Targeted Synthesis of Ferromagnetically Coupled Complexes with Modified 1,3,5-Trihydroxybenzene Ligands**

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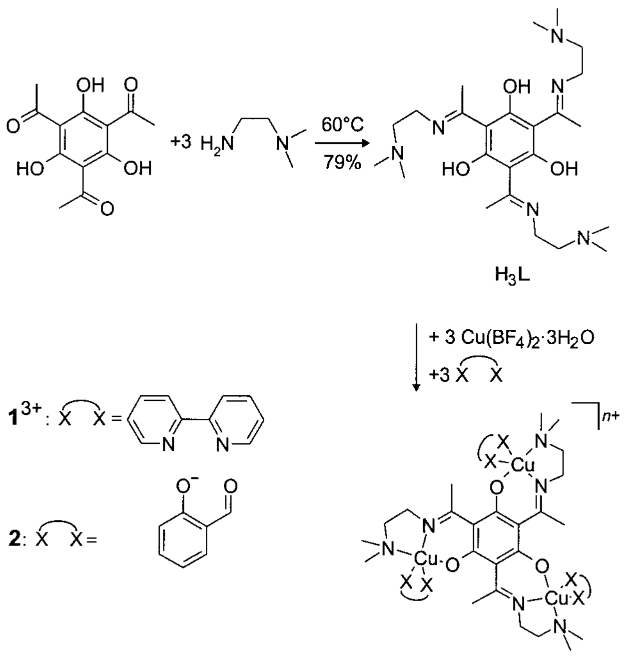
Dedicated to Professor Wieghardt
on the occasion of his 60th birthday

The design and synthesis of molecule-based magnets has attracted considerable interest over the past decade. The synthetic efforts have focused on the assembly of molecular building blocks to form supramolecular magnetic materials.[1] As Kahn emphasized, the design of molecular building blocks with *ferromagnetic* interactions between the paramagnetic centers is essential for the development of new types of molecule-based magnets.[2] One strategy for synthesizing materials with ferromagnetic interactions is provided by the *m*-phenylene linkage of organic radicals, utilizing the spin-polarization mechanism.[3] This concept was applied to binuclear transition metal complexes containing pyrimidine or resorcinol as bridging ligands.[4] One trinuclear complex with 1,3,5-trihydroxybenzene (phloroglucinol) as bridging ligand was reported which exhibits ferromagnetic interactions between the three coordinated (Tp*)Mo^{V}OCl fragments (Tp* = tris((3,5-dimethylpyrazolyl)hydroborate).[5]

The synthesis of phloroglucinol-bridged trinuclear complexes with first-row transition metals is hindered because of the low stability of such complexes. To overcome this problem we have developed an approach in which the stability is enhanced by attaching pendant arms with additional coordinating groups in the 2,4,6-position of phloroglucinol. An analogous approach was used by Abrahams et al. with azophenyl groups in 2,4,6-position.[6] Here we report on the phloroglucin-based ligand H_3L and its ability to bridge three paramagnetic copper centers (Scheme 1) that are ferromagnetically coupled to give the highest possible spin ground state.

The ligand H_3L in reasonable yields was prepared by the condensation of 2,4,6-triacetyl-1,3,5-trihydroxybenzene with three equivalents of *N*,*N*-dimethylethylenediamine (Scheme 1). The reaction of H_3L with $Cu(BF_4)_2 \cdot 3H_2O$ in the presence of NEt_3 yielded a green solution that is typical of Cu^{II}–phenolato complexes. The coordination sphere of the three cooper ions was completed by addition of three equivalents of a bidentate chelate ligand: the use of bipyridine (bpy) gave $[L\{Cu^{II}(bpy)\}_3](BF_4)_3$ (**1**-$(BF_4)_3$) and the use of salicylaldehyde (Hsal) gave $[L\{Cu^{II}(sal)\}_3]$ (**2**). Large single crystals of **1**-$(BF_4)_3 \cdot 2MeOH \cdot HNMe_2 \cdot 1.5H_2O$ suitable for an X-ray structure analysis[7] were grown by slow diffusion of *n*-pentane into the reaction solution. Figure 1a shows the structure of $\mathbf{1}^{3+}$ and illustrates the ability of the ligand L^{3-} to bridge three metal centers. Each of the three copper ions is coordinated by one phenolato oxygen and two nitrogen atoms of the ligand L^{3-}, and two nitrogen atoms of bpy. The coordination geometry of the three copper ions is square pyramidal; however, Cu1 and Cu2 show considerable distortion towards trigonal bipyramidal. Based on the comparable characterization of **2** and **1**-$(BF_4)_3$ by elemental analysis, FT-IR, ESI-MS, UV/Vis/NIR absorption and EPR spectroscopy, and magnetic measurements complex **2** can be formulated as $[L\{Cu^{II}(sal)\}_3]$.



Scheme 1. Synthesis of the ligan H_3L and the reaction to give complexes $\mathbf{1}^{3+}$ and **2**.

Temperature-dependent magnetic susceptibility measurements (SQUID, 2–300 K, 1.0 T) on powdered samples of **1**-$(BF_4)_3$ and **2** revealed an increase of the effective magnetic moment (μ_{eff}) with decreasing temperature, indicative of ferromagnetic interactions between the metal centers (Figure 2). Below 4 K μ_{eff} decreases for **2** due to weak intermolecular antiferromagnetic couplings. The diamagnetic dilution by the three anions in **1**-$(BF_4)_3$ increases the distances between the trinuclear units and thus reduces these antiferromagnetic interactions. A Weiss constant ϑ was used in the fitting procedure to reflect these intermolecular couplings. Despite the small structural differences of the three copper centers in **1**-$(BF_4)_3$, a good fit to the experimental data was obtained with three equal J values ($H = -2J(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_3\mathbf{S}_1) + \Sigma\mu_B g_i S_i B_i$)). The best fit results in $J = +1.96\ cm^{-1}$ for **1**-$(BF_4)_3$ and $J = +3.31\ cm^{-1}$ for **2**. Both complexes exhibit ferromagnetic interactions between the copper centers. The

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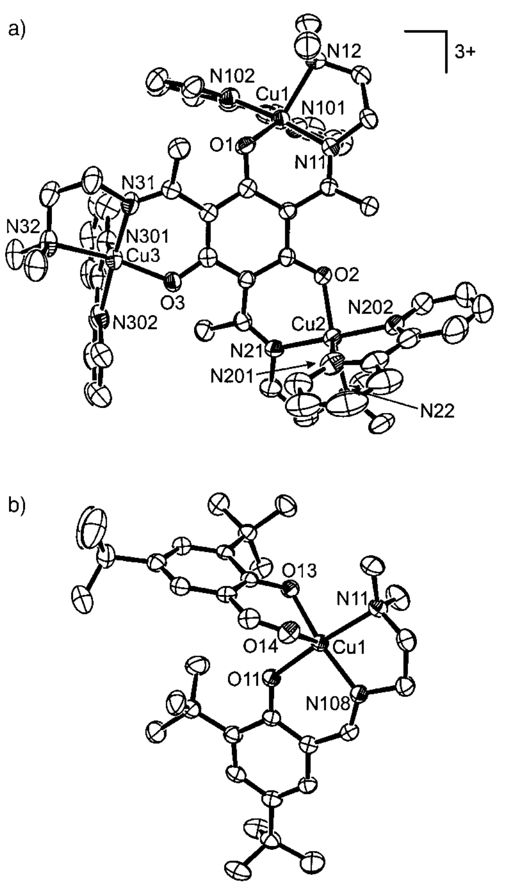


Figure 1. a) Molecular structure (50% probability; H atoms omitted) of 1^{3+}: Selected distances [Å]: Cu1-O1 1.932(4), Cu2-O2 1.937(4), Cu3-O3 1.930(4). b) Molecular structure (50% probability; H atoms omitted) of **3**: Selected distance [Å]: Cu1-O11 1.915(2).

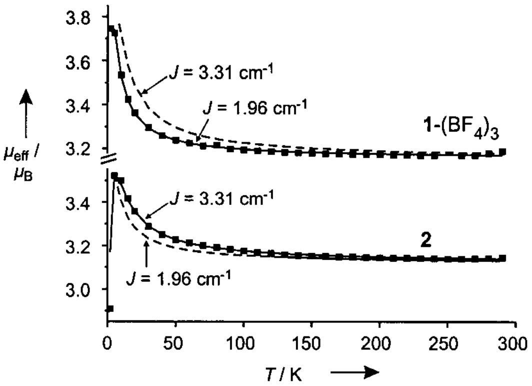
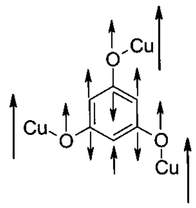


Figure 2. Temperature dependence of μ_{eff} for **1**-$(BF_4)_3$ and **2**. The solid lines represent the best fits ($J = 1.96\,cm^{-1}$, $g = 2.10$, $\chi_{TIP} = 246 \times 10^{-6}\,cm^3mol^{-1}$, $\theta = -0.083$ K for **1**-$(BF_4)_3$; $J = 3.31\,cm^{-1}$, $g = 2.08$, $\chi_{TIP} = 100 \times 10^{-6}\,cm^3mol^{-1}$, $\theta = -1.03$ K for **2**). The dashed lines represent simulations with interchanged J values to demonstrate the accuracy of the obtained values.

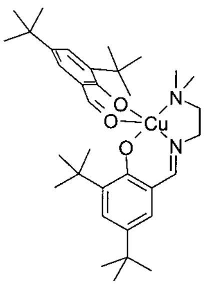
results show that complexes with ferromagntic interactions can be constructed by using phloroglucinol as bridging ligand.

In analogy to a phloroglucin-bridged complex synthesized by Ung et al.,[5] the spin-polarization mechanism should account for these ferromagnetic interactions (Scheme 2). The ferromagnetic interaction in **2** is somewhat larger than that in **1**-$(BF_4)_3$. We assume this reflects differences in the coordination geometry of the copper ions between the two complexes. To investigate this further, we synthesized complex **3**, a mononuclear analogue of **2**, which owing to the coordination of the sal⁻ ligand displays a square-pyramidal structure (Figure 1b). In such a structure, the magnetic $d_{x^2-y^2}$ orbital is directed towards the orbitals of the oxygen donor atom of L^{3-} resulting in better overlap. The distortion to a trigonal-bipyramidal coordination environment in **1**-$(BF_4)_3$ rotates the magnetic orbital out of the basal plane and leads to a worse overlap with the orbitals of the oxygen donor atom of L^{3-} and consequently to weaker coupling.



Scheme 2. Schematic representation of the spin-polarization mechanism. The two large arrows represent the unpaired spin on each of the three Cu^{II} ions; the small arrows represent the direction of polarization of the electron clouds on the intervening atoms. Note that the spin densities of the Cu^{II} centers and the coordinated oxygen atoms have the same directions due to spin-delocalization.

In conclusion, the phloroglucinol-based ligand H_3L allows the bridging of three copper ions in a *m*-phenylene arrangement. The two copper complexes **1**-$(BF_4)_3$ and **2** exhibit ferromagnetic interactions between the paramagnetic copper centers, which are produced by the spin-polarization mechanism. In pursuit of new magnetic materials we aim to use this new class of ligands in two ways: 1) synthesis of trinuclear complexes with high local spin states and magnetic anisotropy through use of metal ions such as Mn^{III} and Cr^{III} as potential single-molecule magnets, and 2) synthesis of two-dimensional networks and magnetic dendrimers as candidates for molecule-based magnets.



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Experimental Section

1-$(BF_4)_3$: A solution of H_3L (0.127 g, 0.275 mmol) in methanol (15 mL) was added to a stirred solution of $Cu(BF_4)_2 \cdot 3H_2O$ (240 mg, 0.824 mmol) in methanol (20 mL) resulting in an olive-green solution. A solution of bpy (0.129 g, 0.824 mmol) and NEt_3 (83 mg, 0.824 mmol) in methanol (15 mL) was added dropwise. Upon slow diffusion of *n*-pentane into the filtered solution large black single crystals were obtained which were washed with diethyl ether and dried in vacuum. Yield: 170 mg (43%). ESI-MS (methanol) of **1**-$(ClO_4)_3$: *m/z* (%): 608.8 (28) $[\mathbf{1}\text{-}(ClO_4)_3{-}2ClO_4]^{2+}$, 530.7 (51) $[\mathbf{1}\text{-}(ClO_4)_3{-}bpy{-}2ClO_4]^{2+}$, 373.0 (100) $[\mathbf{1}\text{-}(ClO_4)_3{-}3ClO_4]^{3+}$; IR (KBr): $\tilde{\nu} = 1568$ (m, br, (C=N)), 1341 (w, (C-O)), 1084 (w, bpy), 1058 (s, br, BF_4^-), 778 cm^{-1} (m, bpy); UV/Vis/NIR (acetonitrile): λ_{max} (ε) = 243 (51000), 304 (73000), 322 (57000), 468 (2700), 598 nm (1100); elemental analysis calcd for $C_{54}H_{67}N_{12}O_5Cu_3B_3F_{12}$ (%): C 45.83, H 4.77, N 11.88; found: C 45.63, H 4.42, N 11.67.

2: A solution of H_3L (147 mg, 0.318 mmol) in ethanol (12 mL) was added to a stirred solution of $Cu(BF_4)_2 \cdot 3H_2O$ (278 mg, 0.954 mmol) in ethanol (10 mL) resulting in an olive-green solution. After addition of a solution of Hsal (116 mg, 0.954 mmol) and NEt_3 (257 mg, 2.53 mmol) in ethanol (10 mL), the resulting solution was stirred for 4 h. Olive-green microcrystals separated which were washed with diethyl ether and dried in vacuum. Yield: 120 mg (37%). ESI-MS (methanol) of **2**: *m/z* (%): 802.3 (12) $[\mathbf{2}{-}2sal{+}CH_3O]^+$, 788.2 (19) $[\mathbf{2}{-}2sal{+}OH]^+$, 712.3 (12) $[\mathbf{2}{-}3sal{-}$

sal+2 $CH_3O]^+$; 385.7 (11) $[\mathbf{2}-2\,\mathrm{sal}]^{2+}$, 333.6 (100) $[\mathbf{2}-3\,\mathrm{sal}+\mathrm{OH}]^{2+}$; IR (KBr): $\tilde{\nu}=1645$ (s, (C=O)), 1568 (m, br, (C=N)), 1352 (w, sal (C−O)), 1341 (w, L^{3-} (C-O)), 897 (w, sal), 762 cm^{-1} (w, sal); UV/Vis/NIR (acetonitrile): λ_{max} $(\varepsilon)=238$ (72000), 327 (47000), 445 (sh), 602 nm (600); elemental analysis calcd for $C_{45}H_{54}N_6O_9Cu_3$ (%): C 53.32, H 5.37, N 8.29; found: C 52.98, H 5.22, N 8.23.

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[7] X-ray structure analysis data of **1**-$(BF_4)_3\cdot 2\,MeOH\cdot HNMe_2\cdot 1.5\,H_2O$: formula $C_{58}H_{81}N_{13}O_{6.5}Cu_3B_3F_{12}$, $M_r=1515.41$, black crystal $0.30\times 0.30\times 0.10$ mm, $a=19.243(1)$, $b=16.521(1)$, $c=21.633(1)$ Å, $\beta=92.18(1)^\circ$, $V=6872.4(6)$ Å^3, $\rho_{calcd}=1.465\ \mathrm{g\,cm^{-3}}$, $\mu=10.10\ \mathrm{cm^{-1}}$, empirical absorption correction by using SORTAV $(0.751\leq T\leq 0.906)$, $Z=4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda=0.71073$ Å, $T=198$ K, ω and φ scans, 23777 reflections collected $(\pm h, \pm k, \pm l)$, $((\sin\theta)/\lambda)=0.62$ Å^{-1}, 13898 independent $(R_{int}=0.032)$ and 9859 observed reflections $(I\geq 2\sigma(I))$, 756 refined parameters, $R=0.087$, $wR^2=0.256$, max. residual electron density 1.68 (−1.12) e Å^{-3}, close to the BF_4^-, refinement with split positions did not improve the model, therefore the anions were refined with isotropic thermal displacement parameters, the solvent molecules (2 methanol, 1 dimethylamine, and 1.5 water) were refined with one common isotropic thermal parameter each, hydrogen atoms on the nitrogen atom of the dimethylamine and at the water molecules not localized, other calculated and refined as riding atoms. X-ray structure analysis data of **3**: formula $C_{34}H_{52}N_2O_3Cu$, $M_r=600.32$, green-yellow crystal $0.25\times 0.15\times 0.03$ mm, $a=9.382(1)$, $b=13.052(1)$, $c=13.789(1)$ Å, $\alpha=87.25(1)$, $\beta=86.88(1)$, $\gamma=87.79(1)^\circ$, $V=1683.0(3)$ Å^3, $\rho_{calcd}=1.185\ \mathrm{g\,cm^{-3}}$, $\mu=6.82\ \mathrm{cm^{-1}}$, empirical absorption correction by using SORTAV $(0.848\leq T\leq 0.980)$, $Z=2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda=0.71073$ Å, $T=198$ K, ω and φ scans, 10380 reflections collected $(\pm h, \pm k, \pm l)$, $((\sin\theta)/\lambda)=0.62$ Å^{-1}, 6793 independent $(R_{int}=0.052)$ and 5042 observed reflections $(I\geq 2\sigma(I))$, 375 refined parameters, $R=0.064$, $wR^2=0.142$, max. residual electron density 0.98 (−0.54) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. For data collection and programs used see H. P. Wu, R. Aumann, R. Fröhlich, E. Wegelius, *Eur. J. Org. Chem.* **2002**, 361–368. CCDC-181141 (**1**-$(BF_4)_3\cdot 2\,MeOH\cdot HNMe_2\cdot 1.5\,H_2O$) and CCDC-181142 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

Supramolecular Engineering with Macromolecules: An Alternative Concept for Block Copolymers[**]

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Block copolymers represent an important class of materials, which have received widespread attention because of their remarkable micro- and nanophase morphology. This morphology leads to unique properties compared to homopolymers or their blends. Classical examples of block-copolymer morphology are lamellae, hexagonal-packed cylinders and body-centered-cubic arrays of spheres.[1] During the last decades, important advances have been made in the synthesis, characterization, and application of block copolymers. In particular, anionic polymerization has been successfully applied in their controlled synthesis.[2] Several other routes have been realized as well, for example, controlled radical polymerization,[3] cationic polymerization,[4] group transfer,[5] and metathesis,[6] or combinations of such techniques. Nevertheless, block-copolymer synthesis remains a challenge for certain materials and several interesting combinations could not be realized to date. On the other hand, recent developments in the field of supramolecular chemistry have shown that small (self-)complementary building blocks can lead, through self-organization processes, to large, well-defined structures, which are held together by noncovalent interactions such as hydrogen bonds[7] and metal-to-ligand coordination.[8] Herein we present a new highly controlled and well-defined construction principle for block copolymers that utilize supramolecular interactions, in this case metal-to-ligand coordination. By this method new combinations of block copolymers can be prepared, which are not accessible, or have been very difficult to access to date. This allows a comparison of the new metallo-supramolecular compounds with classical well-documented covalent block copolymers. For this purpose we chose the terpyridine ligand as the central building unit, which is well-known for its outstanding ability to form stable bis complexes with a large variety of transition-metal ions (Figure 1).[9] The main advantage of having a metal complex as the bridging unit is the possibility of cleavage at this junction point. Therefore new "smart materials" are accessible. Moreover, the metal ion being at the interface between the blocks may cause additional interesting features regarding morphology, thermal and mechanical as well as photophysical properties.

The construction of the supramolecular block copolymers works along the same principle as their covalent counterparts.

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