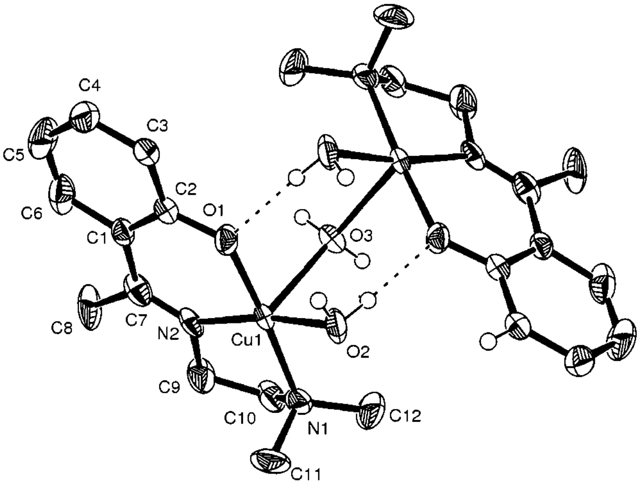

Figure 1. ORTEP view of the dinuclear cation of **1** positioned on the twofold axis of the unit cell.

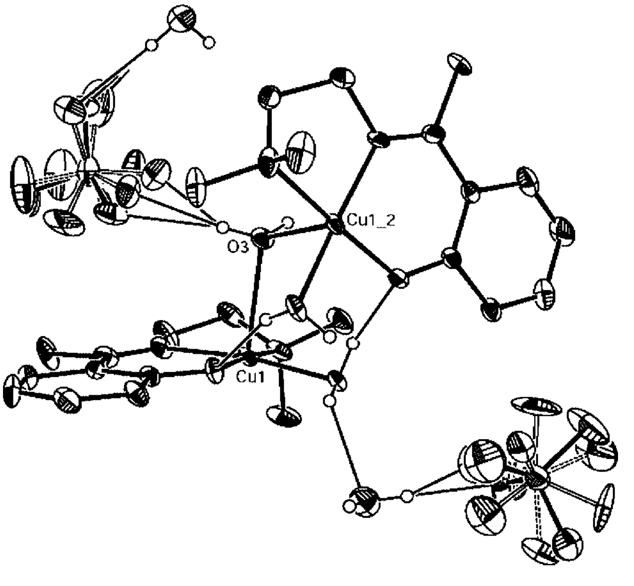

Figure 2. View of the hydrogen bonding (thin lines) in compound **1** (ClO_4^- is threefold disordered).

Table 1. Hydrogen bonds for complex **1**.

D–H···A[a]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O(2)–H(2A)···O(8)	0.85	2.13	2.644(14)	118.9
O(2)–H(2B)···O(1)#1	0.85	1.81	2.627(9)	161.1
O(3)–H(3)···O(4A)#1	0.85	2.27	3.101(18)	165.9
O(3)–H(3)···O(4B)#1	0.85	2.09	2.72(5)	129.7
O(3)–H(3)···O(4C)#1	0.85	2.04	2.88(2)	168.0
O(8)–H(8D)···O(4B)#2	0.85	2.66	3.24(12)	127.2
O(8)–H(8D)···O(6A)#2	0.85	1.91	2.76(14)	178.8
O(8)–H(8D)···O(6B)#2	0.85	2.19	3.04(14)	177.3
O(8)–H(8D)···O(6C)#2	0.85	1.66	2.46(13)	156.2
O(8)–H(8E)···O(4B)#3	0.85	2.48	3.25(9)	152.3
O(8)–H(8E)···O(7A)#3	0.85	1.75	2.54(10)	152.5
O(8)–H(8E)···O(7C)#3	0.85	2.21	2.90(11)	137.5
O(8)–H(8E)···O(5B)#3	0.85	2.65	3.34(11)	140.0

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 2, -y, z$; #2: $-x + 2, -y, z - 1$; #3: $x, y, z - 1$. The O atoms belonging to ClO_4^- are O(4), O(5), O(6) and O(7).

The phenoxo oxygen atom (O1) is deprotonated, producing a negative charge on the Schiff-base moiety. The square base of each polyhedron is nearly planar, with the Cu atoms being shifted by 0.1171 Å from the mean plane containing the four basal atoms in the direction of the oxygen atom (O3) of the bridging water molecule. The least-squares deviations of the basal atoms from their mean plane are –0.0414, 0.0421, –0.0420 and 0.0414 Å for N1, N2, O1 and O2, respectively. The benzene ring and the six-membered metallochelate ring are puckered. The dihedral angle between the planes of the six-membered and five-membered metallochelate rings is 6.32°. The Cu–Cu distance in the dimer is 4.079 Å.

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**.

Cu(1)–O(1)	1.870(7)	O(1)–C(2)	1.322(11)
Cu(1)–N(2)	1.959(8)	O(2)–H(2A)	0.850
Cu(1)–O(2)	1.980(8)	Cl(1)–O(5C)	1.383
Cu(1)–N(1)	2.018(9)	Cl(1)–O(4B)	1.394
Cu(1)–O(3)	2.496(7)	Cl(1)–O(5A)	1.396
		Cl(1)–O(7A)	1.400
O(1)–Cu(1)–N(2)	92.9(3)	O(2)–Cu(1)–N(1)	89.7(4)
O(1)–Cu(1)–O(2)	90.2(3)	O(1)–Cu(1)–O(3)	87.4(3)
N(2)–Cu(1)–O(2)	170.2(3)	N(2)–Cu(1)–O(3)	96.5(3)
O(1)–Cu(1)–N(1)	175.6(4)	O(2)–Cu(1)–O(3)	93.0(3)
N(2)–Cu(1)–N(1)	86.5(4)	N(1)–Cu(1)–O(3)	97.1(3)
Cu(1)–O(3)–H(3)	108.0	Cu(1)–O(3)–Cu(1)#1	109.6(4)

The perchlorate counterion shows threefold disorder. The disordered perchlorate counterion, the two lattice waters as well as the coordinated terminal and bridging water molecules are extensively hydrogen-bonded. The multiple hydrogen bonds are shown in Figure 2 and the interactions are listed in Table 1.

Spectroscopic Properties

The IR spectrum of complex **1** shows a sharp band at 1600 cm^{-1} assigned to the δ(H–OH) mode. Again, a band at 410 cm^{-1} may be assigned to the $\rho_W(H_2O)$ mode and the bands at 846 and 857 cm^{-1} to the $\rho_r(H_2O)$ vibrations, thereby showing presence of both coordinated and uncoordinated lattice water in the complex.[9] This also confirms the presence of hydrogen bonding in the complex.[10] The strong $\nu_{C=N}$ band occurring at 1635 cm^{-1}, which is shifted considerably towards lower frequencies compared to that of the free Schiff base (1650 cm^{-1}), suggests coordination of the imino nitrogen atom. The phenolic stretching band is found at 1258 cm^{-1}. The band at 1160 cm^{-1} for the $\nu_3(F_2)$ ClO_4^- mode is broadened and split, thus indicating the involvement of this anion in hydrogen bonding, as established from the X-ray analysis.[11] Ligand coordination to the metal centre is substantiated by two bands appearing at 405 and 332 cm^{-1} for $\nu_{M–N}$ and $\nu_{M–O}$, respectively.

The electronic spectroscopic data for **1** in acetonitrile solvent are in good agreement with its geometry. A charge-transfer transition (CT) in the range 400–360 nm may be assigned to a ligand-to-metal charge-transfer transition. Much weaker, less well-defined shoulders are found in the lower energy region and are associated with d–d transitions. The d–d bands generally fall below 700 nm and are more consistent with a square-pyramidal geometry for **1**, as in certain related Cu^{II} complexes.[12]

Magnetic Properties

The temperature dependence of the molar magnetic susceptibility, χ_M, for compound **1** was measured on a polycrystalline sample in the temperature range 2–300 K. The plot of $\chi_M T$ vs. T for the dinuclear Cu^{II} compound is shown in Figure 3. At 300 K the value of $\chi_M T$ is 0.76 cm^3 K mol^{-1}, in good agreement with the value expected for two non-interacting Cu^{II} ions. This value decreases very slightly as the temperature is lowered to 100 K, and below this temperature it decreases rapidly to reach 0.03 cm^3 K mol^{-1} at 2 K, thereby revealing the occurrence of antiferromagnetic interactions between the Cu^{II} centres. A classical Bleaney–Bowers law, using the phenomenological Hamiltonian $H = -J\boldsymbol{S}_1\cdot\boldsymbol{S}_2$, is suitable to simulate the magnetic behaviour for compound **1**, the resulting expression for $\chi_M T$ is given below. The best fit of this expression to the experimental data yields the exchange parameter $J = -13.23 \pm 0.01$ cm^{-1} with $g = 2.03$.

$$\chi_M T = \frac{2Ng^2\beta^2}{k[3 + \exp(-J/kT)]}$$

The structural data for compound **1** indicate that the bridging H_2O ligand is connected in an apical position to both the linked Cu ions. As a consequence, there is no overlap with the magnetic orbitals of the metal centres and the exchange interaction through this bridging ligand is expected to be very weak.[13] The magnitude found for J is thus surprisingly high and suggests the occurrence of alternative exchange pathways. In order to clarify the origin of this magnetic coupling, density functional calculations were carried out.

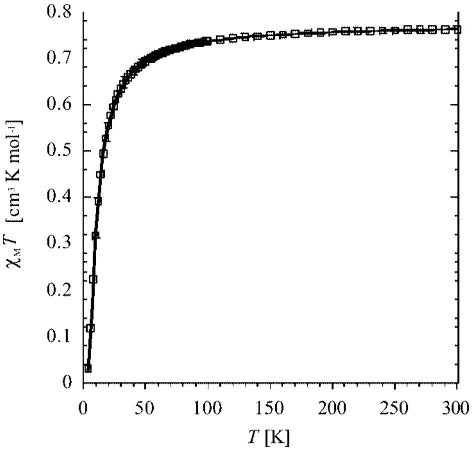

Figure 3. Experimental (□) and calculated (−) temperature dependence of $\chi_M T$ for compound **1**.

Computational Methodology for the Density Functional Calculations

The calculated coupling constant, J, was deduced from two separate density functional computations carried out for the highest-spin state (triplet state for compound **1**) and for the broken-symmetry state. The hybrid B3LYP[14] functional was used, as implemented in Gaussian98.[15] The basis set used in all calculations was the triple-ζ basis-set proposed by Ahlrichs et al.[16] for transition metals and the double-ζ basis set proposed by the same authors for the other atoms.[17] The obtained J values were deduced from the energy difference $E_{HS} - E_{BS} = -J$, where E_{HS} and E_{BS} are the energies of the high-spin and broken-symmetry states, respectively. We consider that the energy of the broken-symmetry state is a good approximation of the low-spin state energy, according to Ruiz et al.[18] The spin densities on the atoms were calculated according to the NBO method.[19]

DFT Calculations for Compound 1

Sets of calculations were carried out for the whole Cu dimer of compound **1** and for the same dimer but without the bridging H_2O molecule. The isotropic interaction parameters that were obtained in both cases were very similar (J = –8.1 and –7.9 cm^{-1}, respectively), in rather good agreement with the experimental exchange parameter. The spin

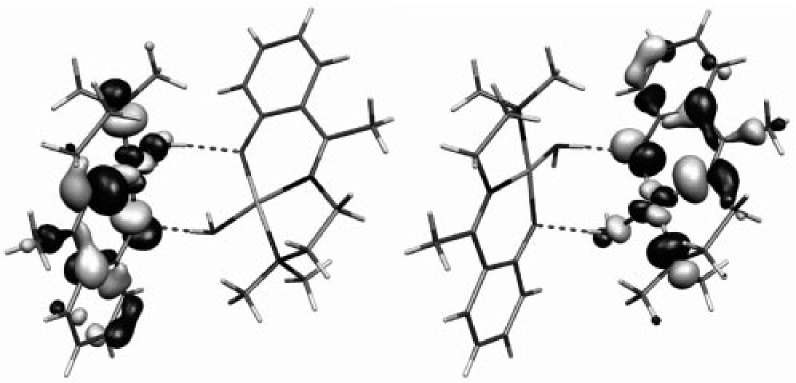

Figure 4. Localised magnetic orbitals issuing from the broken symmetry of the dehydrated compound.

density found on the two equivalent copper atoms is +0.577, whereas that located on the oxygen atoms is +0.116 for O1, +0.051 for O2 and –0.0007 for O3.

The negligible spin density on the bridging oxygen atom is in line with the very small difference in the calculated *J* values for a dimer with and without a bridging H_2O ligand. This result clearly confirms that the bridging water molecule is in no way responsible for the magnetic behaviour exhibited by the complex. In order to rationalise this behaviour, the localised magnetic orbitals issuing from the broken-symmetry state were scrutinised. These orbitals are represented in Figure 4 for the complex without the bridging H_2O ligand (those of the H_2O-bridged system have exactly the same shapes). As expected from simple ligand-field models, the magnetic orbitals are directed towards the four short Cu–N/O distances. Indeed, in a square-pyramidal environment (C_{4v} point group), the five d orbitals split into four sets: d_{xz} and d_{yz} (e); d_{yx} (b_2); d_{z^2} (a_1); and $d_{x^2-y^2}$ (b_1). As it is the only orbital involved in four bonds, the $d_{x^2-y^2}$ orbital has the highest energy and is singly occupied in a d^9 configuration. This explains the negligible influence of the bridging water molecule, which is in an apical position and therefore has no overlap with the magnetically active orbitals of the Cu^{II} ions. Conversely, a significant amount of spin density is found on the oxygen atoms located in the equatorial positions (O1 and O2). The hydrogen bonds linking these atoms within a dimer (dashed lines in Figure 4) may thus provide an alternative pathway for the magnetic interaction between the two Cu^{II} centres.[20] As a matter of fact, doubly H-bridged copper dimers can exhibit experimental coupling constants between limiting values of –4[21] and –94 cm^{-1}.[22] Different intermediate values have also been reported,[23] as well as density functional calculations on these dimers.[24] For compound **1**, the relatively weak exchange interaction is essentially due to the fact that the two basal planes of the copper geometry are not coplanar. This reduces the overlap of the magnetic orbitals, which causes decreased interactions between the two coppers centres.

This study clearly establishes that the main exchange interaction for compound **1** proceeds through the hydrogen bonds existing within the dimer, whereas the H_2O ligand bridging the two Cu ions has a poor contribution.

Conclusions

A rare example of a [(Schiff-base)Cu^{II}] dimer with a single H_2O ligand bridging the two metal ions has been characterised. A striking feature of this compound is the absence of the μ_2-coordination of the phenolato oxygen atoms often observed for such compounds. Instead, these atoms are involved in hydrogen bonds with the adjacent Cu unit, which reinforce the cohesion of the dimer. These hydrogen bonds are also the pathway for the antiferromagnetic interaction (J = –13.2 cm^{-1}) between the Cu centres of the dimer. This is strongly supported by density functional calculations, which show that the contribution of the H_2O bridge is negligible.

Experimental Section

Materials: 2-Hydroxyacetophenone, 2-(dimethylamino)ethylamine and copper perchlorate were used as supplied by Aldrich. All other chemicals or solvents used were of reagent or analytical grade and used without further purification.

Synthesis of the Ligand and Complex: ***Caution!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of the material should be prepared and should be handled with caution*. The ligand LH was prepared by refluxing 2-hydroxyacetophenone (0.60 mL, 5 mmol) and 2-(dimethylamino)-ethylamine (0.545 ml, 5 mmol) in methanol (30 mL) for 0.5 h. The resulting mixture gave a yellow solution containing the tridentate ligand (LH). The ligand was used without further purification. The complex $[Cu_2(\mu_2\text{-}H_2O)L_2(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**1**) was prepared by slowly adding 10 mL of a methanolic solution of LH (2 mmol) to 20 mL of an aqueous solution of copper(II) perchlorate (0.740 g, 2 mmol). The mixture was kept at room temperature. After a few days, green crystals of **1** had formed on slow evaporation of the solvent. Crystals suitable for X-ray diffraction were collected. Yield: 0.541 g (65%). $C_{24}H_{44}Cl_2Cu_2N_4O_{15}$ (826.61): calcd. C 34.9, H 5.4, N 6.8; found C 34.2, H 5.3, N 6.1.

Physical Measurements: Elemental analyses were carried out using a Perkin–Elmer 2400 II elemental analyser. The IR spectrum was recorded with a Perkin–Elmer Spectrum RX FTIR instrument in the range of 4000–350 cm^{-1} as KBr pellets. The electronic spectrum was measured with a Perkin–Elmer Lambda-40 (UV/Vis) spectrophotometer in dichloromethane. Magnetic susceptibility measurements were carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe. Magnetic data were corrected for diamagnetic contributions estimated from Pascal tables and for the sample holder contribution.

X-ray Data Collection and Structure Refinement: Single crystals of the copper complex (0.29 × 0.22 × 0.04 mm) were grown from a methanol/water medium. Diffraction measurements were carried out at 153(2) K with an Enraf–Nonius CAD-4 MACH 3 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å): orientation matrices and unit-cell parameters from the setting angles of 25 centred medium-angle reflections; collection of the diffraction intensities by ω scans. The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms by employing the WinGX package[25] and the relevant programs (SIR-97,[26] SHELXL-97,[27] ORTEP-3[28]) implemented therein. All hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with isotropic displacement parameters fixed at 1.2-times U_{eq} of their parent atoms. $C_{24}H_{44}Cl_2Cu_2N_4O_{15}$ (826.61); orthorhombic, *Fdd*2, a = 18.853(4), b = 36.452(8), c = 9.816(2) Å, V = 6746(2) Å^3, Z = 8, $d_{calcd.}$ = 1.628 Mg m^{-3}, μ(Mo-K_α) = 1.493 mm^{-1}; F(000) = 3424; 2.23° ≤ Θ ≤ 25.56°, 2482 reflections collected ($-2 \le h \le 22$, $-2 \le k \le 44$, $-2 \le l \le 11$; including Friedel pairs), 2075 independent reflections (R_{int} = 0.0988); Completeness to θ = 25.56°: 100.0%; absorption correction: none; 267 parameters and 121 restraints (ClO_4^- anion as geometrically idealised tetrahedron); final R indices [$I > 2\sigma(I)$]: R_1 = 0.0629, wR_2 = 0.1738; R indices (all data): R_1 = 0.0825, wR_2 = 0.1853; absolute structure parameter x = –0.01(4);[29] largest difference peak/hole: 0.844/–1.478 e Å^{-3}. CCDC-279057 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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