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Synthesis and characterization of trinuclear square-planar Ni^{II}_3 and Cu^{II}_3 complexes of an extended phloroglucinol ligand: Experimental evidence for the relative contributions of benzene-like and radialene-like resonance structures

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ABSTRACT

The synthesis and characterization of the extended phloroglucinol ligand H_3felddien, its trinuclear Ni^{II} complex [(felddien)Ni_3]$(BF_4)_3$ and its trinuclear Cu^{II} complex [(felddien)Cu_3]$(ClO_4)_3$ is presented. Detailed NMR studies provide strong evidence that the ligand H_3felddien has to be described as the N-protonated tautomer and not as the O-protonated tautomer, with strong contribution of a radialene-like keto-enamine resonance structure resulting in a C_s and a C_{3h} isomer. The trinucleating tris(tetradentate) ligand provides three donor sets comprised of a phenolate, an imine, and two tertiary amine donors. This donor set enables the synthesis of the diamagnetic square-planar coordinated Ni^{II} complex [(felddien)Ni_3]$(BF_4)_3$ which provides the opportunity to perform detailed NMR spectroscopic characterizations for the evaluation of the electronic structure of the central phloroglucinol unit. In conjunction with a single-crystal X-ray diffraction and a UV–vis absorption spectroscopic analysis, these data indicate that in the coordinated form, the benzene-like phenolate-imine and the radialene-like keto-enamine resonance structures have contributions to the overall resonance hybrid. The weakening of the central π system as a consequence of the contribution of the keto-enamine resonance structure explains the relative small ferromagnetic interactions in the trinuclear Cu^{II} complex [(felddien)Cu_3]$(ClO_4)_3$. This detailed analysis identifies the strong resonance with unsaturated groups in 2,4,6 position of phloroglucinol as the main source for the low ferromagnetic couplings by the spin-polarization mechanism in all our extended phloroglucinol ligands. A replacement of the unsaturated imine functions by saturated amine functions may be a synthetic opportunity to enhance the ferromagnetic interactions by the spin-polarization mechanism in this ligand system.

1. Introduction

The synthesis of molecule-based magnets has attracted considerable interest over the past two decades [1,2]. For a rational development of new types of molecule-based magnets, the design of molecular building blocks with ferromagnetic interactions between the paramagnetic centers was supposed to be essential [3]. In this respect, we have recently established a family of trinucleating ligands sharing a common bridging phloroglucinol (1,3,5-trihydroxybenzene) unit consisting of tris(tridentate) ligands like H_3L [4] and the tris(tetradentate) triplesalen ligands $H_6talen^{X_2}$ [5,6] (Scheme 1a), as well as further modifications [7–10]. The phloroglucinol bridging unit was chosen to behave as a ferromagnetic coupler by the spin-polarization mechanism [11–23]. Indeed, trinuclear Cu^{II} [4,7,24,25] and V^{IV} [26] complexes exhibit weak but ferromagnetic interactions, while in Mn^{III} [10,27,28] and Fe^{III} [8] complexes antiferromagnetic interactions prevail. Moreover, severe ligand foldings have been observed in the complexes of the ligand $H_6talen^{t\text{-}Bu_2}$ resulting in overall bowl-shaped molecular structures [6,23,25]. We have taken advantage of this ligand folding by using the trinuclear complexes $[(talen^{t\text{-}Bu_2})\{M^t(solv)_n\}_3]^{m+}$ to act as molecular building blocks [23] with hexacyanometallates $[M^c(CN)_6]^{3-}$ for the formation of heptanuclear complexes $\mathbf{[M^t_6M^c]^{n+}}$ $([\{(talen^{t\text{-}Bu_2})M^t_3\}_2\{M^c(CN)_6\}]^{3+})$: $\mathbf{[Mn^{III}_6Cr^{III}]^{3+}}$, [29] $\mathbf{[Mn^{III}_6Fe^{III}]^{3+}}$, [30] and $\mathbf{[Mn^{III}_6Co^{III}]^{3+}}$ [31] with $\mathbf{[Mn^{III}_6Cr^{III}]^{3+}}$ being a single-molecule magnet (SMM) [23].

The syntheses of the ligands H_3L and $H_6talen^{X_2}$ are based on the triketone **1** (Scheme 1a). Recently, we have been able to synthesize the ligand H_3felden [32] (Scheme 1b) following a protocol for the trialdehyde **2** established by MacLachlan et. al. [33]. A detailed analysis of the ligand H_3felden and its trinuclear Cu^{II} complex [(felden){Cu(bpy)}$_3$]$(ClO_4)_3$ revealed, that the central phloroglucinol backbone is not in the anticipated conventional phenol form, that is mainly described by the benzene-like enol-imine resonance structure **I** (Scheme 1c), but in the N-protonated tautomer with se-

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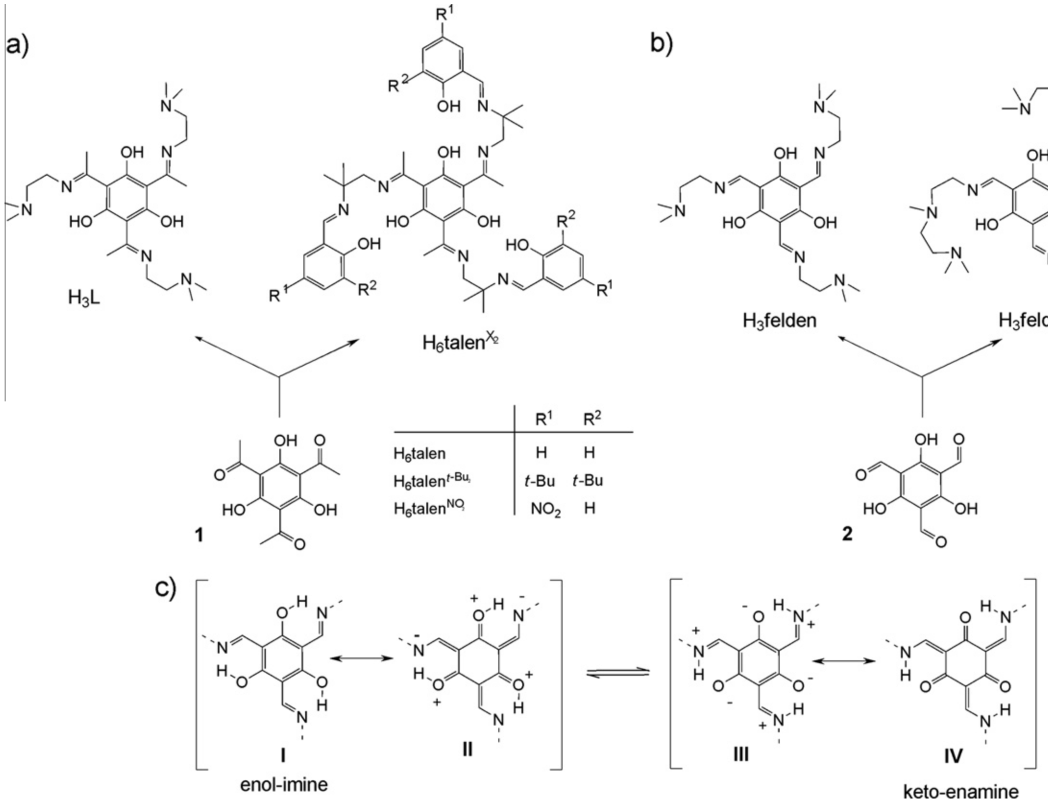


Scheme 1.

vere contributions from the keto-enamine resonance structure **IV**, which may be described as radialene-like [32].

Herein, we present the synthesis of the ligand H_3felddien (Scheme 1b). This ligand was chosen to provide tetradentate ligand compartments to allow the synthesis of four-coordinate diamagnetic Ni^{II} complexes, which have not been accessible with the ligand H_3felden. The diamagnetic trinuclear Ni^{II}_3 complex should allow a NMR spectroscopic study, enabling to estimate relative contributions of the benzene-like and the radialene-like resonance structures in the complexes. In this respect, the synthesis and characterization of the two complexes [(felddien)Ni_3]$(BF_4)_3$ and [(felddien)Cu_3]$(ClO_4)_3$ is presented.

2. Experimental section

2.1. Preparation of compounds

Solvents and starting materials were of the highest commercially available purity and used as received. The synthesis of 2,4,6-triformylphloroglucinol (**2**) [33] and of the triamine **3** [34,35] has already been published.

2.1.1. H_3felddien

2,4,6-Triformylphloroglucinol (**2**) (36 mg, 0.15 mmol) and triamine **3** (135 mg, 0.93 mmol) were stirred in dichloromethane (12 mL) for 16 h. The resulting yellow solution was dried over sodium sulfate and the volatiles were removed under vacuum, yielding the product as a viscous yellow oil. Yield 79 mg (78%). ^{1}H NMR (500.25 MHz; $CDCl_3$): $\delta = 11.32$ (m, $NH_{2a} + NH_{2b}$), 10.95 (m, $NH_{2c} + NH_{2d}$), 8.22 (d, $^3J(H,H) = 14$ Hz, *H*CN 1b), 8.20 (d, $^3J(H,H) = 14$ Hz, *H*CN 1c), 8.12 (d, $^3J(H,H) = 14$ Hz, *H*CN 1a), 8.08 (d, $^3J(H,H) = 14$ Hz, *H*CN 1d), 3.45 (m, CH_2 3a–d), 2.62 (m, CH_2 4a–d), 2.53 (m, CH_2 6a–d), 2.41 (m, CH_2 7a–d), 2.29 (m, CH_3 5a–d), 2.23 (s, CH_3 8a–d). ^{13}C NMR (125.75 MHz, $CDCl_3$): $\delta = 187.89$, 185.23, 182.78, 181.14 (all C_{ar}O); 158.13, 157.58, 157.25, 156.53 (all C1a–d); 104.92, 104.88, 104.73, 104.67 (all C_{ar}CN); 58.13, 58.08, 57.96, 57.92 (all CH_2 4a–d); 57.32, 57.24 (all CH_2 7a–d); 55.97, 55.95, 55.88, 55.85 (all CH_2 6a–d); 48.01, 48.00, 47.97, 47.92 (all CH_2 3a–d); 45.84, 45.81(all CH_3 8a–d), 42.63, 42.62 (all CH_3 5a-d). ESI-MS (positive ion mode): m/z = 296.7 $[M+2H]^{2+}$, 592.3 $[M+H]^+$. IR (KBr): ν_{max}/cm^{-1} 2951br, 2857w, 2822br, 1611s, 1547m, 1462m, 1356w, 1325w. Elemental analysis: Found: C, 57.91; H, 9.44; N, 20.77. Calc. for H_3felddien·$1.5H_2O$ ($C_{30}H_{60}N_9O_{4.5}$): C, 58.22; H, 9.77; N, 20.37.

2.1.2. [(felddien)Ni_3]$(BF_4)_3$

A solution of H_3felddien (191 mg, 0.32 mmol) in methanol (17 mL) was added dropwise to a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (335 mg, 0.98 mmol) in methanol (30 mL). The resulting suspension was heated to reflux for 2 min during which the precipitate dissolves. While the solution was still warm, triethylamine (98 mg, 0.97 mmol) dissolved in methanol (2 mL) was added. After cooling to room temperature the complex can be isolated as a red solid. Yield: 194 mg (59%). ESI-MS (positive ion mode) m/z = 254.6 $[(\text{felddien})Ni_3]^{3+}$. IR (KBr): ν_{max}/cm^{-1} 3013w, 2932m, 1605s, 1514s, 1470m, 1439w, 1420m, 1400w, 1375w, 1362w, 1343w, 1329w, 1298w, 1285w, 1254m, 1244m, 1055br, 950w, 889w, 797m, 766w, 638w, 584w, 523w. Elemental analysis: Found: C, 35.04; H, 5.21; N, 12.13. Calc. for [(felddien)Ni_3]$(BF_4)_3$ ($C_{30}H_{54}N_9O_3Ni_3B_3F_{12}$): C, 35.14; H, 5.31; N, 12.30. To enhance the solubility in noncoordinating solvents (see text for details), [(felddien)Ni_3]$(BF_4)_3$ has been converted into the $B(Ar^F)_4$-salt ($B(Ar^F)_4^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) *via* salt-metathesis. All NMR-spectra have been collected from this salt. ^{1}H NMR (500.25 MHz; CD_2Cl_2): $\delta = 7.77$ (s, $B(Ar^F)_4^-$), 7.59 (s, $B(Ar^F)_4^-$), 7.33 (s, $C_{Ar}C$*H*CN), 3.79–2.10 (m, CH_2, CH_3). ^{13}C NMR

(125.75 MHz, CD_2Cl_2): δ = 169.3 (s, $C_{Ar}O$), 162.3 (q, ${}^1J_{BC}$ = 50 Hz, $B(Ar^F)_4^-$), 153.4 (s, $B(Ar^F)_4^-$), 125.2 (q, ${}^1J_{CF}$ = 270 Hz, $B(Ar^F)_4^-$), 129.5 (q, ${}^2J_{CF}$ = 32 Hz, $B(Ar^F)_4^-$), 118.1 (s, $B(Ar^F)_4^-$), 106.1 (s, $C_{Ar}CCN$), 62.1, 61.5, 59.4, 59.2, 50.1, 48.2, 42.8.

2.1.3. *[(felddien)Cu_3](ClO_4)$_3$*

A solution of H_3felddien (228 mg, 0.39 mmol) in methanol (27 mL) was added dropwise to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (431 mg, 1.16 mmol) in methanol (30 mL). The resulting suspension was heated to reflux for 2 min and triethylamine (117 mg, 1.16 mmol) dissolved in methanol (2 mL) was added. After cooling to room temperature the reaction mixture was filtered. Vapor diffusion of diethyl ether into the filtrate results in the deposition of small needles. Yield: 147 mg (35%). ESI-MS (positive ion mode) m/z = 259.7 [(felddien)Cu_3]$^{3+}$. IR (KBr): ν_{max}/cm^{-1} 2980m, 2926m, 2878m, 1609s, 1499s, 1466s, 1412m, 1360m, 1343m, 1329m, 1296w, 1248m, 1227m, 1090s, 963w, 941m, 926m, 883w, 791m, 760m, 923s, 579w, 503m. Elemental analysis: Found: C, 31.99; H, 5.12; N, 11.01. Calc. for [(felddien)Cu_3]$(ClO_4)_3{\cdot}3H_2O$ ($C_{30}H_{60}N_9O_6Cu_3Cl_3O_{12}$): C, 31.84; H, 5.34; N, 11.14.

2.2. X-Ray crystallography

Single-crystals of [(felddien)Ni_3]$(BF_4)_3{\cdot}0.5C_3H_6O$ suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of the complex in an acetone/cyclohexane mixture, removed from the mother liquor and immediately cooled to 100(2) K on a Bruker KAPPA APEX II CCD diffractometer at a detector distance of 3.51 cm. Crystal data for [(felddien)Ni_3]$(BF_4)_3{\cdot}0.5C_3H_6O$: M = 1054.42 g mol^{-1}, $C_{31.5}H_{57}F_{12}B_3Ni_3N_9O_{3.5}$, triclinic, space group $P\bar{1}$, a = 11.6183(11), b = 14.3983(13), c = 14.7360(15) Å, α = 69.698(4)°, β = 74.652(5)°, γ = 71.889(4)°, V = 2163.1(4) Å^3, Z = 2, ρ = 1.619 g cm^{-3}, μ = 1.390 mm^{-1}, F (0 0 0) = 1088, Crystal size = 0.10 × 0.04 × 0.02 mm^3. A total of 105492 reflections ($2.18 < \Theta < 25.00°$) were collected of which 7606 reflections were unique (R(int) = 0.0501). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2008/1 [36]. The structure was solved with the program SHELXS-97 [37,38] and refined using SHELXL-97 [38] to R = 0.0397 for 6003 reflections with $I > 2\sigma(I)$, R = 0.0589 for all reflections; Max/min residual electron density 0.538 and −0.318 e Å^{-3}. Two of the ligand arms were found to be disordered over two positions (see text). The three BF_4^- anions are so severely disordered, that not all found fluorine positions can be assigned to well resolved BF_4 tetrahedra.

2.3. Other physical measurements

Infrared spectra (400–4000 cm^{-1}) of solid samples were recorded on a Shimadzu FTIR-8400S spectrometer as KBr disks. UV–vis–NIR absorption spectra of solutions were measured on a Shimadzu UV-3101PC spectrophotometer in the range of 200–1200 nm at ambient temperatures. ESI mass spectra were recorded on a Bruker Esquire 3000 ion trap mass spectrometer equipped with a standard ESI source. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX500 or a Bruker AV300 spectrometer using the solvent as an internal standard. The electrochemical experiments were performed on Ar-flushed CH_3CN solutions containing 0.1 M $[NBu_4]PF_6$ in a classical three electrode cell. The working electrode was a platinum electrode, the counter electrode a platinum wire and the reference electrode was Ag/0.01 M $AgNO_3/CH_3CN$. All potentials are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple used as an internal standard. The electrochemical cell was connected to an EG&G potentiostat/galvanostat (VersaStat). Temperature-dependent magnetic susceptibilities were measured by using a SQUID magnetometer (MPMS XL-7 EC, Quantum Design) at 1 T (2–290 K). For calculations of the molar magnetic susceptibilities, χ_m, the measured susceptibilities were corrected for the underlying diamagnetism of the sample holder and the sample by using tabulated Pascal's constants. The JULX program package was used for spin-Hamiltonian simulations and fitting of the data by a full-matrix diagonalization approach [39].

3. Results and discussion

3.1. Synthesis and characterization

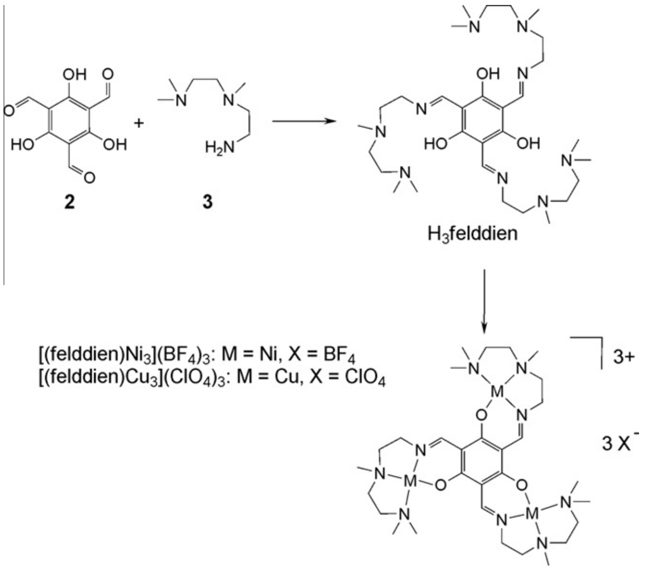
The ligand H_3felddien has been synthesized analogous to the previously reported ligands H_3L [4] and H_3felden [32] by a Schiff-base condensation of the triamine **3** and 2,4,6-triformylphloroglucinol (**2**) (Scheme 2). NMR spectroscopy, FTIR spectroscopy, mass spectrometry, and elemental analysis confirmed the successful synthesis of the ligand H_3felddien. The reaction of H_3felddien with nickel tetrafluoroborate hexahydrate in methanol in presence of triethylamine affords red solid [(felddien)Ni_3]$(BF_4)_3$. The trinuclear copper complex [(felddien)Cu_3]$^{3+}$ can be obtained in analogy to the nickel complex with copper perchlorate hexahydrate as starting material. Vapor diffusion of diethyl ether into the reaction mixture yielded the complex as green needles. The identity and purity of the complexes has been confirmed by FTIR spectroscopy, mass spectrometry, and elemental analysis.

3.2. NMR spectroscopy

3.2.1. H_3felddien

The ^{1}H NMR spectrum of the ligand H_3felddien exhibits multiple signals between 8.3–8.0 and 11.4–10.8 ppm for the imine and for the "phenolic OH" protons, respectively (Fig. 1a). This is not in agreement with the ligand as it is pictured in Scheme 2, since the imine and the phenolic OH protons should only give rise to singlets. However, this splitting pattern of the NMR spectra and various NMR experiments (see below) provide evidence that the ligand has to be described as the N-protonated tautomer, where the radialene-like resonance structure **IV** has strong contributions (Scheme 1c). Additionally, due to the radialene-like description, two different geometrical isomers (with C_{3h} and C_s symmetry, Scheme 3) are present [32,33,40–43].

It is possible to simplify the observed ^{1}H NMR spectra notably in order to facilitate the assignment of the resonances. The exchange



Scheme 2.

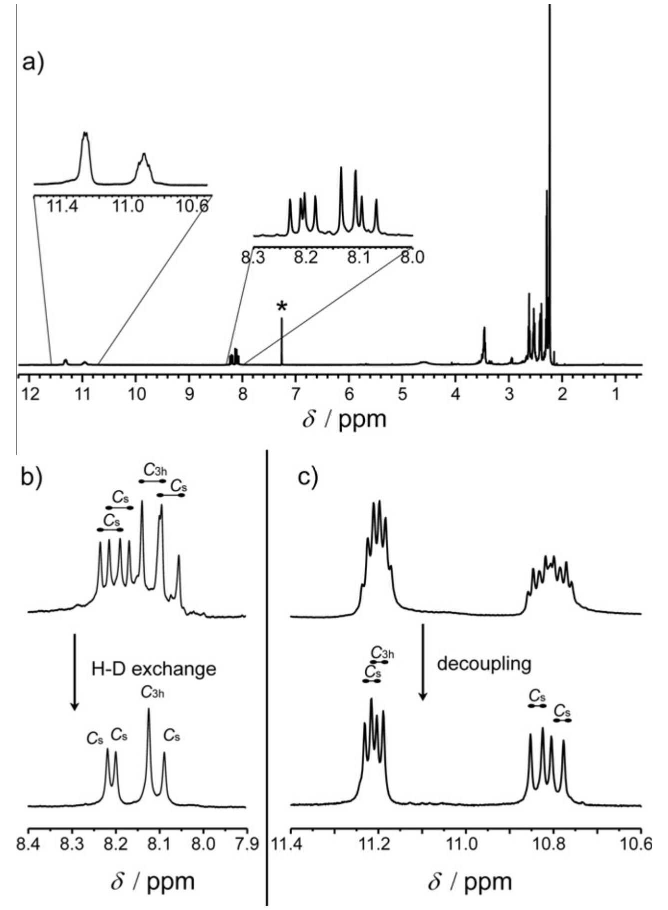
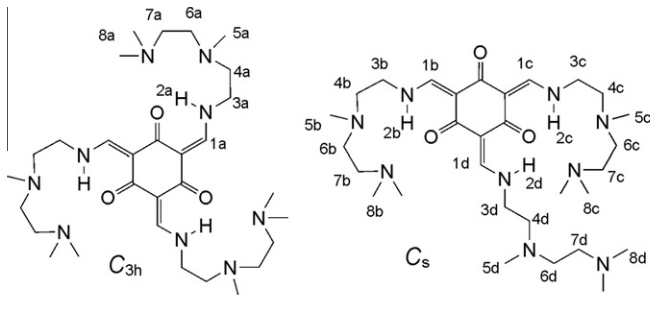


Fig. 1. (a) ^{1}H NMR spectrum of H_3felddien in $CDCl_3$ measured at 500 MHz (* = $CHCl_3$) (b) simplification of the ^{1}H NMR spectrum *via* substitution of NH with deuterium oxide in $CDCl_3$ measured at 300 MHz. (c) Simplification of the ^{1}H NMR spectrum in dmso-d_6 *via* irradiation in the resonances at 3.5 ppm.



Scheme 3.

of the acidic NH-protons (proton 2a–d in Scheme 3) with deuterium by addition of D_2O to a NMR sample leads to the collapse of the doublets between 8.3 and 8.0 ppm of the vinylic protons (1a–d) to four singlets (Fig. 1b). The singlet at 8.12 ppm can be assigned to the three equivalent vinylic protons of the C_{3h} isomer (1a in Scheme 3) and the three singlets at 8.22, 8.20, and 8.08 ppm to the three protons (1b, 1c, and 1d) of the particular arms of the C_s isomer. This experiment also simplified the determination of the ratio of the two isomers to be *ca.* 1:1.6 (C_{3h}/C_s) in $CDCl_3$. This divergence from a statistically ratio of the isomers, generated by a randomly orientation of the three enamines, of 1:3 (C_{3h}/C_s) in favor of the more symmetric compound can be attributed to the NH-ketone hydrogen bonds in the C_{3h} isomer without competition. The spectra exhibit no temperature dependence up to 140 °C, demonstrating a very strong energy barrier for rotation, which is a clear indication of the double bond character for the C_{Ar}–C_{imine} bond.

NMR spectra recorded in $CDCl_3$ and CD_2Cl_2 solutions result in only poorly resolved multiplets between 11.4 and 10.8 ppm, probably due to fast exchange of the acidic NH protons 2a–d with residual water in the solvents. However, the use of dmso-d_6 (upper spectrum in Fig. 1c) or conducting the NMR experiment at low temperatures enhanced the resolution of the multiplets notably. Coupling of the NH protons 2a–d with the vinylic protons 1a–d and with the methylene unit next to it (3a–d) leads to the observed coupling pattern. Irradiation into the resonance for the methylene protons 3a–d leads to a collapse of the multiplets into a set of four doublets due to the remaining coupling with the vinylic protons 1a–d (Fig. 1c).

The ^{13}C NMR spectra exhibit four sets of signals for each carbon atom, which is consistent with the presence of the C_{3h} and C_s isomers. The carbonyl resonances of the two isomers can be assigned to the signals between 188.0 and 181.0 ppm, confirmed by HMQC and HMBC experiments. These chemical shifts are more characteristic for a C=O double bond rather than for a phenolic C–OH single bond. Already Claramunt et al. remarked that the $C_{Ar}O$ resonance varies from 151 ppm for an enol-imine, like in resonance structure **I**, to 180 ppm for a pure keto-enamine tautomer, like in resonance structure **IV**, and is therefore the parameter which is most sensitive towards the relative tautomeric population [44].

In conclusion, the aldimine-based ligand H_3felddien has to be described, like the recently reported H_3felden, [32] as the N-protonated tautomer with strong contributions of the radialene-like resonance structure **IV**. Moreover, this appears to apply not only for our aldimine-based compounds, but to all our ketimine-based triplesalen ligands which exhibit either broad (H_6talen$^{t\text{-}Bu_2}$: 185.6 ppm, H_6talen^{NO_2}: 185.9 ppm) [6] or even multiple signals (H_6talen [5]: 185.0–186.2 ppm) for the chemical shift of the $C_{Ar}O$ resonance in the ^{13}C NMR spectra. This indicates on the one hand a strong contribution of a N-protonated radialen-like resonance structure and on the other hand that also the triplesalen ligands exist as two isomers in solution.

3.2.2. *[(felddien)Ni$_3$]$^{3+}$*

Since the $C_{Ar}O$ resonance appears to be a good measure for the relative contribution of a radialene-like resonance structure, we synthesized the diamagnetic four-coordinate square-planar complex $[(\text{felddien})Ni_3](BF_4)_3$ to investigate the electronic structure of the central unit after metal coordination by NMR spectroscopy. NMR experiments have been conducted in acetone-d_6, dmf-d_7, CD_3CN and dmso-d_6. However, all spectra exhibit significant line broadening of the signals which we refer to some paramagnetism due to coordination of solvent molecules to the Ni^{II} ions. Since the BF_4-salt of the complex is insoluble in non-coordinating solvents we performed a salt metathesis. The exchange of BF_4^- with $B(Ar^F)_4^-$ (=tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) enhanced the solubility in CD_2Cl_2 significantly allowing a detailed NMR spectroscopic analysis of the complex. The proton NMR spectra are complicated since all protons of the ethylene bridges are diastereotopic leading to multiplets between 3.8 and 2.1 ppm. Additionally, this demonstrates that the interconversion of the λ and the δ conformations of the chelate rings (vide infra) is slow on the NMR time scale. This is different to the behavior of $[(\text{talen}^{X_2})Ni_3]$ [6]. A characteristic signal of the complex is the imine proton which shows one single resonance at 7.33 ppm. This is comparable to resonances reported for several Ni^{II} salen complexes [45–47]. Of special interest are the ^{13}C NMR resonances of the central ring. The $C_{Ar}O$ resonances can be assigned to a signal at 169.3 ppm, which has been confirmed by HMQC and HMBC experiments. The triplesalen complexes $[(\text{talen}^{X_2})Ni_3]$ exhibit this resonance between 170.8 and 172.3 ppm [6], while the mononuclear analog [(salen)Ni] shows this signal at 161.0 ppm. Apparently, the NMR shifts observed for the trinuclear complex $[(\text{felddien})\text{Ni}_3]^{3+}$ as well as the trinuclear nickel triplesalen complexes are ∼10 ppm higher compared to those reported for mononuclear Ni^{II} salen complexes.

In this respect, it is interesting to analyze the relative contributions of the phenolate-imine and keto-enamine resonance structures in the mononuclear Ni^{II} salen complex. Mg-phenolate complexes exhibit $\text{C}_{\text{Ar}}\text{O}$ resonances between 161 and 165 ppm, [48,49] while Zn-phenolate complexes exhibit these resonances between 166 and 167 ppm [50]. Quite astonishing, the chemical shift of Zn^{II} salen complexes has been described between 168 and 174 ppm, [51,52] which is significantly higher compared to those of 161 ppm in Ni^{II} salen complexes. These data exemplify that there is no simple relation between the extent of a keto-enamine contribution and the ^{13}C NMR chemical shifts for metallated phenolates, as it is seen in the free ligands. However, the direct comparison of the mononuclear Ni^{II} salen complex to the trinuclear phloroglucinol-bridged complexes demonstrates that in the latter there is a significant contribution from the radialene-like resonance structure, but it appears that this contribution is less strong than in the free ligand.

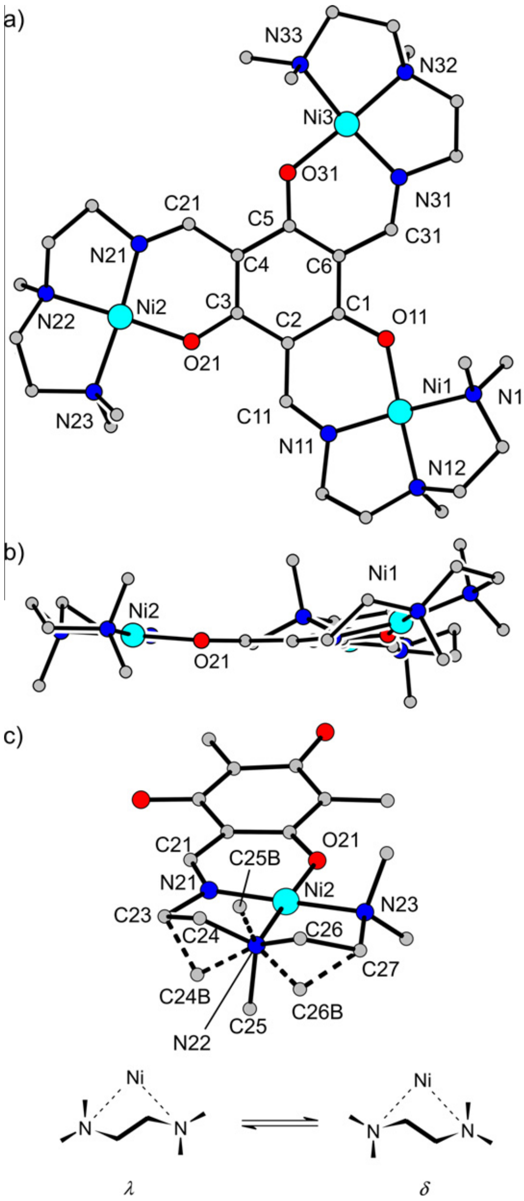


Fig. 2. Molecular structure of $[(\text{felddien})\text{Ni}_3]^{3+}$ in crystals of $[(\text{felddien})\text{Ni}_3](\text{BF}_3)_4 \cdot 0.5$ acetone (a) drawn perpendicular to the central benzene ring of the phloroglucinol backbone, and (b) drawn parallel to the central benzene ring of the phloroglucinol backbone. (c) Disorder of the ethylene bridge enclosing Ni2 in the conformation $\lambda\delta$ 75% (solid line) and $\delta\lambda$ 25% (dashed line). See text for details. Hydrogen atoms are omitted for clarity.

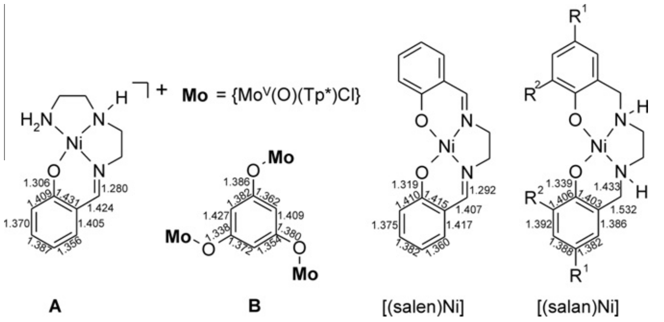
3.3. Structural characterization

The crystal structure of $[(\text{felddien})\text{Ni}_3](\text{BF}_4)_3 \cdot 0.5$acetone incorporates one cation $[(\text{felddien})\text{Ni}_3]^{3+}$ in the asymmetric unit, which exhibits no crystallographically imposed symmetry (Fig. 2). Selected interatomic distances and angels are summarized in Table 1. The deprotonated ligand felddien^{3-} acts as a triple(tetradentate) ligand for three Ni^{II} ions. The Ni^{II} ions are in a square-planar coordination environment coordinated by one phenolate, one imine, and two amine donors of the ligand. In contrary to the nickel triplesalen complexes the molecule $[(\text{felddien})\text{Ni}_3]^{3+}$ shows no significant ligand folding (Fig. 2b). This is manifested by small distances of the Ni^{II} ions to the best plane through the central ring ($d_{\text{Ni}_1} = 0.43$ Å, $d_{\text{Ni}_2} = 0.13$ Å, $d_{\text{Ni}_3} = 0.07$ Å). The mean values of the Ni–O, $\text{Ni–N}^{\text{imine}}$, $\text{Ni–N}^{\text{amine}}$, and $\text{Ni–N}^{\text{term-amine}}$ bond lenghts are 1.84, 1.84, 1.90, and 1.95 Å, respectively. The C–O and the C–C bond distances of the central ring have mean values of 1.30 and 1.43 Å, respectively.

Of particular value for the experimental evaluation of the relative contributions of a radialen-like and a benzene-like resonance structure in the complex are the bond lengths of the central ring compared with related structures from the literature. A good comparison for $[(\text{felddien})\text{Ni}_3]^{3+}$ are its mononuclear analog, the phenol complex **A** [53–55] (Scheme 4), and [(salen)Ni] [56]. Both complexes exhibit the same mean value for the C–C bond distances of the central ring of 1.39 Å which is particularly smaller than the value observed for $[(\text{felddien})\text{Ni}_3]^{3+}$ (1.43 Å). This might indicate a prevalence of the benzene-like enolate-imine resonance structure for the mononuclear compounds [(salen)Ni] and **A**, and of the radialene-like keto-enamine resonance structure (**IV** in Scheme 1c) for $[(\text{felddien})\text{Ni}_3]^{3+}$. However, a close inspection of

Table 1
Selected interatomic distances [Å] and angles [°] for $[(\text{felddien})\text{Ni}_3](\text{BF}_4)_3 \cdot 0.5$acetone.

Ni1–O11	1.824(2)	O11–Ni1–N11	94.32(11)
Ni1–N11	1.841(3)	O11–Ni1–N12	176.71(12)
Ni1–N12	1.903(3)	O11–Ni1–N13	90.36(12)
Ni1–N13	1.950(3)	N11–Ni1–N12	87.13(12)
Ni2–O21	1.839(2)	N11–Ni1–N13	170.58(13)
Ni2–N21	1.832(3)	N12–Ni1–N13	88.63(13)
Ni2–N22	1.901(3)	O21–Ni2–N21	94.65(11)
Ni2–N23	1.941(3)	O21–Ni2–N22	177.99(12)
Ni3–O31	1.849(2)	O21–Ni2–N23	90.47(11)
Ni3–N31	1.841(3)	N21–Ni2–N22	87.03(13)
Ni3–N32	1.910(3)	N21–Ni2–N23	173.51(13)
Ni3–N33	1.956(3)	N22–Ni2–N23	87.93(14)
O11–C1	1.302(4)	O31–Ni3–N31	95.15(11)
O21–C3	1.305(4)	O31–Ni3–N32	174.62(13)
O31–C5	1.303(4)	O31–Ni3–N33	91.22(11)
N11–C11	1.292(4)	N31–Ni3–N32	86.33(12)
N21–C21	1.294(4)	N31–Ni3–N33	168.67(13)
N31–C31	1.288(4)	N32–Ni3–N33	88.19(13)
C1–C2	1.421(4)	Ni1–O11–C1	128.5(2)
C2–C3	1.434(4)	Ni2–O21–C3	128.7(2)
C3–C4	1.411(5)	Ni3–O31–C5	127.7(2)
C4–C5	1.448(4)		
C5–C6	1.410(4)		
C1–C6	1.413(5)		
C2–C11	1.419(5)		
C4–C21	1.414(4)		
C6–C31	1.426(4)		



Scheme 4. Mean value of the bond distances [Å] of three reported structures of the mononuclear analog of $[(\text{felddien})\text{Ni}_3]^{3+}$ the complex **A**, [53–55] phloroglucinol bridged **B**, [57] [(salen)Ni] [56] and the mean value of two tetrahydro salen [(salan)Ni] complexes.[83,84] (Tp* = tris(3,5-dimethylpyrazolyl)hydroborate).

the central ring of [(salen)Ni] and **A** reveals a strong spread of the C–C bond distances which is not observed in the reduced analog [(salan)Ni] (Scheme 4), although this compound exhibits the same mean value of 1.39 Å for the central ring. This distribution of the bond distances indicates a significant contribution of the keto-enamine resonance structure even in the mononuclear [(salen)Ni] and phenol complex **A**. Another interesting comparison is the phloroglucinol-bridged trinuclear molybdenum complex **B** [57], which has a mean value for the central C–C bond lengths of 1.38 Å. This implies that $[(\text{felddien})\text{Ni}_3]^{3+}$ but also [(salen)Ni] and complex **A** cannot be regarded as pure phenolate-imine resonance structures. This remarkable result has also been observed by other authors for salphen complexes [58–60] and recently discussed by us for [(salen)Cu] and $[(\text{felden})\{\text{Cu(bpy)}\}_3](\text{ClO}_4)_3$ [32].

The structure of $[(\text{felddien})\text{Ni}_3]^{3+}$ exhibits an interesting disorder phenomenon concerning the ethylene diamine units of the chelating arms of Ni1 and Ni2 (Fig. 2c). Coordinated ethylene diamine units are not planar but exhibit a *gauche* conformation. The five-membered chelate rings can adopt two enantiomeric conformations, labeled by λ and δ (Fig. 2c). The two chelate rings of Ni3 are in the $\lambda\delta$ conformations, where the first designation (λ) refers to the conformation of the chelate ring involving N31 and N32, while the second designation (δ) refers to the chelate ring involving N32 and N33. The chelate ring of the pendent arms around Ni2 and Ni3 exhibit a disorder of $\lambda\delta$ and $\delta\lambda$ orientations of 3:1 ratio.

For each of the three ligand compartments of felddien^{3-} exist four different stereoisomers: $\lambda\lambda$, $\lambda\delta$, $\delta\lambda$, $\delta\delta$. Statistically, the trinuclear unit may exhibit 64 conformations ($2^3 \times 2^3$), where several of these conformations are equivalent by symmetry. However, considering the situation in Fig. 2c, the position of the methyl group C25 defines the conformation of *both* chelate rings: position C25 (i.e. pointing downwards) forces the configuration λ in the chelating Ni2–N22–C24–C23–N21 and the configuration δ in the chelate ring Ni2–N22–C26–C27–N23. The orientation C25B of the methyl group results in the opposite $\delta\lambda$ configuration. Thus, the covalent connection of the two chelate rings reduces the accessible number of stereoisomers per ligand compartment to two: $\lambda\delta$ and $\delta\lambda$; $\lambda\lambda$ and $\delta\delta$ conformations are not accessible due to the sp^3-type hybridization of the amine nitrogen donor. This restriction reduces the overall number of stereoisomers to four: the enantiomeric pairs ($\lambda\delta$, $\lambda\delta$, $\lambda\delta$) and ($\delta\lambda$, $\delta\lambda$, $\delta\lambda$) on the one hand and ($\lambda\delta$, $\lambda\delta$, $\delta\lambda$) and ($\delta\lambda$, $\delta\lambda$, $\lambda\delta$) on the other hand (note that e.g. ($\lambda\delta$, $\lambda\delta$, $\delta\lambda$), ($\lambda\delta$, $\delta\lambda$, $\lambda\delta$) and ($\delta\lambda$, $\lambda\delta$, $\lambda\delta$) are equivalent by symmetry). These two pairs are diasteromeric and therefore different in energy.

The crystal structure (space group $P\bar{1}$ would require two independent positions for one enantiomer of the two enantiomeric pairs. The other enantiomer would then be generated by the crystallographic center of inversion. However, the asymmetric unit consists only of one position for the trinuclear complex. The position shown in Fig. 2 is a 3:1 mixture of ($\lambda\delta$, $\lambda\delta$, $\lambda\delta$) and ($\delta\lambda$, $\delta\lambda$, $\lambda\delta$), since the chelating arm of Ni3 exhibits no disorder in the solid state. The enantiomeric position generated by the crystallographic center of inversion therefore consists of a mixture of ($\delta\lambda$, $\delta\lambda$, $\delta\lambda$) and ($\lambda\delta$, $\lambda\delta$, $\delta\lambda$), with the same ratio 3:1, which leads overall to an excess of the more symmetric isomers compared to a statistical mixture. The fact that the two isomers can be packed in the same position in the crystal structure without loss of the 3D regularity shows, that the alteration in the molecule structure for the isomers is small. This might be an explanation for the problems we experienced by obtaining a single-crystal of $[(\text{felddien})\text{Cu}_3]^{3+}$ suitable for single-crystal X-ray diffraction. Moreover, the knowledge of the presence of these two diasteromeric pairs in solution is important for the use of these trinuclear complexes for the construction of heptanuclear complexes by reaction with hexacyanometallates. Only the symmetric ($\lambda\delta$, $\lambda\delta$, $\lambda\delta$) and ($\delta\lambda$, $\delta\lambda$, $\delta\lambda$) isomers appear to be ideally preorganized for the reaction with a hexacyanometallate.

3.4. Electronic absorption spectroscopy

The electronic absorption spectra of the ligands $\text{H}_3\text{felddien}$, H_3felden, $\text{H}_6\text{talen}^{t\text{-Bu}_2}$, and H_2salen (Fig. 3a) as well as of their Ni^{II} (Fig. 3b) and Cu^{II} complexes (Fig. 3c) are compared to obtain more insight into the variation of the electronic structures.

H_2salen (Fig. 3a) exhibits a transition involving the imine group around 32000 cm^{-1} and a transition above 36000 cm^{-1} which has been assigned to the phenolic chromophores [61–63]. Contrary, the spectrum of the ketimine-based ligand $\text{H}_6\text{talen}^{t\text{-Bu}_2}$ [6] as well as the aldimine-based ligands $\text{H}_3\text{felddien}$ and H_3felden [32] exhibit two stronger absorption features in the region 26000–35000 cm^{-1}. Therefore, these features cannot be assigned as a three-fold superposition of the electronic structure of a salen ligand. This has already been realized in the study on the triplesalen ligands [6,25] and supports the interpretation of the NMR spectra that the ligand systems cannot be described in the anticipated benzene-like, but rather in the radialene-like resonance structure. The absorption features above 36000 cm^{-1} are absent in the spectra of $\text{H}_3\text{felddien}$ and H_3felden consistent with the assignment of these transitions to the terminal enol-imine chromophores of H_2salen and $\text{H}_6\text{talen}^{t\text{-Bu}_2}$.

The spectrum of [(salen)Ni] (Fig. 3b) consists of one weak band at 18400 cm^{-1} ($\varepsilon \approx 10\ \text{M}^{-1}\ \text{cm}^{-1}$) assigned to the d–d transition ($^1A_{1g} \rightarrow {}^1A_{2g}$; C_{2v} symmetry: $d_{xy} \rightarrow d_{x^2-y^2}$) [62,64–66], three resolved absorption features in the 21000–27000 cm^{-1} region assigned to CT transitions, and absorption features between 27000 and 35000 cm^{-1} originating from imine π–π^* transitions.[61] The complex $[(\text{felddien})\text{Ni}_3]^{3+}$ exhibits absorptions in the 20000–35000 cm^{-1} region that are distinct from [(salen)Ni] as well as from $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$, [6] which allows a self-consistent assignment of these transitions. The absorptions of $[(\text{felddien})\text{Ni}_3]^{3+}$ between 27000 and 35000 cm^{-1} are much more intense than those of [(salen)Ni] while the CT bands in the 21000–27000 cm^{-1} region are missing. On the other hand, $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$ not only exhibits these CT bands but also shows stronger intensities in the 27000–35000 cm^{-1} region. This is consistent with the transitions between 27000 and 35000 cm^{-1} being characteristic for the central bridging unit being a resonance hybrid of a benzene-like and a radialene-like resonance structure. In addition to this feature, $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$ has additional intensity of imine π–π^* transitions of the terminal phenolate-imine donors in this 27000–35000 cm^{-1} region. The intensity in the 21000–27000 cm^{-1} region of $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$ can thus be assigned to CT transitions of the terminal Ni^{II}-phenolate-imine units. The d–d transition (inset in Fig. 3b) is shifted from 18000 cm^{-1} in $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$ to 22200 cm^{-1} in $[(\text{felddien})\text{Ni}_3]^{3+}$, which is a remarkable experimental signature of the stronger ligand field of felddien^{3-} in comparison to $(\text{talen}^{t\text{-Bu}_2})^{6-}$ due to strong σ-donating amine donors and the absence of the terminal strong π-donor phenolate.

The overall assignment of the nickel complexes can be also applied to the copper complexes (Fig. 3c). The complex $[(\text{felddien})\text{Cu}_3]^{3+}$ has a strong absorption feature between 27000 and 35000 cm^{-1} attributed to the central bridging chromophore. Despite this feature, $[(\text{talen}^{t\text{-Bu}_2})\text{Cu}_3]$ has additional intensity between 24000 and 27000 cm^{-1} and a strong feature at 36000 cm^{-1}, [25] which are also observed for [(salen)Cu] and are therefore mainly assigned to the terminal Cu$^{\text{II}}$-phenolate-imine chromophore. The additional strong intensity in $[(\text{felden})\{\text{Cu(bpy)}\}_3]^{3+}$ [32] around 32000 is due to $\text{Cu}^{\text{II}} \rightarrow \pi^*$ MLCT transitions involving the bpy ligands.

A GAUSSIAN analysis of the d–d transitions of $[(\text{felddien})\text{Cu}_3]^{3+}$ is provided in Fig. 3d. The fitting process was performed with a minimum number of GAUSSIANS and the line widths of the ligand field transitions have been correlated to the same value. In order to obtain a good reproduction of the experimental data, the incorporation of four GAUSSIAN peaks at 13400, 16900, 19500 and 23400 cm^{-1} and a less intense but clearly distinct band at 9700 cm^{-1} was necessary. These d–d transitions are all shifted by $\sim$1500 cm^{-1} to higher energy in comparison to $[(\text{felden})\{\text{Cu(bpy)}\}_3]^{3+}$ reflecting the stronger σ-donation of the sp^3-hybridized terminal amines in $[(\text{felddien})\text{Cu}_3]^{3+}$ compared to the sp^2-hybridized N-donor bipyridine ligands in $[(\text{felden})\{\text{Cu(bpy)}\}_3]^{3+}$. Contrarily, the comparison of the d–d transitions of the square-planar coordinated Cu$^{\text{II}}$ complex of the tris(tetradentate) triplesalacen ligand H$_6$talacen $[(\text{talacen})\text{Cu}_3]$ [7] to those of $[(\text{felddien})\text{Cu}_3]^{3+}$ reveals larger shifts in the lower energy d–d transitions and smaller shifts in the higher energy d–d-transitions indicative of significant π-contributions in $[(\text{talacen})\text{Cu}_3]$ as compared to $[(\text{felddien})\text{Cu}_3]^{3+}$.

This reduced π-contribution (mainly π-acceptor) in complexes of felddien^{3-} shifts the ligand field from a typical ligand field of four-coordinate Ni$^{\text{II}}$ complexes to a ligand field which may also stabilize six-coordinate Ni$^{\text{II}}$ complexes. This is consistent with the experimental observation of paramagnetic affected NMR spectra of $[(\text{felddien})\text{Ni}_3]^{3+}$ measured in coordinating solvents as CD$_3$CN indicating an equilibrium between Ni$^{\text{II}}$ in a diamagnetic square-planar form and a paramagnetic octahedral form.

This is in conjunction with measurements of the effective magnetic moment in CD$_3$CN solution by the Evans method [67,68]. A rough estimate of 7% Ni$^{\text{II}}$ in the paramagnetic octahedral form has been calculated from the solution magnetic moment [69].

The weak band around 11000 cm^{-1} ($\varepsilon \approx 6$ M^{-1} cm^{-1}) of $[(\text{felddien})\text{Ni}_3]^{3+}$ in acetonitrile (Fig. 4) may be assigned to the $^3A_2 \rightarrow {}^3T_1$ transition in octahedral Ni$^{\text{II}}$ complexes. Recording the UV–vis spectra in the stronger donor solvent pyridine, a clear new absorption with small extinction arises at 10950 cm^{-1} ($\varepsilon = 26$ M^{-1} cm^{-1}). Concomitantly, the intensity of the bands as-

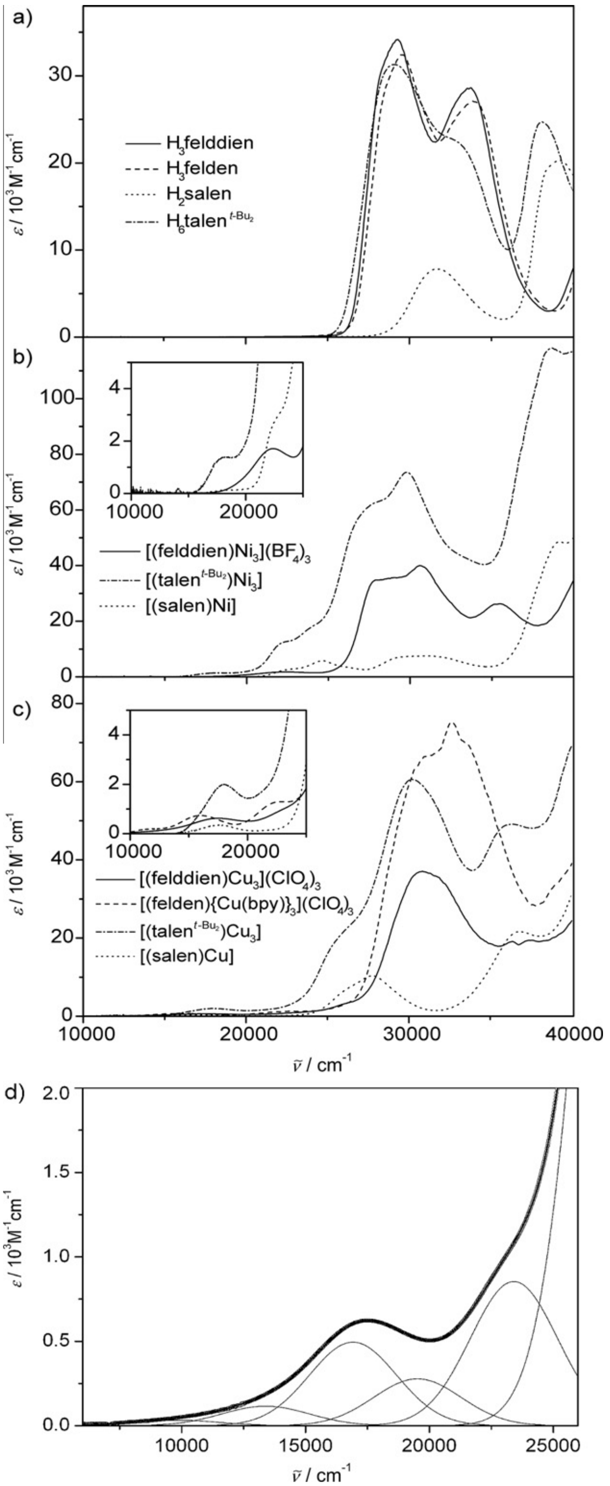


Fig. 3. (a) Electronic spectra of the ligands H$_3$felddien, H$_3$felden, H$_2$salen, and H$_6$talen$^{t\text{-Bu}_2}$ all measured in CH$_3$CN. (b) Electronic spectra of the complexes $[(\text{felddien})\text{Ni}_3](\text{BF}_4)_3$ (CH$_3$CN), $[(\text{talen}^{t\text{-Bu}_2})\text{Ni}_3]$ (CH$_2$Cl$_2$), and [(salen)Ni] (CH$_3$CN). (c) Electronic spectra of the complexes $[(\text{felddien})\text{Cu}_3](\text{ClO}_4)_3$ (CH$_3$CN), $[(\text{felden})\{\text{Cu(bpy)}\}_3](\text{ClO}_4)_3$ (CH$_3$CN), $[(\text{talen}^{t\text{-Bu}_2})\text{Cu}_3]$ (CH$_2$Cl$_2$), and [(salen)Cu] (CH$_3$CN). (d) GAUSSIAN fit to the d–d region of $[(\text{felddien})\text{Cu}_3](\text{ClO}_4)_3$. Thin lines represent the GAUSSIAN peaks, the thick solid line their sum, and the open circles the experimental data.

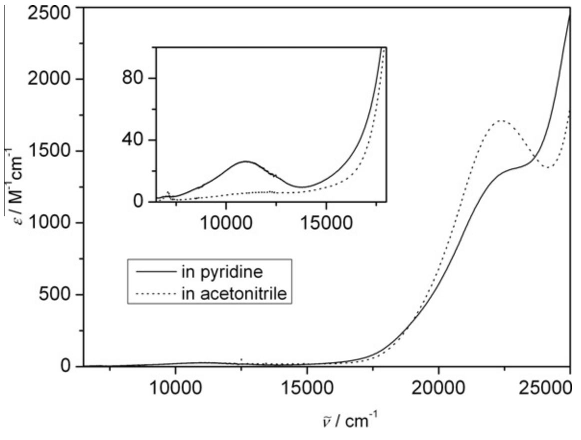


Fig. 4. d–d Region of the electronic spectra of $[(\text{felddien})\text{Ni}_3](\text{BF}_4)_3$ in pyridine and CH$_3$CN.

signed to the d–d transitions of the square-planar Ni^{II} ions decreases roughly by 30% in intensity. This indicates that even in pyridine solution the major species is still four-coordinate. However, this borderline situation of the ligand field between favoring a four- and a sixfold-coordination for Ni^{II} might make the complex suitable for the preparation of a $\mathbf{[Ni^{II}_6M^c]^{n+}}$ heptanuclear compound by reaction with hexacyanometallates. The electrostatic interactions between the [(felddien)Ni_3]$^{3+}$ cation and the [$M^c(CN)_6$]$^{3-}$ anion should be an additional driving force for the formation. Such a heptanuclear complex should have interesting magnetic properties, as the interaction of a central metal ion like Cr^{III}, Fe^{III} l.s., Os^{III} l.s., Mn^{III} l.s. with unpaired electrons in the t_{2g} orbitals and Ni^{II} with unpaired electrons in the e_g. orbitals might lead to ferromagnetic exchange couplings by the orthogonality of the magnetic orbitals [70–73].

3.5. Electrochemistry

Cyclic and square-wave voltammograms of [(felddien)Ni_3](BF_4)$_3$ and [(felddien)Cu_3](ClO_4)$_3$ have been recorded in acetonitrile solutions containing 0.1 M [NBu_4]PF_6 as supporting electrolyte and representative examples of the CVs are provided in Fig. 5. The CV of [(felddien)Ni_3]$^{3+}$ shows three reversible reduction waves with $E_{1/2}$ of −1.69, −1.88, and −2.10 V (all potentials are referenced vs Fc^+/Fc couple) which might be attributed to Ni^{II}/Ni^{I} couples [74,75] and one irreversible oxidation wave with $E_{p,ox}$ = 1.27 V. By contrast, the triplesalen complex [(talen$^{t\text{-}Bu_2}$)Ni_3] exhibits no reduction waves and three reversible oxidation waves with $E_{1/2}$ of 0.22, 0.55 and 1.00 V [6].

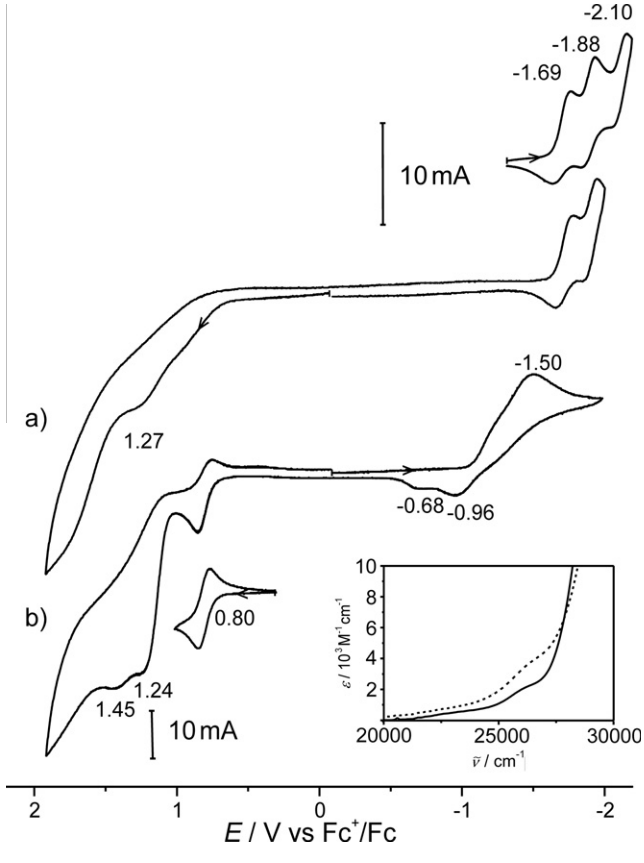


Fig. 5. (a) CV of [(felddien)Ni_3](BF_4)$_3$ and (b) CV of [(felddien)Cu_3](ClO_4)$_3$. Both spectra recorded at a platinum working electrode at 20 °C {0.1 M [NBu_4]PF_6} in CH_3CN solution. Scan rate 200 mV s^{-1}. The inset shows the UV–vis spectra of [(felddien)Cu_3](ClO_4)$_3$ before (solid line) and after oxidation at 1.1 V (dashed line) in a CV in an OTTLE cell.

The CV of [(felddien)Cu_3]$^{3+}$ shows one irreversible reduction wave at $E_{p,red}$ = −1.50 V, which can be assigned to the Cu^{II}/Cu^{I} redox couple [76]. At positive potentials [(felddien)Cu_3]$^{3+}$ shows a reversible oxidation at $E_{1/2}$ = 0.80 V followed by two irreversible oxidation waves at $E_{p,ox}$ = 1.24 and 1.45 V. The triplesalen complex [(talen$^{t\text{-}Bu_2}$)Cu_3] exhibits at −30 °C three reversible waves at 0.26, 0.59, and 0.81 V oxidation waves [25].

The overall anodic shift of the potentials of the complexes with felddien^{3-} versus (talen$^{t\text{-}Bu_2}$)$^{6-}$ might reflect the strong electron density provided by π-donor effects of the terminal phenolato donor ligand in triplesalen complexes.

3.6. Spectroelectrochemistry

We have followed the formation of the oxidized species [(felddien)Cu_3]$^{4+}$ by UV–vis spectroscopy during a CV in an OTTLE cell at ambient temperature, which took roughly 2 min (inset of Fig. 5b). The oxidized species exhibits an increased absorption at 26800 cm^{-1}, which is characteristic for the formation of phenoxyl radicals [77–80]. A similar intensity increase has been observed in [(talen$^{t\text{-}Bu_2}$)Cu_3]$^+$, but was obscured by the strong absorbance of the central unit (vide supra), which we have assigned to the oxidation of the central phloroglucinol unit [25]. Due to the absence of terminal phenolate units in [(felddien)Cu_3]$^{3+}$, the band observed here is a strong support for this assignment. Further attempts to isolate the oxidized species are currently in progress in our laboratory.

3.7. Magnetochemistry

Temperature-dependent measurements of the magnetic susceptibility (SQUID, 2–290 K) at different magnetic fields of samples of [(felddien)Cu_3]$^{3+}$ were performed. The effective magnetic moment, μ_{eff}, is 3.07 μ_B at 290 K and varies barely by lowering the temperature and increases only slightly at $T \approx 60$ K and then rapidly drops below this maximum to a value of 3.02 μ_B at 2 K. This temperature behavior indicates that there are two weak couplings effective in the system: a weak ferromagnetic coupling and a weak antiferromagnetic coupling. Both couplings seem to be of the same order of magnitude and it is therefore difficult to assign either one to an intra- or an intermolecular interaction. We tried to simulate the temperature-dependence of μ_{eff} with the appropriate spin-Hamiltonian (1) for an equilateral Cu^{II}_3 ($S_i = 1/2$) triangle by a full-matrix diagonalization approach including *Heisenberg-Dirac-van Vleck* (HDvV) exchange and *Zeeman* interactions using the program package JULX [39]. In this procedure, saturation effects are taken into account. Intermolecular interactions are modeled by a Weiss temperature Θ. Fitted values of χ_{TIP} are subtracted from the simulated and experimental data.

$$H = -2J(S_1S_2 + S_2S_3 + S_1S_3) + \sum_{i=1}^{3}[g_i\mu_B S_i B] \qquad (1)$$

The overall temperature-dependence of μ_{eff} can be modeled in two different scenarios: 1. using a weak ferromagnetic intramolecular coupling modeled by the HDvV term including a weak antiferromagnetic intermolecular interaction modeled by a negative Weiss temperature Θ; 2. a weak antiferromagnetic intramolecular interaction modeled by a negative J value including a ferromagnetic intermolecular interaction modeled by a positive Weiss temperature Θ. While the observed temperature-dependence of the data excludes a definite assignment to one of the two scenarios, the second scenario seems to be rather unlikely, as it would exhibit a ferromagnetic intermolecular pathway through space and via non-magnetic orbitals. Therefore, the scenario of an intramolecular interaction as observed for all other Cu^{II}_3 complexes seems to be more realistic. The solid line provided in Fig. 6 is obtained for

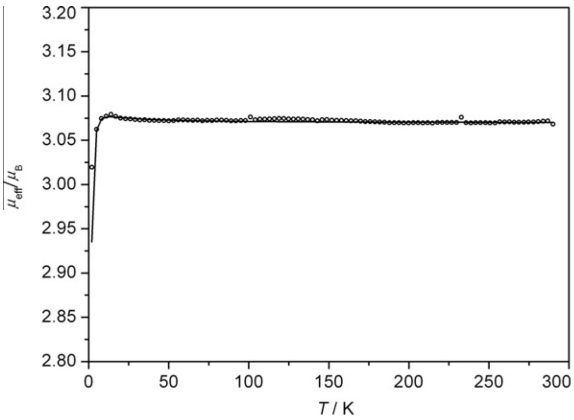


Fig. 6. Temperature-dependence of the effective magnetic moment, μ_{eff}, of $[(felddien)Cu_3](ClO_4)_3 \cdot 3H_2O$. The solid line corresponds to the best fits: $J = 0.57\ cm^{-1}$, $g = 2.05$, $\chi_{TIP} = 430 \times 10^{-6}\ cm^3\ mol^{-1}$ and $\Theta = -0.70\ K$.

$J = 0.57\ cm^{-1}$, $g = 2.05$, $\chi_{TIP} = 430 \times 10^{-6}\ cm^3\ mol^{-1}$, and $\Theta = -0.70\ K$. The decrease of μ_{eff} at lower temperatures is thus due to the combined effect of Zeeman interactions (taken into account in our analysis), intermolecular antiferromagnetic interactions, and anisotropy of the $S_t = 3/2$ ground state. The latter has been observed in several ferromagnetically coupled Cu^{II}_3 complexes [24,81,82].

All trinuclear copper complexes based on extended phloroglucinol ligands exhibit ferromagnetic interactions with coupling constants in the range of $J = 1.02–3.31\ cm^{-1}$ [4,7,24,25,32]. This means, that $[(felddien)Cu_3]^{3+}$ has the lowest coupling constant yet observed in extended phloroglucinol ligands. The pronounced low coupling in $[(felddien)Cu_3]^{3+}$ can probably be attributed to the interplay of ferromagnetic and antiferromagnetic interactions. As we already discussed for Cu^{II} triplesalen complexes [22,25] the ligand folding of the complexes is crucial for a ferromagnetic interaction *via* the central ring. In almost planar complexes the magnetic $Cu^{II}d_{x^2-y^2}$ orbital and the phenolate O p^{π} orbital are orthogonal to each other and therefore the overlap integral is zero, resulting in no spin-delocalization onto the phenolate oxygen atom [22]. A slight bending of the basal plane relative to the central phloroglucinol ring opens a bonding path for delocalization of spin density from the $Cu^{II}d_{x^2-y^2}$ orbital in the O p^{π} orbitals. This increase of spin density strengthens the ferromagnetic contribution by the spin-polarization mechanism. It might therefore be supposed, that the almost planar structure of $[(felddien)Ni_3]^{3+}$ retains in the complex $[(felddien)Cu_3]^{3+}$ and is thus one possible reason for the weak ferromagnetic coupling in $[(felddien)Cu_3]^{3+}$.

Moreover, the spin-polarization mechanism is thought to be a π mechanism [22,23] and the lack of the π system of the central ring in the radialene-like resonance structures could explain the relatively weak couplings observed not only in $[(felddien)Cu_3]^{3+}$ but in all our trinuclear copper complexes of modified phloroglucinol ligands.

4. Conclusions

We have synthesized the new ligand H_3felddien, which is an extension of our previously reported ligand H_3felden, and its trinuclear nickel and copper complexes. Detailed NMR spectroscopic investigations on the ligand revealed that H_3felddien as well as H_3felden and all our triplesalen ligands have to be described as the N-protonated tautomer and not as the O-protonated tautomer, with main contribution of the radialene-like keto-enamine resonance structure with two geometrical isomers (C_{3h} and C_s). The analysis of the structural and spectroscopic data of the trinuclear nickel complex $[(felddien)Ni_3]^{3+}$ indicates that after coordination both resonance structures, a radialene-like keto-enamine and a benzene-like phenolate-imine, have strong contributions. This reduced central π system leads to a relative weak ferromagnetic coupling not only in the trinuclear copper complex of H_3felddien but also in all our other trinuclear copper complexes of modified phloroglucinol ligands.

The substitution of the terminal phenolate-imine donor set in H_2salen and $H_6talen^{t\text{-}Bu_2}$ by a bis terminal amine donor set changes the preference of the ligand field from a four-coordinate square-planar coordination environment to a borderline situation for Ni^{II} between a four-coordinate square-planar versus a six-coordinate octrahedral coordination environment. This tendency of the Ni^{II} ions in $felddien^{3-}$ complexes to accept suitable donors in the axial positions makes this complex suitable for the preparation of heptanuclear complexes of the kind $\mathbf{[Ni^{II}_6M^c]^{n+}}$. These complexes promise interesting magnetic properties, as the interaction of a central metal ion like Cr^{III}, Fe^{III} l.s., Os^{III} l.s., Mn^{III} l.s. with unpaired electrons in the t_{2g} orbitals and Ni^{II} with unpaired electrons in the e_g. orbitals may lead to ferromagnetic exchange couplings by the orthogonality of the magnetic orbitals [70–73].

Acknowledgment

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Appendix A. Supplementary data

CCDC-802298 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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