The novel triplesalen ligand bridges three Ni^II-salen subunits in a *meta*-phenylene linkage †

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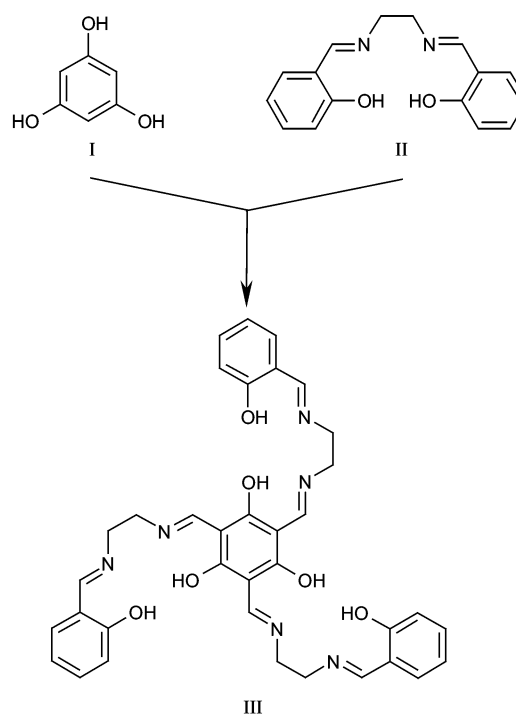
An unique trinickel(II) complex has been synthesized and characterized using the novel triplesalen ligand H$_6$talen which bridges three Ni^II-salen units in a *meta*-phenylene linkage.

The development of new types of molecule-based magnets requires the design of molecules with ferromagnetic interactions between the paramagnetic centers.[1] One strategy for synthesizing materials with ferromagnetic interactions is provided by the *meta*-phenylene linkage of organic radicals and carbenes, utilizing the spin-polarization mechanism.[2] This concept was applied to binuclear transition metal complexes containing pyrimidine or resorcinol as bridging ligands.[3,4] One trinuclear complex with phloroglucinol (1,3,5-trihydroxy-benzene) as bridging ligand was reported which exhibits ferromagnetic interactions between the three coordinated (Tp*)-Mo^VOCl fragments (Tp* = tris((3,5-dimethylpyrazolyl)-hydroborate).[4] Recently, we reported the use of a modified phloroglucinol ligand as ferromagnetic coupler between three Cu^II ions through the spin-polarization mechanism to give a S_t = 3/2 spin ground state.[5] Polynuclear transition metal complexes with high spin ground states and strong magnetic anisotropy of the easy axes type exhibit slow relaxation of the magnetization at low temperature resulting in a hysteresis of the magnetization of pure molecular origin (single-molecule magnets, SMM).[6] Here, we report a further development of the modified phloroglucinol ligands in our efforts for the rational synthesis of a SMM. The design, synthesis, and characterization of a hybrid ligand which combines the phloroglucinol bridging unit with three salen-like coordination environments is described. Metal complexes with salen-like coordination environments exhibit a pronounced magnetic anisotropy due to the strong ligand field in the basal plane. A well studied example is the Jacobsen catalyst [(salen′)Mn^IIICl] with salen′ = (*R,R*)-*N,N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine.[7] Campbell *et al.* studied the catalyst upon addition of substrate by dual-mode EPR spectroscopy and determined a zero-field splitting of $D = -2.5$ cm^{-1} for the Mn^III ($S = 2$) species.[8] The new hybrid ligand reported here is capable of bridging three metal–salen units in a *meta*-phenylene linkage demonstrated by the synthesis and characterization of its trinuclear Ni^II complex.

In order to combine the phloroglucinol bridging unit **I** with salen-like ligand units **II**, we designed the hybrid ligand **III** (Scheme 1) which we term 'triplesalen'. The requirement for a successful synthesis was a differentiation of the reactivity of the two amine functions of the ethylenediamine component. The sterically more shielded amine group of 1,2-diamino-2-methyl-propane does not react with ketones.[9] Thus, the reaction of the triketone **H$_3$1** with this diamine yielded regioselectively the triplesalen half-unit **H$_3$2** (Scheme 2). The ESI mass spectrum confirms the condensation of three diamine molecules with one molecule of **H$_3$1**. The NMR spectra of **H$_3$2** (^{1}H NMR: 3

† Electronic supplementary information (ESI) available: synthesis and characterization of compounds, temperature dependent NMR spectra of H$_6$talen. See http://www.rsc.org/suppdata/dt/b3/b303290f/
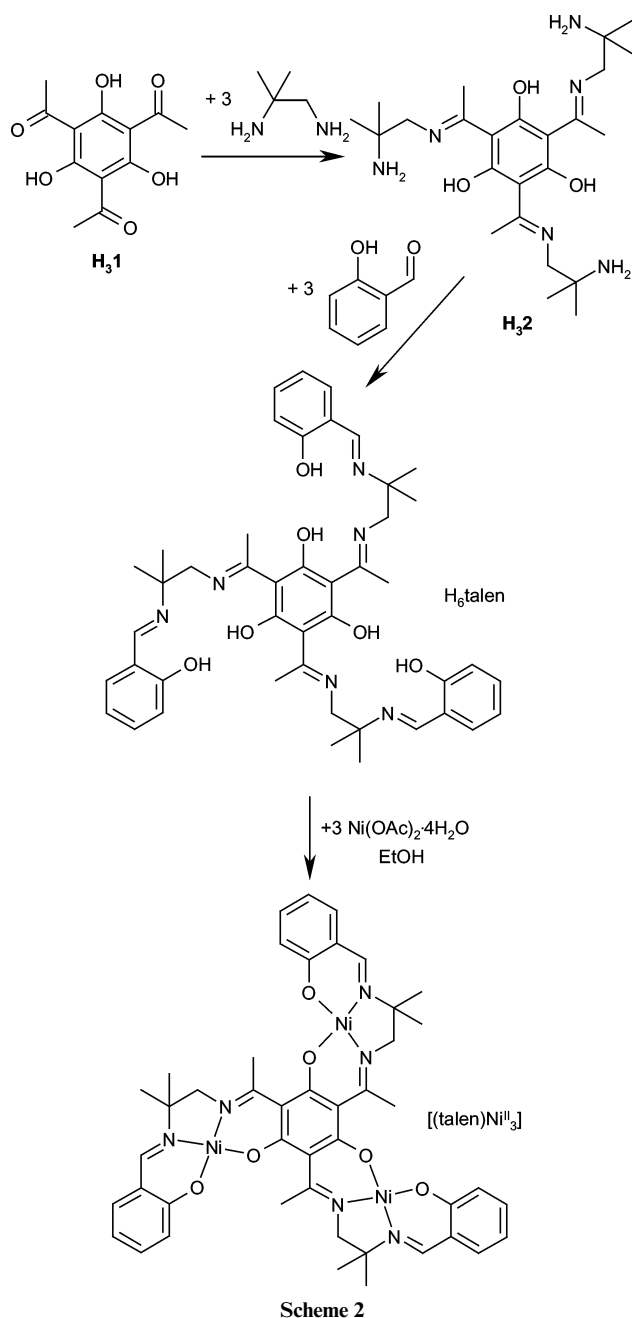

Scheme 1

resonances; ^{13}C NMR: 7 resonances) prove the regioselectivity of the reaction and the threefold symmetry of the molecule (C_{3h}). The two methylene protons exhibit a hyperfine inter-action with the phenolic proton. This J(H,H) coupling including an O–H · · · N hydrogen bond is corroborated by the low C=N stretching frequency at 1538 cm^{-1} in the IR spectrum of **H$_3$2**. Treatment of **H$_3$2** with salicylaldehyde gave the *triple-salen* ligand H$_6$talen (= 2,4,6-tris(1-(2-salicylaldimino-2-methyl-propylimino)-ethyl)-1,3,5-trihydroxybenzene) as a yellow solid. The ^{1}H NMR spectra of H$_6$talen exhibit a temperature depend-ence (Fig. S1).† At 40 °C the expected 8 resonances for a three-fold symmetry (C_{3h}) are observed. Lowering the temperature leads to complicated spectra with splittings of the resonances for the OH protons, the aldimine proton, and the methylene doublet. The ^{13}C NMR spectrum at 25 °C corroborates this dynamic behavior. We attribute this temperature-dependence of the NMR spectra to some hindered rotations. H$_6$talen exhibits a C=N stretching frequency at 1630 cm^{-1} for the aldimine C=N bond and in accordance to **H$_3$2** a low C=N stretching frequency at 1536 cm^{-1} for the ketimine C=N bond.

Reaction of H$_6$talen with 3 equivalents of Ni^II(OAc)$_2$·4H$_2$O in EtOH resulted in an orange–red microcrystalline solid. MALDI-TOF mass spectra and elemental analysis confirmed the successful synthesis of [(talen)Ni^II$_3$]. The ^{1}H NMR and ^{13}C NMR spectra of [(talen)Ni^II$_3$] exhibit sharp resonances con-sistent with the diamagnetism of square-planar coordinated Ni^II (d^8, $S = 0$) and demonstrate the threefold symmetry of

H₃1

H₃2

H₆talen

+3 Ni(OAc)₂·4H₂O
EtOH

[(talen)Ni^{II}₃]

Scheme 2

a)

b)

Fig. 1 Molecular structure of [(talen)Ni₃]. Selected bond lengths [Å]: Ni1–O11 1.832(2), Ni1–O12 1.852(3), Ni1–N11 1.859(3), Ni1–N12 1.851(3), O11–C1 1.291(4), O12–C101 1.310(4), N11–C11 1.299(4), N12–C17 1.284(5), Ni2–O21 1.814(2), Ni2–O22 1.852(2), Ni2–N21 1.851(3), Ni2–N22 1.845(3), O21–C5 1.293(4), O22–C201 1.305(4), N21–C21 1.313(4), N22–C27 1.289(4), Ni3–O31 1.827(2), Ni3–O32 1.862(2), Ni3–N31 1.851(3), Ni3–N32 1.852(3), O31–C3 1.296(4), O32–C301 1.314(4), N31–C31 1.309(4), N32–C37 1.287(4); metal–metal distances [Å]: Ni1 ⋯ Ni2 7.000(1), Ni2 ⋯ Ni3 7.169(1), Ni3 ⋯ Ni1 7.132(1).

[(talen)Ni^{II}₃] in solution (C_{3h}). Additionally, no temperature-dependence was observed showing that the rotations observed in the free ligand are blocked by complexation. The C=N stretching frequencies for [(talen)Ni^{II}₃] appear at 1615 cm^{-1} (aldimine) and 1551 cm^{-1} (ketimine). A detailed picture of its molecular structure was provided by X-ray crystallography. ‡

The structure analysis revealed discrete trinuclear nickel complexes [(talen)Ni^{II}₃] (Fig. 1a). The complex has no crystallographically imposed symmetry. However, the threefold axes perpendicular to the molecular plane observed in solution by NMR spectroscopy remains as a pseudo C_3 axes. The whole molecule is not flat but bowl-shaped (Fig. 1b). The two methyl groups of each dimethyl unit are discriminated: one methyl group lies in the plane of the salen sub-unit (equatorial; C16, C26, C36) whereas the other is directed perpendicular to the salen sub-unit (axial; C15, C25, C35). The Ni–Ni distances are 7.00, 7.17, and 7.13 Å. All nickel centers are square-planar co-ordinated by two phenolato donors and two imine nitrogen donors. The Ni–O bond distances of the central phenolato donors are slightly shorter (1.82 Å) as compared to the terminal phenolato donors (1.86 Å). The Ni–N bond distances of 1.85 Å of the ketimine and aldimine nitrogen donors do not differ in
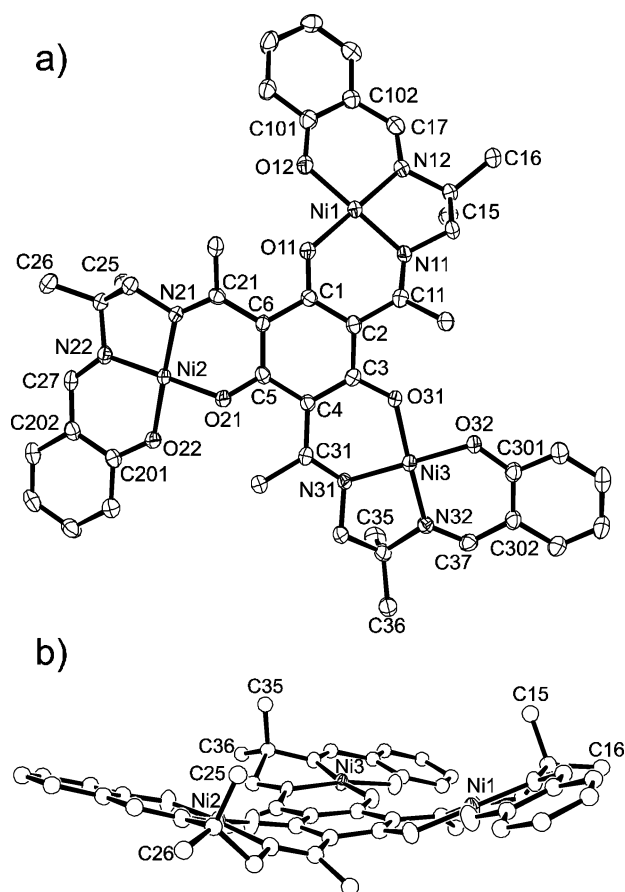
the experimental limit (±3σ). Thus, the metal–ligand bond distances reveal a slightly stronger Ni–O bond involving the central phenol ligand as compared to the terminal phenol ligands. The crystal structure exhibits some close contacts between two [(talen)Ni^{II}₃] along the *a*-axes with the shortest C–C distance of 3.05 Å.

In order to get some insights into the variation of the electronic structure by going from the mononuclear salen units to the trinuclear triplesalen units, the electronic absorption spectra of H₆talen and [(talen)Ni^{II}₃] were measured and compared to the spectra of H₂salen and [(salen)Ni^{II}] (Fig. 2). H₂salen exhibits three strong absorption maxima assigned to π⟶π* transitions of the phenolic chromophores at 214 and 256 nm and of the imine group at 316 nm.[10] The electronic spectrum of H₆talen in CH₃CN shows absorption maxima at 215, 253, 309, and 347 nm. The energies and line shapes of the two high energy bands resemble those of H₂salen with an increase of the intensity by a factor of 2 consistent with 4 benzene moieties in H₆talen and 2 benzene moieties in H₂salen. In contrast, the overall intensity in the 275–400 nm region of H₆talen is approximately ten times larger compared to H₂salen. Thus, the electronic structure of H₆talen cannot be described as a threefold superposition of the electronic structure of H₂salen. The topology of the triplesalen ligand with the shared, bridging phloroglucinol unit results in an electronic communication between the π systems of the three salen sub-units resulting in increased absorption intensity at lower energy. The absorption spectrum of [(salen)Ni^{II}] consists of a weak band at 543 nm
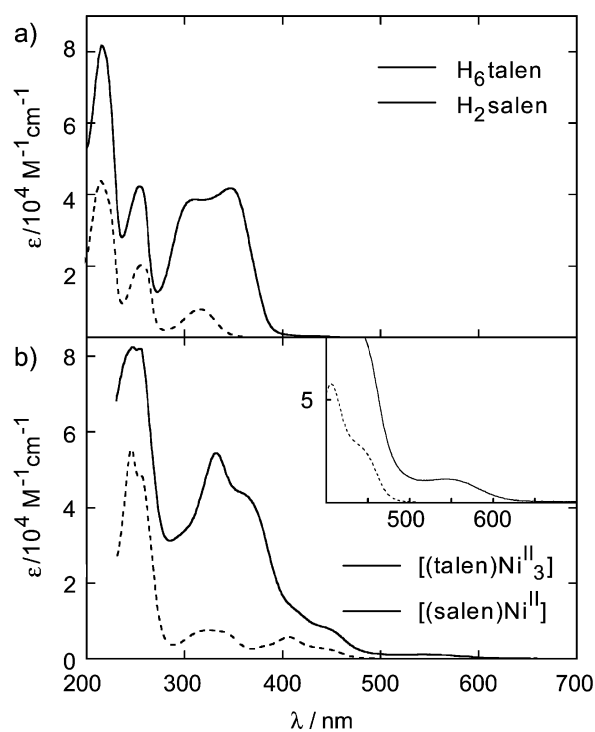
Fig. 2 Electronic spectra of H₆talen (———) and H₂salen (---) (a), and of [(talen)Ni^{II}₃] (———) and [(salen)Ni^{II}] (---) (b). All spectra were measured in CH₃CN despite the spectrum of [(talen)Ni^{II}₃] which was measured in CH₂Cl₂.

(d–d), three absorption features in the 375 to 460 nm range (MLCT C=N), and two bands in the 300–350 nm region ($\pi \rightarrow \pi^*$ C=N).[10] Below 280 nm, the spectrum of [(talen)Ni^{II}₃] exhibits strong absorption features which are similar in shape and position to those of [(salen)Ni^{II}]. The spectral region from 280 to 400 nm exhibits strong absorptions with a tenfold intensity compared to [(salen)Ni^{II}] which may be attributed to a coupling of the phenolate $\pi \rightarrow \pi^*$ and LMCT transitions over the π system of the central benzene ring. The intensity of the d–d transition at 544 nm in the trinuclear complex is increased by a factor of 8 consistent with more pronounced symmetry lowering by the differentiated Ni^{II}-phenolato bonds. In summary, the observed changes in the electronic absorption spectra by going from H₂salen to H₆talen and from [(salen)Ni^{II}] to [(talen)Ni^{II}₃] may be interpreted by a strong electronic communication between the three salen units involving π molecular orbitals.

A versatile synthetic route for the novel triplesalen ligand H₆talen has been worked out. The synthesis of the trinuclear complex [(talen)Ni^{II}₃] demonstrates that the strong coordinating properties of H₂salen are still present in H₆talen. The analysis of the electronic absorption spectra indicates that

an electronic interaction between the three salen sub-units exist which is probably propagated by the π system of the bridging phloroglucinol backbone. This hybrid ligand has been designed for the synthesis of trinuclear complexes with high spin ground states and pronounced magnetic anisotropy. Thus, the synthesis of trinuclear Cr^{III}, Mn^{III}, and Fe^{III} complexes with the triplesalen ligand is an attractive goal. We consider such derivatives as potential candidates for rationally designed SMM.

References

‡ Crystal data for [(talen)Ni^{II}₃]·CHCl₃·0.5C₆H₅CH₃: C₄₉.₅H₅₃Ni₃N₆O₆Cl₃, M = 1110.46, monoclinic, a = 26.4321(10), b = 12.7252(5), c = 30.8525(11) Å, β = 110.7210(10)°, V = 9706.1(6) Å³, T = 153 K, $C2/c$, Z = 8, μ(Mo-Kα) = 1.373 mm^{-1}, 38565 reflections measured, 8551 unique (R_{int} = 0.061), 6771 observed [$I > 2\sigma(I)$], 614 parameters, final $R[I > 2\sigma(I)]$ = 0.045, R_w = 0.105. CCDC reference number 196942. See http://www.rsc.org/suppdata/dt/b3/b303290f/ for crystallographic data in CIF or other electronic format.

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