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From Triplesalen to Triplesalophen: Ferromagnetic Interactions through Spin-Polarization in a Trinuclear Ni^{II} Triplesalophen Complex

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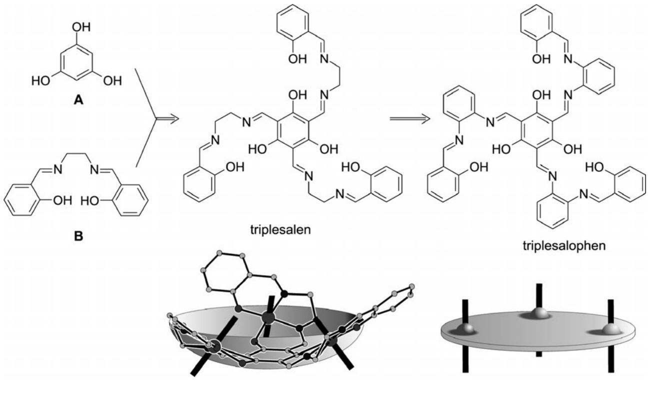
The synthesis and characterization of the ligand triplesalophen is presented. This ligand is the all sp^2-hybridized analogue of the ligand triplesalen, which was designed for the synthesis of single-molecule magnets with a supramolecular building block approach. The triplesalophen ligand allows the isolation of a trinuclear Ni^{II} complex with one square-planar Ni^{II} ion ($S = 0$) and two paramagnetic octahedral Ni^{II} ($S = 1$) ions. Magnetic measurements demonstrate ferromagnetic interactions in agreement with the spin-polarization mechanism.

Introduction

The design and synthesis of molecule-based magnets has attracted considerable interest over the past two decades, and ferromagnetic interactions between the paramagnetic centers have been identified as a key element in this process.[1] In this respect, we have recently developed a trinucleating ligand system comprising three salen-ligand compartments bridged in a *meta*-phenylene arrangement by a central phloroglucinol backbone (Scheme 1).[2,3] These triplesalen ligands are intended to combine phloroglucinol **A**, as a ferromagnetic coupler by the spin-polarization mechanism,[4] and the salen-like coordination environment **B**, which enforces a strong magnetic anisotropy in selected metal ions.[5] Indeed, the characterization of trinuclear Cu^{II} and $V^{IV}=O$ complexes demonstrate the targeted ferromagnetic interactions,[6–8] while in Mn^{III}[9] and Fe^{III}[10] complexes, antiferromagnetic interactions prevail. Moreover, the trinuclear complexes of the *tert*-butyl derivative H_6-$talen^{tBu_2}$ exhibit a strong ligand folding, which leads to an overall bowl-shaped molecular structure (Scheme 1).[3,7] We have taken advantage of this by reacting two trinuclear Mn^{III} triplesalen complexes with hexacyanometalates to obtain the heptanuclear complexes $[\{(talen^{tBu_2})Mn^{III}{}_3\}_2\{M(CN)_6\}]^{3+}$ (M = Cr^{III},[11] Fe^{III},[12] Co^{III}[13]) in a supramolecular approach, and $Mn^{III}{}_6Cr^{III}$ is a single-molecule magnet.[11]



Scheme 1.

In order to rationally improve the magnetic properties of these supramolecular aggregates, we are trying to optimize its molecular building blocks.[14] One strategy is to employ less-folded trinuclear building blocks, which can be used to form triple-stranded 1D chains or nonanuclear complexes of the type $M_3'M_3M_3'$. Thus, we thought the all sp^2-derivative triplesalophen ligand system would be a good candidate (Scheme 1). Herein, we present the successful synthesis of the first triplesalophen ligand H_6baron^{Br} and its trinuclear Ni^{II} complex that comprises a diamagnetic square-planar Ni^{II} ion and two paramagnetic octahedral Ni^{II} ions. Magnetic measurements confirm ferromagnetic coupling between the two Ni^{II} ($S = 1$) ions by the spin-polarization mechanism. This is the first ferromagnetic interaction propagated by an extended phloroglucinol ligand for spins with $S_i > 1/2$.

Results and Discussion

H_6baron^{Br} was isolated as a bright yellow solid in 92% yield by reacting 2-[(2-aminophenylimino)(phenyl)methyl]-

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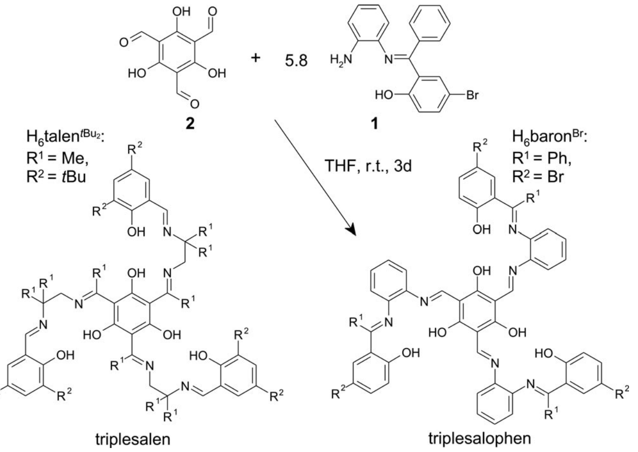
4-bromophenol (**1**) and 2,4,6-triformylphloroglucinol (**2**) in a Schiff base condensation reaction (Scheme 2). The successful synthesis was confirmed by FTIR spectroscopy, mass spectrometry, and elemental analysis. The FTIR spectrum shows strong bands at 1611 and 1578 cm^{-1}, which are assigned to the aldimine and ketimine C=N bond, respectively. The aldimine C=N stretch corresponds well with that of H$_2$salophen at 1613 cm^{-1}.[15]



Scheme 2.

Reaction of H$_6$baron$^{\mathrm{Br}}$ with three equivalents of Ni$^{\mathrm{II}}$(OAc)$_2$·4H$_2$O in pyridine afforded a deep red solid **3**. The C=N stretches are shifted to lower energy (1558 cm^{-1} for ketimine, 1591 cm^{-1} for aldimine), in accordance with coordination of the ligand to Ni$^{\mathrm{II}}$. However, the aldimine C=N stretching band is significantly lower in comparison to that of the corresponding vibration in [(salophen)Ni] at 1605 cm^{-1}.[16] This implies that the double-bond character of the aldimine in **3** is weakened. The MALDI-TOF mass spectra exhibit only signals corresponding to [(baron$^{\mathrm{Br}}$)Ni$_3$], while elemental analysis and single-crystal X-ray diffraction provides the formulation of **3** as [(baron$^{\mathrm{Br}}$)Ni{Ni(py)$_2$}$_2$] in the solid state. This indicates a weak coordination of the pyridine donors to the Ni$^{\mathrm{II}}$ ions and is in agreement with the ligand field being at the borderline between the preference for square-planar and octahedral coordination polyhedra.

The molecular structure of **3** consists of a neutral trinuclear complex in which one sixfold-deprotonated ligand (baron$^{\mathrm{Br}}$)$^{6-}$ coordinates three Ni$^{\mathrm{II}}$ ions as a triple(tetradentate) ligand (Figure 1). One Ni$^{\mathrm{II}}$ ion (Ni2) is four-coordinate in a square-planar coordination environment of two imine and two phenolate donor atoms. Ni1 and Ni3 are hexacoordinate in a distorted octahedral coordination environment by the N$_2$O$_2$ donor set of (baron$^{\mathrm{Br}}$)$^{6-}$ in the equatorial plane and by pyridine nitrogen atoms in the axial positions. These different coordination numbers are also reflected in the bond lengths. The Ni–O bonds of Ni2 are significantly shorter (1.85, 1.82 Å) than those of Ni1 and Ni3 (2.00, 1.96 Å and 2.01, 1.99 Å, respectively). This tendency is reflected in the Ni–N$^{\mathrm{imine}}$ bond lengths (Ni1: 1.98, 2.04 Å; Ni2: 1.83, 1.90 Å; Ni3: 1.99, 2.02 Å). Ni1 and Ni3 exhibit a long Ni–N$^{\mathrm{py}}$ bonds with lengths 2.20 and 2.17 Å and a short one with 2.18 and 2.14 Å, respectively. The angle between the best planes defined by the carbon atoms of the pyridine groups is 75.2° for Ni1 and 84.2° for Ni3, which indicates interactions of the pyridine groups with different orbitals of the Ni$^{\mathrm{II}}$ ions. It is conspicuous that the terminal Ni–O bonds are shorter than the central Ni–O bonds. This is quite contrary to the properties of the M–O bonds in [(talen$^{\mathrm{R}}$)M$_3$].[2,3,6–8] However, Ni–O, Ni–N$^{\mathrm{imine}}$, and Ni–N$^{\mathrm{py}}$ bond lengths are consistent with literature values for square-planar[17] or octahedral[18] Ni$^{\mathrm{II}}$ ions. The triplesalophen complex **3** exhibits no overall planar structure as envisioned but rather some strong ligand foldings. We identified the bent angles[19] $\varphi_{\mathrm{central}}$ and $\varphi_{\mathrm{terminal}}$ as best parameters to quantitatively determine the ligand folding.[3,7] The bent angle is defined by $\varphi = 180° - \angle(\mathrm{M{-}X_{NO}{-}X_R})$ (X$_{\mathrm{NO}}$:

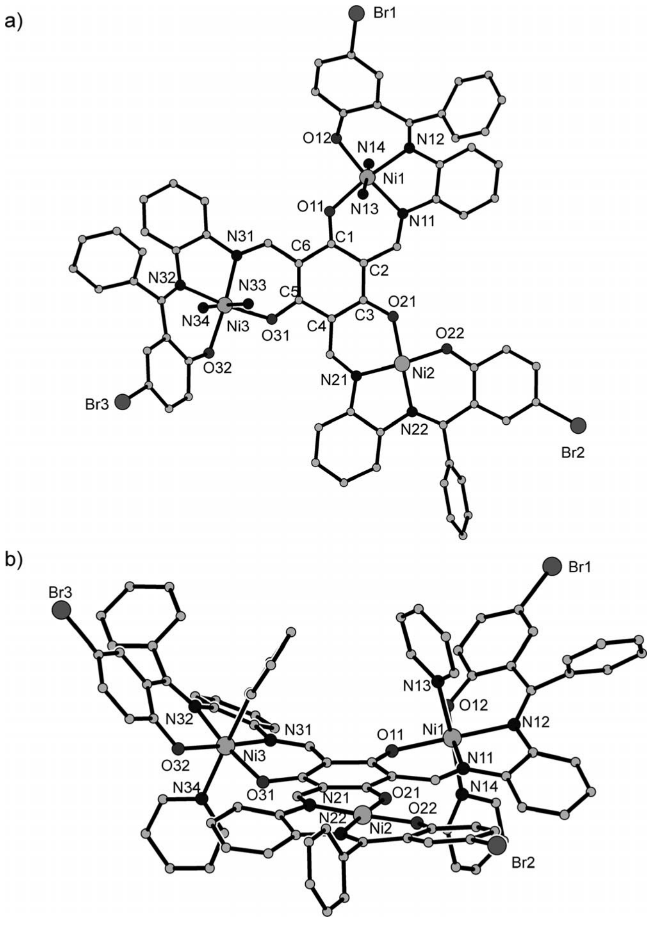


Figure 1. Molecular structure of **3** in crystals of **3**·3py·0.5C$_5$H$_{12}$ (a) drawn perpendicular to the central phloroglucinol ring; carbon atoms of the pyridines are omitted for clarity, and (b) drawn parallel to the central phloroglucinol ring. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ni1–O11 1.996(3), Ni1–O12 1.956(3), Ni1–N11 1.977(4), Ni1–N12 2.037(4), Ni1–N13 2.198(4), Ni1–N14 2.166(4), Ni2–O21 1.854(3), Ni2–O22 1.819(3), Ni2–N21 1.827(4), Ni2–N22 1.896(4), Ni3–O31 2.010(3), Ni3–O32 1.966(3), Ni3–N31 1.985(4), Ni3–N32 2.024(4), Ni3–N33 2.183(4), Ni3–N34 2.144(4), C1–C2 1.456(6), C1–C6 1.460(6), C2–C3 1.432(6), C3–C4 1.417(6), C4–C5 1.452(6), C5–C6 1.423(6), Ni1··Ni2 7.2984(12), Ni1··Ni3 7.3862(12), Ni2··Ni3 7.2115(12).

midpoint of adjacent N and O donor atoms; X_R: midpoint of the six-membered chelate ring containing the N and O donor atoms). In **3**, these angles are smaller for square-planar coordinated Ni2 ($\varphi_{central}$ = 8.5°, $\varphi_{terminal}$ = 14.8°) than for octahedrally coordinated Ni1 ($\varphi_{central}$ = 20.5°, $\varphi_{terminal}$ = 32.1°) and Ni3 ($\varphi_{central}$ = 30.4°, $\varphi_{terminal}$ = 36.1°). For all Ni^{II} ions, $\varphi_{terminal}$ is bigger than $\varphi_{central}$, which is in contrast to that for the trinuclear triplesalen complexes. However, $\varphi_{central}$ of Ni1 and Ni3 is of the same magnitude as in $[(talen^{tBu_2})Cu_3]\cdot 3.5CHCl_3$.[7] A close inspection of the intermolecular interactions reveals π–π interactions between two molecules of **3** by the terminal phenolate and the phenylenediamine bridge of Ni2. The pyridine groups of Ni1 and Ni3 with long $Ni–N^{py}$ bonds exhibit intermolecular interactions as well. They are directed to the terminal phenyl substituent of Ni2 (Figure S1). These intermolecular interactions may cause some of the observed ligand folding.

We performed temperature-dependent magnetic measurements (SQUID, 2–220 K, 1 T) on a sample of $3\cdot 3py\cdot 1.5H_2O$ (Figure 2). The effective magnetic moment, μ_{eff}, increases by lowering the temperature, in agreement with the expected ferromagnetic interactions though the spin-polarization mechanism. Variable temperature-variable field (VTVH) magnetization measurements were performed at 1, 4 and 7 T. The isofield lines exhibit only a small nesting behavior. In order to obtain *J* and *D* values, we performed a full-matrix diagonalization of the appropriate spin-Hamiltonian (Equation 1), including Heisenberg–Dirac–van-Vleck (HDvV), zero-field splitting, and Zeeman interactions using the program package JulX.[20]

$$\hat{H} = -2J\mathbf{S}_1\mathbf{S}_2 + \sum_{i=1}^{2} D_i\left[S_{z,i}^2 - \frac{1}{3}S_i(S_i+1)\right] + \sum_{i=1}^{2} g_i\mu_B S_i B \qquad (1)$$

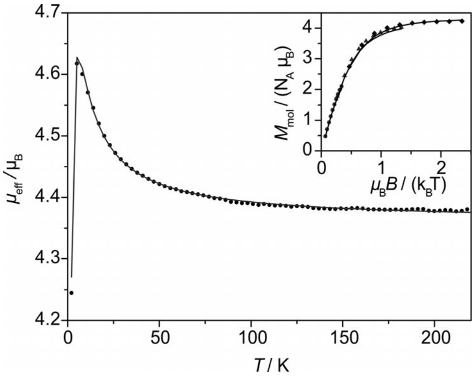


Figure 2. Temperature-dependence of the effective magnetic moment, μ_{eff}, and VTVH magnetization measurements (inset) of $3\cdot 3py\cdot 1.5H_2O$. The solid lines correspond to a fit of the experimental data by using the values given in the text.

In this procedure, saturation effects are taken into account, and intermolecular interactions are modeled by a Weiss temperature θ. The best agreement between experimental and simulated data was obtained for two high-spin Ni^{II} ions (S_i = 1) with $J = +1.05\ cm^{-1}$, g = 2.18, $|D|$ = 2.15 cm^{-1}, TIP = $255 \times 10^{-6}\ cm^3 mol^{-1}$ (subtracted from experimental and simulated data), and θ = –0.51 K. Despite the use of a Weiss-correction for the intermolecular antiferromagnetic interactions, a dimer-of-dimer model was also considered by using an intermolecular exchange coupling of $J' = -0.10\ cm^{-1}$, which then results in $J = +0.98\ cm^{-1}$ (Figure S2 and Scheme S1). The π–π interactions between two molecules of **3** observed in the crystal structure (Figure S1) may account for this antiferromagnetic intermolecular interaction. The intramolecular ferromagnetic coupling is consistent with the anticipated spin-polarization pathway, and the coupling constant is consistent with values in the range 1.02–1.55 cm^{-1}, obtained for trinuclear Cu^{II} triplesalen complexes.[6,7] Although **3** exhibits the same magnitude of ligand folding as $[(talen^{tBu_2})Cu_3]\cdot 3.5CHCl_3$, the coupling constant of the latter is higher ($J = +1.55\ cm^{-1}$).[7] On the other hand, the coupling in related bis(oxamato) Ni^{II} complexes is also slightly stronger, with $J \approx 1.6\ cm^{-1}$.[21]

In conclusion, we have been able to synthesize the all sp^2-hybridized analogue of triplesalen, which we term triplesalophen. This ligand allowed the isolation and characterization of the first trinuclear Ni^{II} complex, which exhibits paramagnetic Ni^{II} ions bridged by a modified phloroglucinol backbone. In accordance to the spin-polarization mechanism, magnetic measurements reveal ferromagnetic interactions between the two paramagnetic Ni^{II} ions. This is the first ferromagnetic interaction observed between metal ions with more than one unpaired electron in phloroglucinol-bridged complexes. We are currently applying trinuclear triplesalophen complexes for the construction of triple-stranded nonanuclear complexes as candidates for SMMs and of 1D triple-stranded chains as candidates for SCMs.

Experimental Section

Synthesis of 2,4,6-Tris{[2-((5-bromo-2-hydroxyphenyl)phenylmethylimino)phenylimino]methyl}-1,3,5-trihydroxybenzene (H_6baron^{Br}): 2,4,6-Triformylphloroglucinol[22] (0.10 g, 0.48 mmol) and 2-[(2-aminophenylimino)phenylmethyl]-4-bromophenol[23] (1.01 g, 2.78 mmol, 5.8 equiv.) were dissolved in anhydrous tetrahydrofuran (30 mL). The resulting orange solution was stirred at room temperature for 3 d. In this time, a yellow precipitate formed, which was collected by filtration, washed with methanol (10 mL), and dried in vacuo. H_6baron^{Br} was isolated as a bright yellow solid. Yield: 0.58 g (92 %). $C_{72}H_{57}Br_3N_6O_{7.5}$ (1365.98): calcd. C 63.31, H 4.21, N 6.15; found C 63.65, H 4.34, N 6.36. MALDI-TOF-MS: *m*/*z* = 1258.5 [M]$^+$, 1281.5 [M + Na]$^+$, 1298.0 [M + K]$^+$. IR (KBr): $\tilde{\nu}$ = 1611 (s), 1578 (s), 1553 (s), 1493 (w), 1443 (m), 1331 (w), 1290 (m), 1265 (m), 1234 (m), 750 (w) cm^{-1}.

Synthesis of $[(baron^{Br})Ni\{Ni(py)_2\}_2]$ (3): A solution of H_6baron^{Br} (300 mg, 0.24 mmol) in pyridine (120 mL) was added dropwise to a solution of $Ni(OAc)_2\cdot 4H_2O$ (182 mg, 0.73 mmol, 3.07 equiv.) in pyridine (75 mL). The resulting deep red solution was stirred at 60 °C for 1 h. The reaction solution was allowed to cool to room temperature and was filtered. Upon slow diffusion of pentane into the reaction solution, red columns were obtained, which were analysed to be $3\cdot 3py\cdot 1.5H_2O$. Yield: 243 mg (51 %).

$C_{101}H_{77}Br_3N_{13}Ni_3O_{7.5}$ (2008.58): calcd. C 60.40, H 3.86, N 9.07; found C 60.45, H 3.82, N 8.95. MALDI-TOF-MS: m/z = 1428.9 $[\{(\text{baron}^{Br})Ni_3\} + H]^+$. IR (KBr): $\tilde{\nu}$ = 1591 (m), 1560 (m), 1501 (s), 1475 (s), 1344 (m), 1240 (m), 1147 (w), 744 (w), 702 (m).

Crystal Data of 3·3py·0.5C$_5$H$_{12}$: $C_{103.5}H_{80}Br_3Ni_3N_{13}O_6$, M = 2017.67, triclinic, a = 13.719(2) Å, b = 19.004(3) Å, c = 19.933(3) Å, α = 65.406(2)°, β = 74.600(3)°, γ = 86.741(3)°, U = 4547.0(11) Å^3, T = 173(2) K, space group $P\bar{1}$, Z = 2, 40896 reflections measured, 15927 unique (R_{int} = 0.0543) were used in all calculations. R_1 = 0.0530 [$I > 2\sigma(I)$], wR_2 = 0.1489 (all data).

CCDC-786851 contains the supplementary crystallographic data for this paper. These data can be obtained free for charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Illustration of two molecules of **3**·3py·0.5C$_5$H$_{12}$, which indicates intermolecular interactions and simulation of the experimental data of temperature-dependent magnetic measurements in a dimer-of-dimer model.

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