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Communication

Ferromagnetic Coupling by Orthogonal Magnetic Orbitals in a Heterodinuclear $Cu^{II}V^{IV}{=}O$ Complex and in a Homodinuclear $Cu^{II}Cu^{II}$ Complex

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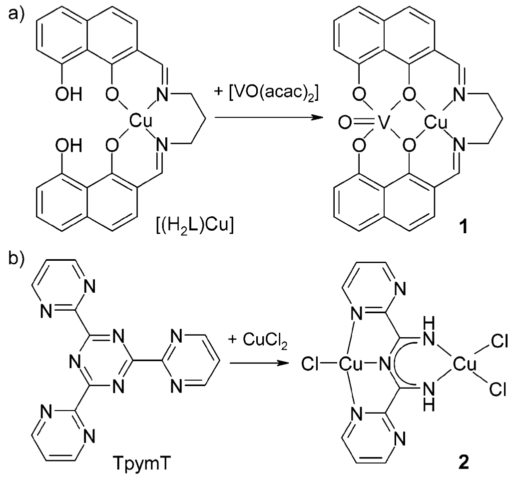
The heterodinuclear complex $[LCu^{II}V^{IV}O]$ **1** was synthesized by using a new unsymmetric dinucleating ligand based on 1,8-naphthalenediol, whereas the homodinuclear $Cu^{II}Cu^{II}$ complex **2** has a bridging β-diketimineamid unit. Here we report on the synthesis, molecular structures, and magnetic properties of **1** and **2**. In the solid state, both complexes dimerize to tetranuclear entities $\mathbf{1}_2$ and $\mathbf{2}_2$. The intradimer interaction in both complexes is ferromagnetic because of the orthogonality of the magnetic orbitals (J_{12} = +45.6 cm^{-1} in **1** and +4.8 cm^{-1} in **2**). The interdimer interaction in **1** is also ferromagnetic, giving a $S_t = 2$ ground state.

The synthesis of molecule-based magnets has attracted considerable interest since the discovery of a molecular compound exhibiting a spontaneous magnetization below a critical temperature.[1] As Kahn emphasized, parallel alignment of neighboring spins is essential for the design of a molecule-based magnet.[2] To establish recipes for parallel spin alignments, we are exploring three different strategies: the spin-polarization mechanism[3] in *m*-phenylene-bridged complexes,[4] the double-exchange mechanism[5] in face-sharing octahedra,[6] and the use of orthogonal magnetic orbitals.[7] In this Communication, the usefulness of the last concept to enforce ferromagnetic interactions is exemplified for both hetero- and homodinuclear complexes.

Scheme 1



We have synthesized the "ring- and donor-increased" derivative of salen-like ligands based on the 1,8-naphthalenediol backbone H_4L to mimic and to study (a) the cooperative action of proximate metal ions as in metalloenzymes[8] and (b) the presence of an electrophilic and a nucleophilic site in metal–salen-derived catalysts.[9] The dinuclear $Cu^{II}Cu^{II}$ complex with this ligand exhibits antiferromagnetic spin coupling with a coupling constant of $J = -371$ cm^{-1}.[10] By reacting H_4L with 1 equiv of a Cu^{II} salt, we obtained the mononuclear complex $[(H_2L)Cu^{II}]$ (Scheme 1a) with the Cu^{II} ion coordinated by the N_2O_2 compartment. The noncoordinated OH groups of the empty O_4 compartment form strong H bonds with the O atoms coordinated to the Cu^{II} ion, resulting in a destabilization of the Cu^{II} oxidation state by 270 mV.[11]

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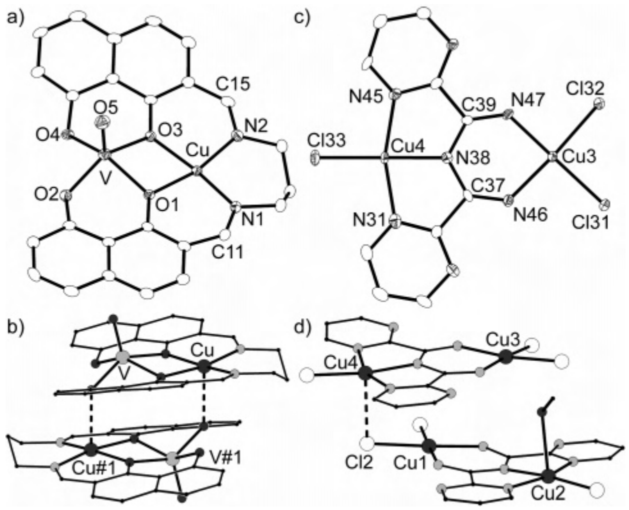

Figure 1. (a) Molecular structure of [LCuVO] **1**. (b) Dimer of dimers $\mathbf{1}_2$. (c) Molecular structure of one of the dimers [L′Cu_2Cl_3] in [{L′Cu_2Cl_3}{L′Cu_2Cl_3(MeOH)}]. (d) Dimer of dimers [{L′Cu_2Cl_3}{L′Cu_2Cl_3(MeOH)}]. 50% ellipsoids and H atoms were omitted for clarity. Selected interatomic distances (Å): **1**, Cu−N1 = 1.955(2), Cu−N2 = 1.961(3), Cu−O3 = 1.974(2), Cu−O1 = 1.991(2), Cu−O4#1 = 2.430(2), Cu−V = 3.0891(8), V−O5 = 1.597(2), V−O2 = 1.890(2), V−O4 = 1.935(2), V−O1 = 1.990(2), V−O3 = 2.004(2), N1−C11 = 1.286(4), N2−C15 = 1.282(4); **2** (**2**·MeOH), Cu3−Cl31 = 2.251(2) (2.230(2)), Cu3−Cl32 = 2.261(2) (2.296(2)), Cu3−N46 = 1.969(7) (1.975(6)), Cu3−N47 = 1.947(6) (1.950(7)), Cu4−Cl33 = 2.198(2) (2.209(2)), Cu4−N31 = 2.037(7) (2.003(7)), Cu4−N38 = 1.964(7) (1.962(6)), Cu4−N45 = 2.038(7) (2.030(7)), Cu4−Cl2 = 2.755(2) (Cu2−O20 = 2.415(6)).

By reacting [(H_2L)Cu^{II}] with 1 equiv of [VO(acac)$_2$],[12a] we obtained the dinuclear complex [L$Cu^{II}V^{IV}$O] **1** (Scheme 1a). The molecular structure of **1** is shown in Figure 1a.[13] The N_2O_2 ligand compartment is occupied by Cu^{II}, while the O_4 compartment hosts a V^{IV}═O unit with a short V−O bond distance of 1.60 Å. Two dinuclear complexes **1** dimerize by weak apical copper−aryl oxide interactions (Cu−O4#1 = 2.43 Å) to a tetranuclear entity $\mathbf{1}_2$ (Figure 1b). The vanadyl O atoms are not involved in this dimerization.

We have utilized substituted 1,3,5-trihydroxybenzene (phloroglucinol) derivatives to synthesize trinuclear complexes with ferromagnetic interactions based on spin polarization.[4] To extend our approach to 1,3,5-triazabenzene (triazine) bridged systems, we changed to 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) but obtained only a dinuclear triazine-bridged $Cu^{II}Cu^{II}$ complex in which two pyridyl side arms form a terpyridine-like compartment while the third pyridyl side arm forms only a bipyridine-like compartment.[14] To provide three *m*-phenylene-bridged terpyridine-like compartments, we have turned our attention to 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TpymT).[15,16] However, in contrast to our experiences with tptz, we obtained by the reaction of TpymT with $Cu^{II}Cl_2$·$2H_2O$ the hydrolytic product **2** (Scheme 1b and Figure 1c).[12b,13] Hydrolytic cleavages of triazine derivatives catalyzed by metal coordination have been frequently observed.[16,17] Interestingly, the bridging *β*-diketimineamid unit results in a relative rotation of the two local Cu coordinate systems by 45°. In the solid state, two dinuclear complexes **2** dimerize through a weak Cu4−Cl2 interaction in combination with one molecule of MeOH to a tetranuclear assembly $\mathbf{2}_2$·MeOH (Figure 1d). The dimers

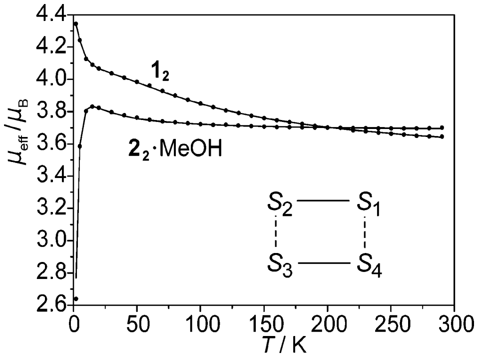

Figure 2. Temperature dependence of μ_{eff} calculated for the tetranuclear assemblies $\mathbf{1}_2$ and $\mathbf{2}_2$·MeOH at 1 T. The solid lines are fits to the experimental data using the appropriate spin Hamiltonian. $\mathbf{1}_2$: $J_{12} = +45.6$ cm^{-1}, $J_{23} = +0.55$ cm^{-1}, $g_1 = 1.89$, $g_2 = 2.11$, $\theta = +0.15$ K, $\chi_{TIP} = 300 \times 10^{-6}$ cm^3 mol^{-1}. $\mathbf{2}_2$·MeOH: $J_{12} = +4.8$ cm^{-1}, $J_{23} = -2.5$ cm^{-1}, $g_1 = g_3$, $g_2 = g_4 = 2.124$, $\chi_{TIP} = 290 \times 10^{-6}$ cm^3 mol^{-1}. The values for χ_{TIP} have been subtracted from the experimental and theoretical data.

exhibit slight differences especially in the interatomic Cu−Cl distances. However, the Cu−N bond distances of the bridging units differ by less than 0.01 Å.

The magnetic susceptibilities were measured in the temperature range 2−290 K for $\mathbf{1}_2$ and $\mathbf{2}_2$·MeOH. Both complexes show an increase of the effective magnetic moment μ_{eff} with decreasing temperature, demonstrating the presence of ferromagnetic interactions (Figure 2). Simulations of the data using a dimer model were not successful in both cases. The sharp increase of μ_{eff} for complex $\mathbf{1}_2$ below 10 K and the steep drop of μ_{eff} for complex $\mathbf{2}_2$·MeOH indicate additional ferromagnetic and antiferromagnetic interactions,

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(12) (a) **[LCuVO] 1.** To a stirred solution of [(H_2L)Cu] (156 mg, 0.33 mmol) in CH_2Cl_2 (100 mL) was added a solution of [VO(acac)$_2$] (87 mg, 0.33 mmol) in EtOH (25 mL). The mixture was heated at reflux for 4.5 h. After cooling to room temperature, the solution was filtered. Evaporation of the solvent caused the deposition of green crystals, which were dried under vacuum (100 mg, 50%). Anal. Calcd for $C_{25}H_{18}O_5N_2CuV$·$0.8CH_2Cl_2$ (608.86): C, 50.90; H, 3.24; N, 4.60. Found: C, 50.79; H, 3.74; N, 4.44. MS (MALDI-TOF): *m/z* 540 [M]$^+$. FT-IR (KBr): $\tilde{\nu}$/cm^{-1} 3059w, 2928w, 2851w, 1632m, 1604s (C═N), 1547m, 1502w, 1425m, 1359s, 1342w, 1323w, 1266m, 1239m, 1147m, 1053s, 976m (V═O), 823m, 768w, 727m, 714m, 688w, 656w, 425w. (b) **[L′Cu_2Cl_3]$_2$·MeOH $\mathbf{2}_2$·MeOH.** A suspension of TpymT (124 mg, 0.39 mmol) and $CuCl_2$·$2H_2O$ (1.01 g, 5.9 mmol) in MeOH (160 mL) was stirred at 40 °C until a green solution resulted. This solution was filtered while still hot. Evaporation of the solvent caused the deposition of dark-blue crystalline needles (32 mg, 17%). Anal. Calcd for $C_{21}H_{20}Cl_6Cu_4N_{14}O$ (951.37): C, 26.51; H, 2.12; N, 20.61. Found: C, 26.33; H, 2.42; N, 20.55. MS (MALDI-TOF): *m/z* 424 [L′Cu_2Cl_2]$^+$. FT-IR (KBr): $\tilde{\nu}$/cm^{-1} 3319m, 3300m, 3280m, 3065w, 1637s (C═N), 1582s, 1557s, 1485s, 1437m, 1401s, 1381s, 1249m, 1187w, 1090m, 1058w, 1017m, 824m, 692s, 677m, 653w.

(13) Crystallographic data: $C_{27}H_{22}Cl_4CuN_2O_5V$ (**1**·$2CH_2Cl_2$), $M = 710.75$, $a = 9.8577(15)$ Å, $b = 12.6070(19)$ Å, $c = 13.008(2)$ Å, $\alpha = 101.433(3)°$, $\beta = 111.687(3)°$, $\gamma = 108.967(3)°$, $V = 1324.2(3)$ Å^3, $Z = 2$, space group $P\bar{1}$, $T = 123(2)$ K, $\lambda = 0.710\,73$ Å, $D_{calcd} = 1.783$ g cm^{-3}, $\mu = 1.604$ mm^{-1}, $R(F_o^2) = 0.0434$, $R_w(F_o^2) = 0.1124$; $C_{21}H_{20}Cl_6Cu_4N_{14}O$ ($\mathbf{2}_2$·MeOH), $M = 951.37$, $a = 6.9771(4)$ Å, $b = 21.6972(14)$ Å, $c = 20.3740(12)$ Å, $\beta = 96.124(6)°$, $V = 3066.7(3)$ Å^3, $Z = 4$, space group $P2_1/c$, $T = 100(2)$ K, $\lambda = 0.710\,73$ Å, $D_{calcd} = 2.061$ g cm^{-3}, $\mu = 3.306$ mm^{-1}, $R(F_o^2) = 0.0703$, $R_w(F_o^2) = 0.1553$.

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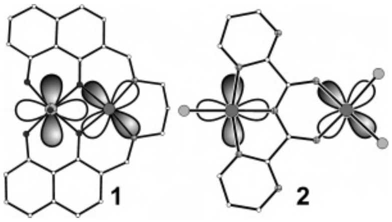
Chart 1



respectively. The magnetic properties could be analyzed by using the isotropic Heisenberg−Dirac−van Vleck (HDvV) exchange Hamiltonian and single-ion Zeeman interactions as given in eq 1 (full-matrix diagonalization).

$$H = H_{\mathrm{HDvV}} + \sum_{i}^{4}[\mu_{\mathrm{B}} g_i \mathbf{S}_i \mathbf{B}]$$

$$H_{\mathrm{HDvV}} = -2J_{12}\mathbf{S}_1\mathbf{S}_2 - 2J_{23}\mathbf{S}_2\mathbf{S}_3 - 2J_{34}\mathbf{S}_3\mathbf{S}_4 - 2J_{41}\mathbf{S}_4\mathbf{S}_1 \quad (1)$$

The molecular topology of $\mathbf{1}_2$ requires the following coupling scheme: $J_{12} = J_{34}$, $J_{23} = J_{41}$, $g_1 = g_3$, and $g_2 = g_4$. We found J_{12} as well as the interdimer coupling J_{23} to be positive, according to the low-temperature rise of μ_{eff}. Because in this situation the g values of $\mathrm{Cu^{II}}$ and $\mathrm{V^{IV}}$ are covariant, the g value for $\mathrm{Cu^{II}}$ was fixed to 2.11 as in [LCuCu][10] and only the g value of $\mathrm{V^{IV}}$ was optimized. Moreover, the large increase of μ_{eff} at the lowest temperatures could not be fully reproduced within the spin tetramer model. Thus, additional intermolecular interactions were taken into account, as parametrized by a positive Curie−Weiss temperature θ. The optimized values are $J_{12} = +45.6 \pm 1.6$ cm^{-1}, $J_{23} = +0.55 \pm 0.02$ cm^{-1}, and $\theta = +0.15$ K. The ground state of $\mathbf{1}_2$ is $S_{\mathrm{t}} = 2$.

For the homonuclear metal compound $\mathbf{2}_2$·MeOH, the following coupling scheme was used: $J_{12} = J_{34}$, $J_{41} = 0$, $g_1 = g_3$, and $g_2 = g_4$. Although the two molecules in $\mathbf{2}_2$·MeOH are not identical, we have assumed the intradimer couplings to be equal, neglecting the small differences in the bridging unit. This reduces the parameter space and avoids ambiguities. Simulation of the data yielded $J_{12} = +4.8 \pm 0.2$ cm^{-1} and $J_{23} = -2.5 \pm 0.2$ cm^{-1}. The g values were constrained to be equal, which yielded a reasonable average value of $g = 2.12$.

The origin of ferromagnetic exchange interaction in the heterodinuclear $\mathrm{Cu^{II}V^{IV}{=}O}$ **1** and the homodinuclear $\mathrm{Cu^{II}}$-$\mathrm{Cu^{II}}$ **2** units can be referred to the same spin-coupling mechanism. In a tetragonal $\mathrm{Cu^{II}}$ complex, the magnetic orbital is of the $d_{x^2-y^2}$ type with its lobes pointing toward the equatorial ligands, whereas the magnetic orbital in a tetragonal $\mathrm{V^{IV}{=}O}$ complex is of the d_{xy} type with its lobes pointing between the equatorial ligands. Chart 1 provides a sketch of the magnetic orbitals in **1** and **2**.

The orthogonality of the magnetic orbitals in complex [$\mathrm{LCu^{II}V^{IV}O}$] **1** (Chart 1) results in a strong ferromagnetic coupling, whereas the nonorthogonality of the magnetic orbitals in the related homodinuclear [$\mathrm{LCu^{II}Cu^{II}}$][10] results in a strong antiferromagnetic coupling. This is a materialization of the classical textbook example of Kahn et al.[18,19] Although other complexes with edge-bridged $\mathrm{Cu^{II}V^{IV}{=}O}$ centers have been synthesized and magnetically characterized,[20,21] the magnitude of the ferromagnetic coupling, which depends on the overlap density, is still under debate.[19] It was suggested that the overlap density depends on the dihedral angle, ϕ, between the two equatorial planes.[20] Because of simple overlap consideration, the coupling should be at a maximum for a coplanar arrangement and lowest for $\phi = 90°$. A linear relationship between the coupling constant and ϕ was proposed based on two experimental points.[21] Considering $\phi = 6.4°$ in **1**, the coupling strength should exceed that of the famous Kahn example with $J = 59$ cm^{-1} ($\phi = 9.8°$). However, the value for **1** ($J = 45.6$ cm^{-1}) is close to the value of Nag et al.[21] ($J = 42.5$ cm^{-1} with $\phi = 32°$). Thus, the magnetostructural correlation for $\mathrm{Cu^{II}V^{IV}{=}O}$ seems to be more complex, and the coupling strengths depend on more than only the dihedral angle. Considering the famous magnetostructural correlation of Gorun and Lippard for $\mathrm{Fe^{III}}$-$\mathrm{OFe^{III}}$,[22] which depends only exponentially on half of the shortest superexchange pathway, a distance dependence seems to be also valid for $\mathrm{Cu^{II}V^{IV}{=}O}$: 2.03 Å (Nag et al.), 1.99 Å (**1**), 1.96 Å (Kahn et al.).

Complex **2** is a scarce example[23] for ferromagnetic coupling in a homonuclear complex due to topological orthogonality of the magnetic orbitals. The 45° rotation of the local coordinate systems provided by the bridging unit enforces the same magnetic orbital topology in the $\mathrm{Cu^{II}Cu^{II}}$ complex as was observed in edge-bridged $\mathrm{Cu^{II}V^{IV}{=}O}$ complexes (Chart 1). Several heteronuclear complexes with bridging units analogous to the β-diketimineamid bridging unit in **2** have been synthesized.[24] This bridging motif seems to be a useful ferromagnetic coupling unit for homonuclear complexes, which are usually more easily accessible than heteronuclear complexes, and we are exploring routes to utilize it for the preparation of high-spin molecules and ferromagnetic chains.

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Supporting Information Available: Full details of single-crystal X-ray diffraction details for **1** and $\mathbf{2}_2$·MeOH in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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