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Communication

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Bioinspired Enhancement of Superexchange: From 1,3,5-Trihydroxybenzene-Bridged to 1,3,5-Trimercaptobenzene-Bridged Trinuclear Copper(II) Complexes

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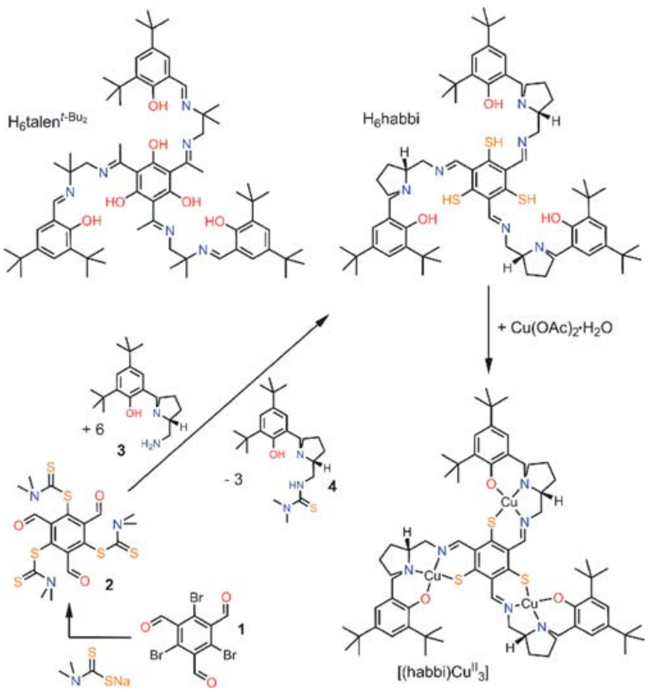
Ⓢ *Supporting Information*

ABSTRACT: An unprecedented trinucleating ligand with a central 1,3,5-trimercaptobenzene unit and its trinuclear Cu^{II}_3 complex are presented. The high covalency of the difficult-to-realize Cu^{II}−SR bond provides an order of magnitude increase in the superexchange interaction in comparison to its oxygen analogue.

For the rational development of single-molecule magnets, we employed phloroglucinol (1,3,5-trihydroxybenzene) as the central *m*-phenylene bridging unit in our triplesalen ligands, e.g., $H_6talen^{t\text{-}Bu_2}$ (Scheme 1).[1,2] The *m*-phenylene linkage is known as an effective ferromagnetic coupling unit for organic radicals and carbenes rationalized by a specific form of superexchange called spin-polarization.[3] Although difficult to measure, exchange coupling constants J ($H = -2J\mathbf{S}_1\mathbf{S}_2$) up to 2000 cm^{-1} have been estimated for the organic systems.[4] However, in trinuclear triplesalen Cu^{II} and $V^{IV}{=}O$ complexes, the exchange coupling is indeed ferromagnetic but with $+0.5 < J < +3.0$ cm^{-1}, much weaker than that in the organic systems.[2,5] Upon evaluation for possible reasons for this discrepancy, the most prominent difference between the organic radicals and carbenes and our complexes appears to be the spin density distribution of the local spins. Whereas in the organic radicals and carbenes the spin density resides in a p_z orbital that is perfectly oriented to interact with the benzene π system, the spin density in our complexes is mostly located in the metal d orbitals, with only a minor portion delocalized to the phloroglucinol oxygen atom by covalent bonding.

Scheme 1



In order to optimize our triplesalen ligands, we have been inspired by the efficient superexchange pathways in metal-based biological electron-transfer (ET) sites. Nature has realized the essential strong covalent interaction at the metal−protein interface through the use of highly covalent metal−sulfur bonds in blue copper and Fe−S ET sites.[6] In analogy, we envisioned that the stronger covalency of a metal−thiolate bond[7] realized by a central 1,3,5-trimercaptobenzene (thiophloroglucinol) should lead to a higher spin density on the sulfur atom, which should result in a more effective spin-polarization mediated by the central benzene. Therefore, we started a project to synthesize extended thiophloroglucinol ligands. Herein, we report the first successful synthesis and characterization of such a ligand (H_6habbi) and its trinuclear copper(II) complex [(habbi)Cu^{II}_3].

There are several synthetic strategies to go from an O-donor to an S-donor ligand. The direct conversion of an OH group by an SH group via a Newman−Kwart rearrangement[8] appears to be straightforward, but we had to realize severe problems following this route.[9] Interestingly, although complexes of the parent thiosalen are known,[10,11] the free thiosalen ligand is unstable because it forms bicyclic dithiocin derivatives,[12] so that usually a ligand precursor is deprotected during the complex formation.[13] Starting from Rubin's aldehyde **1**[14] and sodium dithiocarbamate, we obtained aldehyde **2** (Scheme 1). The reaction of **2** with 6 equiv of the chiral half-unit **3**[15] resulted not only in the 3-fold Schiff-base reaction but also in the nucleophilic deprotection of the thiolate with the formation of byproduct **4**, which was removed by column chromatography. The identity and purity of the ligand H_6habbi was confirmed by Fourier transform infrared (FTIR), NMR, mass spectrometry (MS), and elemental analysis.

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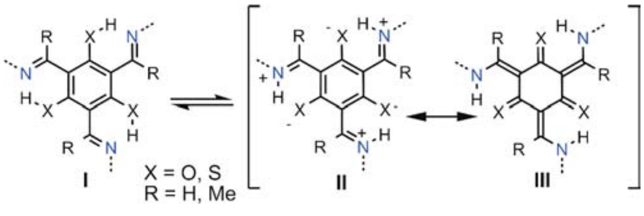
Despite the higher covalency, the sulfur substitution should be of benefit for another reason because we have recently discovered that our triplesalen ligands have to be described not as their O-protonated tautomer **I** but as their N-protonated tautomers with the main contribution of resonance structure **III** (Scheme 2).[16] Because of the resemblance of **III** to [6]radialenes, these compounds have been referred to as heteroradialenes.[17] Radialenes are cross-conjugated alicycles without a delocalized π system. Because a delocalized aromatic π system is central for an efficient superexchange, its loss by heteroradialene formation might also be a reason for the weak coupling in the phloroglucinol-bridged complexes. However, by going from the phloroglucinol to the thiophloroglucinol ligands, we envisioned a reduced contribution of the pure heteroradialene resonance structure **III** because a C=S double bond should be less favorable than a C=O double bond.

Scheme 2



NMR spectroscopy proved already to be a valuable tool to discriminate between several tautomer and resonance contributions in the extended phloroglucinol ligands.[16] In this respect, is the appearance of a broad unresolved multiplet at 14.7 ppm coupled to a doublet at 9.67 ppm in the ^{1}H NMR spectra of H_6habbi (Figures S1 and S2 in the Supporting Information) a clear indication that also H_6habbi is not in the S-protonated tautomer but in the N-protonated tautomer. A comprehensive analysis of the electronic structure of *S*- versus *O*-phloroglucinol ligands including their nickel(II) complexes by NMR, FTIR, UV−vis, and single-crystal X-ray diffraction will be presented in a forthcoming full paper.

The preparation of Cu^{II}−SR complexes is complicated by the frequently observed oxidation of the thiol or deprotonated thiolate by copper(II).[18] However, the reaction of H_6habbi with $Cu(OAc)_2\cdot H_2O$ in ethanol resulted in the clean formation of $[(\text{habbi})Cu^{II}_3]$, as confirmed by FTIR, MS, elemental analysis, and single-crystal X-ray diffraction. The crystal structure of $[(\text{habbi})Cu^{II}_3]\cdot 3CH_2Cl_2\cdot 6CH_3CN$ contains two independent trinuclear complexes.[19] While molecule 1 (Cu1,2,3) exhibits no crystallographically imposed symmetry (Figure 1), molecule 2 (Cu4) possesses crystallographic C_3 symmetry. The mean Cu−S bond length of 2.24 Å is only slightly longer than that in $[(\text{thiosalen})Cu^{II}]$ of 2.22 Å,[11] while the mean Cu−N^{imine} bond length of 1.93 Å is significantly smaller than that in $[(\text{thiosalen})Cu^{II}]$ of 1.98 Å. Interestingly, the mean C−S bond lengths of 1.74 Å (molecule 1) and 1.73 Å (molecule 2) are almost unaffected ($[(\text{thiosalen})Cu^{II}]$: 1.74 Å). While the former result argues in favor of the description of a deprotonated amine in $(\text{habbi})^{6-}$ (analogous to resonance structure **III** for H_6habbi), the latter results do not argue against a deprotonated thiolate (analogous to **II**). However, the mean C−C bond length of 1.42 Å is increased in comparison to 1.39 Å in $[(\text{thiosalen})Cu^{II}]$, although not as much as in the Cu^{II}_3 complexes of the extended phloroglucinol ligands (1.43 Å).[2] Moreover, a close inspection of the individual central C−C bond lengths of molecule 2 in $[(\text{habbi})Cu^{II}_3]$ of 1.402(3) and 1.449(3) Å implies a severe localization of single- and double-bond character, while molecule 1 exhibits only two localized bonds of 1.393(3) and 1.444(3) Å. This is corroborated by the harmonic oscillator model of aromaticity (HOMA),[20] which considers bond lengths and their alternation. It is 1 for the model aromatic system benzene and 0 for the model nonaromatic system (benzene with localized double and single bonds). The HOMA value of 0.91 for $[(\text{thiosalen})Cu^{II}]$ reflects the delocalized π system, while the reduced HOMA values of 0.64 (molecule 1) and 0.50 (molecule 2) demonstrate a severe distortion. Interestingly, the HOMA values are close to those of the trinuclear complexes of the triplesalen ligand $H_6\text{talen}^{t\text{-Bu}_2}$.[2]

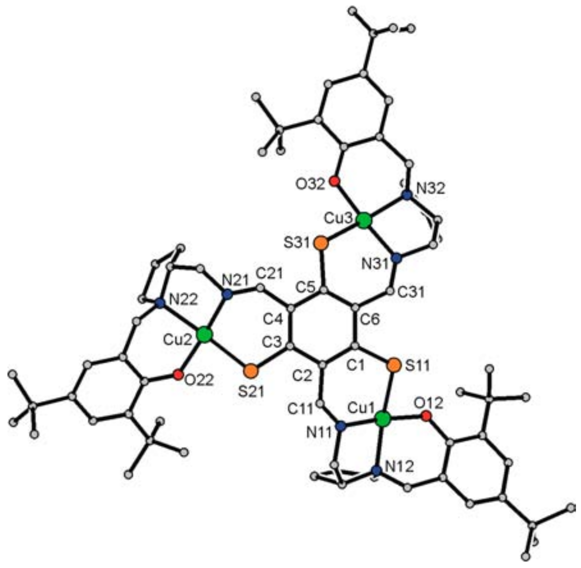


Figure 1. Molecular structure of $[(\text{habbi})Cu^{II}_3]$ (molecule 1). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] for molecule 1: Cu1−S11 2.234, Cu1−O12 1.878, Cu1−N11 1.921, Cu1−N12 2.036, Cu2−S21 2.249, Cu2−O22 1.878, Cu2−N21 1.925, Cu2−N22 2.044, Cu3−S31 2.241, Cu3−O32 1.868, Cu3−N31 1.927, Cu3−N32 2.032, C1−C2 1.418, C2−C3 1.428, C3−C4 1.420, C4−C5 1.430, C5−C6 1.393, C6−C1 1.444. Selected interatomic distances [Å] molecule 2 (not shown): Cu4−S41 2.238, Cu4−O42 1.882, Cu4−N41 1.941, Cu4−N42 2.032, C1B−C2B 1.402, C2B−C1B#2 1.449.

The effective magnetic moment, μ_{eff}, of $[(\text{habbi})Cu^{II}_3]$ at 290 K is 3.02 μ_B (Figure 2), which is slightly smaller than the value for three noninteracting Cu^{II} ($S = {}^1/_2$) ions ($\mu_{\text{eff}} = 3.16\ \mu_B$; $g =$

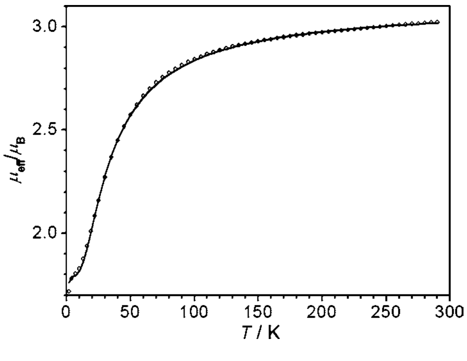


Figure 2. Temperature dependence of the effective magnetic moment, μ_{eff}, of $[(\text{habbi})Cu^{II}_3]$ at 1 T. The solid line represents the simulation (see the text).

2.11). Upon decreasing temperature, μ_{eff} decreases continuously to a small plateau of ~1.79 μ_{B} at low temperature, typical for an antiferromagnetically coupled system with a $S_t = {}^1/_2$ spin ground state. Simulations with the appropriate spin Hamiltonian (eq 1) resulted in $J = -11.93$ cm^{-1}, $g = 2.07$, and $\chi_{\mathrm{TIP}} = 321 \times 10^{-6}$ cm^3 mol^{-1}.

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

Thus, the exchange interaction in [(habbi)Cu$^{\mathrm{II}}_3$] is 1 order of magnitude stronger as that in the extended phloroglucinol ligands, which is enforced by the high covalency of the Cu$^{\mathrm{II}}$−S bonds. This result is even more remarkable considering that the free ligand H$_6$habbi as well as the coordinated ligand (habbi)$^{6-}$ cannot be formulated by the pure aromatic resonance structure **I** (with respective to the deprotonated form). The large mean C−C bond lengths of the central ring manifest a strong reduction of its aromaticity. Moreover, it appears that not only a heteroradialene resonance form but also a strong localization of C═C double bonds in the central ring accounts for this. Hence, there is also no delocalized aromatic π system in the central backbone of [(habbi)Cu$^{\mathrm{II}}_3$] so that the spin-polarization mechanism cannot be effective. This leads to severe localization of the spin density in different parts of the molecule, which may thus be ascribed to disjoint singly occupied molecular orbitals that had already been used to rationalize antiferromagnetic interactions.[21]

In conclusion, the higher covalency of the Cu$^{\mathrm{II}}$−SR bond results in an order of magnitude increase in the superexchange, although the central ring experiences a strong reduction of its aromaticity. To establish stronger and, even more important, ferromagnetic interactions, the imine functions in the 2, 4, and 6 positions, which enables heteroradialene formation, should be replaced by saturated amine functions so that highly covalent Cu$^{\mathrm{II}}$−SR units are *m*-phenylene-bridged by a real delocalized π system. Synthetic strategies to realize such ligand systems are currently explored in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for 1,3,5-tris(dimethyldithiocarbamoyl)-2,4,6-triformylbenzene (**2**), H$_6$habbi, and [(habbi)Cu$^{\mathrm{II}}_3$], ^{1}H and H−H COSY NMR spectra of H$_6$habbi, thermal ellipsoid plots, and crystallographic data (CIF format) of [(habbi)Cu$^{\mathrm{II}}_3$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) Crystal data for [(habbi)Cu$_3$]·3CH$_2$Cl$_2$·6CH$_3$CN: M = 1845.42 g mol^{-1}, C$_{84}$H$_{120}$Cl$_6$Cu$_3$N$_{12}$O$_3$S$_3$, hexagonal, space group $P6_3$, a = 24.936(4) Å, b = 24.936(4) Å, c = 40.088(8) Å, V = 21588(6) Å^3, Z = 8, ρ = 1.136 g cm^{-3}, μ = 2.942 mm^{-1}, T = 100(2), Cu Kα radiation, F(000) = 7752, crystal size = 0.28 × 0.14 × 0.12 mm^3, Flack parameter = 0.046(9). 175349 reflections collected (2.20 < θ < 66.83°), 25404 unique (R_{int} = 0.0484). The structure was refined to R = 0.0360 for 24301 reflections with $I > 2\sigma(I)$. CCDC 893670.

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