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Targeted Ferromagnetic Coupling in a Trinuclear Copper(II) Complex: Analysis of the $S_t = {}^3/_2$ Spin Ground State

Thorsten Glaser,*,† Maik Heidemeier,† Stefan Grimme,‡ and Eckhard Bill§

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster,
Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany, Organisch-Chemisches Institut,
Westfälische Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Germany, and
Max-Planck-Institut für Bioanorganische Chemie, Stiftstr. 34-36, D 45470 Mülheim, Germany

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The trinuclear Cu^{II} complex $[(talen)Cu^{II}_3]$ (**1**) using the new triplesalen ligand H_6talen has been synthesized and structurally characterized. The three Cu^{II} ions are bridged in a *m*-phenylene linkage by the phloroglucinol backbone of the ligand. This *m*-phenylene bridging mode results in ferromagnetic couplings with an $S_t = {}^3/_2$ spin ground state, which has been analyzed by means of EPR spectroscopy and DFT calculations. The EPR spectrum exhibits an unprecedented pattern of 10 hyperfine lines due to the coupling of three Cu^{II} ions ($I = {}^3/_2$). Resonances around $g = 4$ in both perpendicular and parallel mode EPR spectra demonstrate a zero-field splitting of $D \sim 74 \times 10^{-4}$ cm^{-1} arising from anisotropic/antisymmetric exchange interactions. The DFT calculations show an alteration in the sign of the spin densities of the central benzene ring corroborating the spin-polarization mechanism as origin for the ferromagnetic coupling.

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, the parallel alignment of neighboring spins is essential for the design of a molecule-based magnet.[2] Besides the well established use of orthogonal magnetic orbitals,[3] the double exchange mechanism[4] and the spin-polarization mechanism[5] are known for the prospect to stabilize ferromagnetically coupled ground states. The spin-polarization mechanism provides control over the interaction (ferromagnetic vs antiferromagnetic). The *m*-phenylene linkage of organic radicals and carbenes leads to ferromagnetic couplings, whereas the *o*- and *p*-phenylene linkages lead to antiferromagnetic couplings. This concept was applied to transition metal complexes using a variety of ligands which bridge the metal ions in *m*-phenylene arrangements. Some of these compounds indeed exhibit ferromagnetic interactions between the transition metal ions.[6] However, there are complexes with the same or slightly modified bridging ligands that exhibit antiferromagnetic interactions.[7,8] Competing superexchange and spin-polarization mechanisms and the orientation of the magnetic orbitals relative to the bridging ligand plane have accounted for these differences in the exchange interactions.[8,9]

Recently, we reported the use of the modified 1,3,5-trihydroxybenzene (phloroglucinol) ligand H_3L (=2,4,6-tris-

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* To whom correspondence should be addressed. E-mail: tglaser@uni-muenster.de.

† Institut für Anorganische und Analytische Chemie, Universität Münster.

‡ Organisch-Chemisches Institut, Universität Münster.

§ Max-Planck-Institut für Bioanorganische Chemie, Mülheim.

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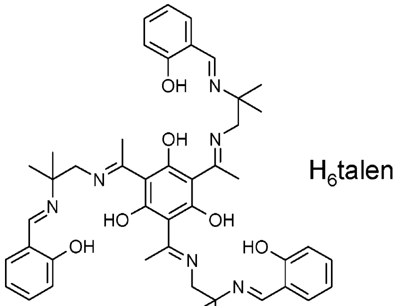
Chart 1



H_6talen

(1-((2-(dimethylamino)ethyl)imino)ethyl)-1,3,5-trihydroxybenzene) to bridge three Cu^{II} ions in a *m*-phenylene linkage.[10] These complexes exhibit ferromagnetic interactions between the three $S_i = {}^1/_2$ sites to result in $S_t = {}^3/_2$ ground states. We proposed that the ferromagnetic coupling originates from the spin-polarization mechanism. The ligand H_3L has been synthesized from the triketone 2,4,6-trisacetyl-1,3,5-trihydroxybenzene. The reactive carbonyl functions provide the opportunity to introduce a variety of pendant arms in 2,4,6 position of phloroglucinol. Thus, this versatile ligand system provides the opportunity to synthesize and study a series of closely related compounds. In this respect, we synthesized the ligand triplesalen, H_6talen (=2,4,6-tris(1-(2-salicylaldimino-2-methylpropylimino)-ethyl)-1,3,5-trihydroxybenzene, Chart 1).[11]

The triplesalen ligand was designed to meet both criteria necessary for single-molecule magnets:[12] high-spin ground states by the *m*-phenylene bridging and magnetic anisotropy by the strong axial ligand field of a salen-like coordination environment.[11] In this study, we report on the synthesis and characterization of the first complex of the triplesalen ligand with paramagnetic transition metal ions, i.e., the ferromagnetically coupled trinuclear Cu^{II} complex $[(talen)Cu^{II}_3]$ (**1**), which has been characterized by means of single-crystal X-ray diffraction, temperature-dependent magnetic susceptibility measurements, EPR spectroscopy, and DFT calculations.

Reaction of H_6talen with $[Cu^{II}_2(OAc)_4(OH_2)_2]$ in EtOH results in a purple solid which was recrystallized from a $CHCl_3$/toluene mixture to afford single-crystals of **1**·$CHCl_3$·0.5toluene. Figure 1a shows the molecular structure of **1**.[13] Three {salenCu^{II}} units are bridged in a *m*-phenylene arrangement. Each copper ion is in a distorted square-planar coordination environment.

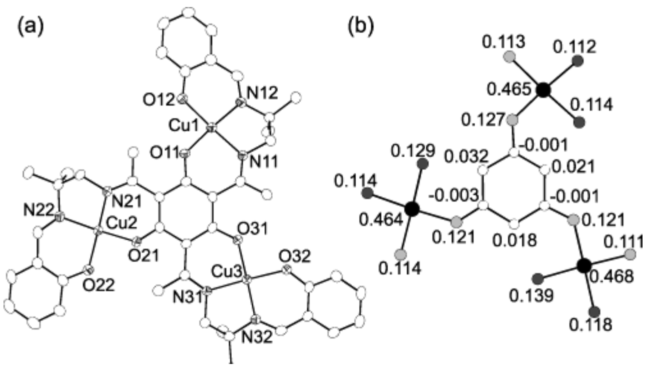


Figure 1. (a) Molecular structure of $[(talen)Cu^{II}_3]$ in crystals of **1**·$CHCl_3$·0.5toluene. Selected bond lengths [Å]: Cu1−O11 1.883(3), Cu1−O12 1.899(3), Cu1−N11 1.942(3), Cu1−N12 1.940(3), Cu2−O21 1.859(3), Cu2−O22 1.899(3), Cu2−N21 1.930(3), Cu2−N22 1.923(3), Cu3−O31 1.883(3), Cu3−O32 1.916(3), Cu3−N31 1.921(3), Cu3−N32 1.935(3). (b) Spin-density distribution of the inner fragment of **1** for the $S_t = {}^3/_2$ ground state obtained from DFT calculations.

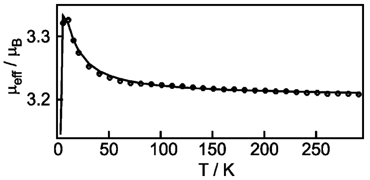


Figure 2. Temperature dependence of μ_{eff} of complex **1**. The solid line is a fit to the experimental data using the values given in the text.

The effective magnetic moment, μ_{eff}, of **1** at 290 K is 3.21 μ_B, consistent with three noninteracting $S_i = {}^1/_2$ spins (g = 2.14). With decreasing temperature, μ_{eff} increases and reaches a maximum of 3.33 μ_B at 10 K (Figure 2) demonstrating a ferromagnetic coupling in **1** with an $S_t = {}^3/_2$ spin ground state. Below 5 K, μ_{eff} drops to 2.53 μ_B at 2 K due to the combined effects of intermolecular antiferromagnetic couplings, saturation, and zero-field splitting in the $S_t = {}^3/_2$ spin ground state.

The experimental magnetic data have been successfully simulated using the spin-Hamiltonian (eq 1) for an equilateral Cu^{II}_3 triangle by a full-matrix diagonalization approach:[14]

$$H = -2J(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_1\mathbf{S}_3) + \sum_{i=1}^{3}[g_i\mu_B S_i B] \qquad (1)$$

In this procedure, saturation effects are already taken into account. The zero-field splitting in the $S_t = {}^3/_2$ spin ground state is too small (see EPR spectroscopy) to cause the sharp decrease of μ_{eff} at low temperatures. Thus, a Weiss constant has been used to account for intermolecular interactions. This yielded $J = +1.52$ cm^{-1}, $g = 2.14$, and $\Theta = -1.1$ K, which renders the excited spin doublets at 4.56 cm^{-1} above the spin ground state.

The cw X-band EPR normal-mode spectrum ($B_1 \perp B_0$) of **1** recorded in a CH_2Cl_2/toluene 1:1 mixture at 2.7 K exhibits an axial powder signal at $g \approx 2$ with 10 resolved $^{63/65}$Cu

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(13) Crystal data for **1**·$CHCl_3$·0.5toluene: formula $C_{49.50}H_{53}Cl_3Cu_3N_6O_6$, $M = 1124.95$, monoclinic, $C2/c$, $a = 26.485(4)$ Å, $b = 12.714(2)$ Å, $c = 31.189$ Å, $\beta = 111.006(6)°$, $V = 9804.6(25)$ Å^3, $Z = 8$, $\mu = 1.509$ mm^{-1}, $R = 0.0458$, $R_w = 0.1088$ (6387 observed reflections, $I > 2\sigma(I)$).

(14) The routine JULIUS was used for spin Hamiltonian simulations of the data (Krebs, C.; Bill, E.; Birkelbach, F.; Staemmler, V. Unpublished results).

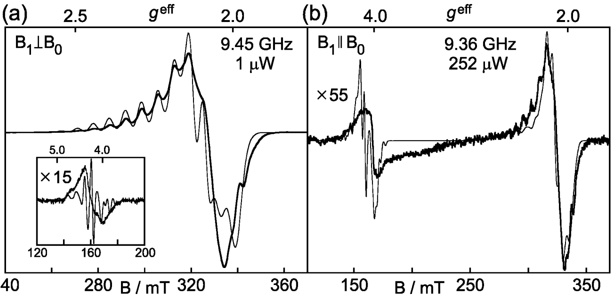

Figure 3. (a) Perpendicular mode and (b) parallel mode EPR spectra of complex **1** in CH_2Cl_2/toluene (1:1) solution at 2.7 K.

hyperfine lines ($=2nI+1$, $I = {}^3/_2$, $n = 3$), and a weak half-field signal at $g \approx 4$ (Figure 3a). Both features demonstrate the $S_t = {}^3/_2$ spin ground state of an equilateral Cu^{II} trimer. The intensity of the half-field transitions increases in a parallel-mode measurement ($B_1 \| B_0$), whereas the allowed transitions are strongly attenuated (Figure 3b). The relative intensities of the $g \approx 4$ signals in both detection modes, as well as the width and the appearance of the $g \approx 2$ pattern, indicate substantial zero-field splitting of the total spin quartet. The spectra were successfully simulated by adopting an effective spin-Hamiltonian (eq 2) for an isolated $S_t = {}^3/_2$ spin ground-state including hyperfine-couplings with three identical $^{63/65}$Cu nuclei.

$$H^{\text{eff}} = D_{3/2}\left(S_z^{\,2} - \frac{1}{3}S(S+1)\right) + \mu_B \mathbf{S}\mathbf{g}_{3/2}\mathbf{B} + \sum_{i=1}^{3}[\mathbf{A}_{3/2,i}\mathbf{S}\mathbf{I}_i] \tag{2}$$

An axial zero-field parameter was found, $D_{3/2} = -74 \times 10^{-4}$ cm^{-1} (along the local z-axes, normal to the molecular xy-plane), which has to be compared with possible dipolar spin coupling contributions for the trimer of $D_{\text{dip},3/2} = +15 \times 10^{-4}$ cm^{-1}. That value is obtained in a point-dipole model[15] with a Cu−Cu pair distance of 7.2 Å, which yields pairwise axial J_{dip} matrices with main components $j_{\max} = -97.5 \times 10^{-4}$ cm^{-1} in the molecular xy-plane. Addition of the local matrices with 120° rotations around z, and considering the corresponding weighting coefficients of $^1/_6$ according to the Wigner−Eckart theorem,[15] yields an axial total dipolar coupling matrix $J_{\text{dip},3/2}$ with positive main component as given above. The deviation from the experimental value (note the difference in signs) strongly supports the presence of substantial anisotropic-antisymmetric exchange contributions to the cluster spin ground state $S_t = {}^3/_2$ zero-field splitting.[15]

The **g**-matrix obtained from the simulations, $\mathbf{g}_{3/2} = 2.050$, 2.050, 2.235, and the hyper-fine tensors $\mathbf{A}_{3/2,i} = (-10, -10, -70) \times 10^{-4}$ cm^{-1}, correspond nicely to the values of mononuclear [(salen)Cu^{II}],[16] due to the relation $\mathbf{g}_{3/2} = \mathbf{g}_i$, and $\mathbf{A}_{3/2,i} = \mathbf{a}_i/3$,[15] which reveals the persistence of the local electronic structure in the spin-coupled system.

In order to obtain insight into the spin-density distribution of the $S_t = {}^3/_2$ spin ground state, we have performed density functional theory (DFT) calculations.[17] The atomic spin density distribution in the quartet ground state, as obtained by Mulliken population analysis, is shown in Figure 1b. The main (positive) spin density is on the three Cu ions. The square-planar coordination geometry observed in **1** is known for strong covalent overlap of the magnetic orbitals on the Cu^{II} ions ($x^2 - y^2$) with the pseudo-σ orbitals of the donor atoms[18] leading to an efficient spin-delocalization (positive spin-density) on the O and N donor atoms. Although the density functional used for the calculations is known to overestimate the covalency of Cu^{II}−ligand bonds,[19] it is expected to provide a qualitatively correct picture of the spin density distribution of the central benzene ring. As predicted by the spin-polarization mechanism, an alteration of negative and positive spin densities on adjacent C atoms is obtained by the DFT calculations. These results are in strong support that the origin of the ferromagnetic coupling observed in **1** is the spin-polarization mechanism.

In conclusion, the m-phenylene linkage of the three Cu^{II} ions by the triplesalen ligand in **1** results in ferromagnetic interactions and an $S_t = {}^3/_2$ spin ground state via the spin-polarization mechanism. The EPR spectra exhibit to the best of our knowledge the unprecedented pattern of 10 hyperfine lines due to the interaction of the total electron spin with the individual nuclear spins of the three Cu^{II} ions. We are currently investigating trinuclear Cr^{III}, Fe^{III}, and Mn^{III} complexes of the triplesalen ligand as candidates for single-molecule magnets and related ligand systems based on other phloroglucinol derivatives for the preparation of higher dimensional compounds.

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Supporting Information Available: Experimental details describing the synthesis and characterization of **1**; complete single-crystal X-ray diffraction details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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