Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 4102

A streamlined synthesis of extended thiophloroglucinol ligands and their trinuclear Ni^{II}_3 complexes†

Bastian Feldscher, Hubert Theil, Anja Stammler, Hartmut Bögge and Thorsten Glaser*

Received 9th December 2013,
Accepted 11th January 2014

DOI: 10.1039/c3dt53457j

www.rsc.org/dalton

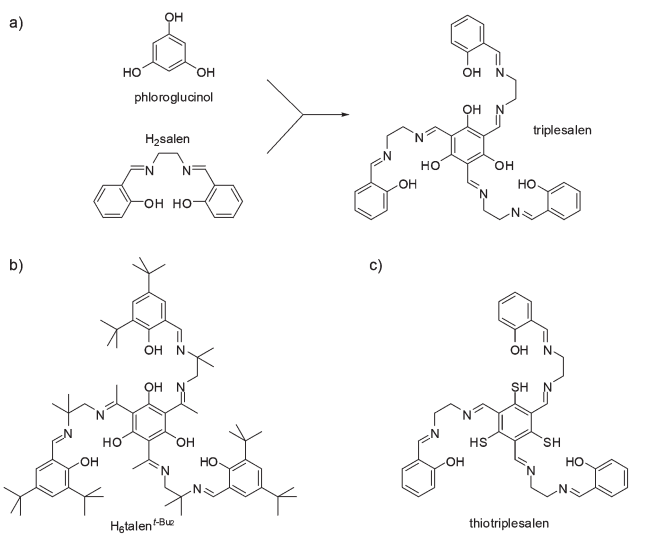
A protocol for the synthesis of trinucleating C_3-symmetric ligands based on a central *meta*-phenylene bridging 1,3,5-trimercaptobenzene (thiophloroglucinol) backbone has been established. The key compound turned out to be the trialdehyde obtained from the triple nucleophilic attack of dimethyldithiocarbamate at 1,3,5-tribromo-2,4,6-triformylbenzene. Reacting this trialdehyde with six equivalents of a primary amine results in the simultaneous dithiocarbamate cleavage and Schiff-base formation providing the extended thiophloroglucinol ligands H_3bertdien, H_6bert^{Me}, H_6bert$^{t\text{-}Bu_2}$, and H_6habbi. Reaction with Ni^{II} leads to the formation of the trinuclear Ni^{II}_3 complexes [(bertdien)Ni^{II}_3](X)$_3$ (X = BPh_4^-, BF_4^-), [(bert^{Me})-Ni^{II}_3], [(bert$^{t\text{-}Bu_2}$)Ni^{II}_3], and [(habbi)Ni^{II}_3], which are characterized spectroscopically, electrochemically, and crystallographically.

Introduction

The discovery of single-molecule magnets (SMMs)[1–3] and their potential applications[4–7] has attracted much interest for new types of SMMs. We have developed the trinucleating ligand system triplesalen which combines a central phloroglucinol (=1,3,5-trihydroxybenzene) bridging unit with three salen-like coordination compartments (Scheme 1a) for the rational synthesis of SMMs.[8–11] Trinuclear Cu^{II}_3 [12,13] and V^{IV}_3 [14] complexes exhibit the anticipated ferromagnetic interactions by the spin-polarization mechanism[15–22] although the interactions are only weak ($+0.5 < J < +3.0$ cm^{-1}, $H = -2J\mathbf{S_1S_2}$). Trinuclear complexes of the triplesalen ligand H_6talen$^{t\text{-}Bu_2}$ (Scheme 1b) react with hexacyanometallates to heptanuclear complexes $[\mathbf{M^t_6M^c}]^{n+}$ (= $[\{(\text{talen}^{t\text{-}Bu_2})M^t_3\}_2\{M^c(CN)_6\}]^{n+}$) by molecular recognition.[23–29] $[\mathbf{Mn^{III}_6Cr^{III}}]^{3+}$ is a SMM with a relatively high anisotropy barrier of $U^{eff} \sim 25.4$ K and a blocking temperature of $T_B \sim 1.5$ K depending on the counter-anion and the solvate,[23,26] while $[\mathbf{Mn^{III}_6Mn^{III}}]^{3+}$ is a SMM with a low anisotropy barrier but which exhibits a hysteretic opening up to 10 T at 0.3 K due to high molecular and crystal symmetry.[27,28]

Detailed magnetic studies demonstrated that the coupling between Mn^{III} [23–28,30,31] and Fe^{III} [32,33] ions through the triplesalen ligand is slightly antiferromagnetic. This result was especially unexpected, as the *meta*-phenylene linkage is a well established ferromagnetic coupling unit in organic chemistry,[15,18,20,34–37] where coupling constants up to 1700–1800 cm^{-1} have been estimated.[38–40]

In order to optimize our ligand system we have to understand this discrepancy of efficiency in the spin-polarization mechanism in transition metal complexes[16,21,22,41–58] *vs.* organic systems. In organic radicals and carbenes as the



Scheme 1

Lehrstuhl für Anorganische Chemie I, Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, D-33615 Bielefeld, Germany. E-mail: tglaser@uni-bielefeld.de

†Electronic supplementary information (ESI) available: Thermal ellipsoid plots and crystallographic data (CIF format) of all structures. CCDC 901451, 901452, 901454 and 901455. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53457j

archetype 1,3-dimethylenebenzene (*meta*-quinodimethane)[38,39] there is a strong π overlap of the p_z orbitals containing the unpaired electrons and the p_z orbitals of the central bridging benzene unit. In a simple Hückel-MO-treatment (one-electron theory), two degenerate π MOs result with one unpaired electron in each MO. Application of Hund's rule (as in molecular O_2) leads to the energetically favored parallel orientation of the two spins (ferromagnetic interaction).[59,60] Incorporation of electron–electron repulsion results in the stabilization of the triplet, mainly by the exchange integral (which is of course the physical origin of Hund's rule). Thus, the stronger the π interaction of the p_z orbitals the stronger is the spin-polarization effect.

An obvious difference noticed by comparing *e.g.* 1,3-dimethylenebenzene with a trinuclear transition metal triplesalen complex is the localization of the magnetic orbitals. Whereas in the organic radical the magnetic orbital is the p_z orbital that is perfectly oriented for a π interaction with the bridging π system, in triplesalen complexes the magnetic orbitals are metal d orbitals. Although the covalent metal–ligand interaction provides some spin-density on the phloroglucinol oxygen atom (for an educational review on spin-density transfer from metal d orbitals to ligand orbitals see ref. 19), this spin-density is much smaller and is not necessarily as well oriented as in the organic radicals. This comparison implies that a stronger metal–ligand covalency would transfer more spin-density to the ligand atom and thus would provide a more efficient spin-polarization over the *meta*-phenylene linkage.

In this respect, biological electron-transfer (ET) sites are a good guide. Nature has solved the problem of a necessary strong metal–ligand covalency for a fast and directed superexchange ET pathway by using metal–thiolate (cysteine) coordination in iron–sulfur clusters and blue copper centers.[61–66] The metal–sulfur bond has a stronger covalency than a corresponding metal–oxygen bond due to the energetically higher lying and more diffuse sulfur 3p orbitals than the oxygen 2p orbitals.[67–71] Based on these considerations, we started a project to substitute the central phloroglucinol unit by a central thiophloroglucinol (=1,3,5-trimercaptobenzene) unit leading to extended thiophloroglucinol and in particular thiotriplesalen ligands (Scheme 1c).

Our first synthetic route to thiotriplesalen ligands was based on the Newman–Kwart rearrangement,[72–74] which is an established route from phenols to thiophenols *via* the thermal rearrangement of the *O*-thiocarbamate (synthesized from the phenol with carbamoylchloride) to the *S*-thiocarbamate. Thus, we reacted our starting material 2,4,6-triacetyl-1,3,5-trihydroxybenzene for the triplesalen ligands H_6talen^R with dimethylthiocarbamoyl chloride to afford the tris(*O*-thiocarbamate) and rearranged it to the tris(*S*-thiocarbamate). However, cleavage of the tris(*S*-thiocarbamate) resulted not in the free thiol, but in the formation of polycyclic products.[75]

Herein, we present the successful realization of extended thiophloroglucinol ligands. This proved to be a versatile route to such ligands with varying pendant arms. Furthermore, the trinuclear Ni^{II}_3 complexes of the extended thiophloroglucinol ligands have been synthesized. The synthesis of the ligand H_6habbi and its trinuclear copper complex [(habbi)Cu^{II}_3] has only recently been communicated.[76]

Experimental section

Preparation of compounds

Solvents and starting materials were of the highest commercially available purity and were used as received. 1,3,5-Tribromo-2,4,6-triformylbenzene (**1**),[77] half-units **3**,[32] and **6**,[78] and 2,4,6-triformylphloroglucinol[79] were prepared according to reported procedures. Trialdehyde **4** and H_6habbi were synthesized as described previously.[76] The assignments of the NMR resonances in all products were supported by 2D COSY, HMBC, and HMQC spectroscopy and the numbering was done according to the numbering scheme in Fig. 1.

1,3,5-Tri(*tert*-butylmercapto)-2,4,6-triformylbenzene (2). Under standard Schlenk-conditions NaS*t*-Bu (147 mg, 1.31 mmol) and **1** (166 mg, 0.42 mmol) were dissolved in dmf (4 mL) at 0 °C. The resulting mixture was stirred at room temperature for 24 h and subsequently Et_2O (10 mL) was added. The precipitating salts were separated and the filtrate was evaporated to dryness to afford **2** as a yellow powder (143 mg, 0.34 mmol, 81% yield). ^{1}H NMR (500.25 MHz, $CDCl_3$): δ = 10.52 (s, O=C*H*), 1.28 (s, *t*-Bu). ^{13}C NMR (125.80 MHz, $CDCl_3$): δ = 192.5 (s, *C*=O), 153.3 (s, C^{Ar}C), 132.7 (s, C^{Ar}S), 52.1 (s, $C(CH_3)_3$), 31.4 (s, CH_3). EI MS (positive ion mode) *m*/*z* = 426 $[M]^+$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2964m, 2926w, 2901w, 2858w, 1707s, 1460m, 1366m, 1161m, 987m. Elemental analysis: Found: C, 58.49; H, 7.05; N, 0.17. Calc. for $C_{21}H_{30}O_3S_3$·0.15dmf ($C_{21.45}H_{31.5}N_{0.15}O_{3.15}S_3$) C, 58.81; H, 7.25; N, 0.48.

***t*-Bu$_3$H$_3$bert^{Me}.** Aldehyde **2** (90 mg, 0.211 mmol) and half-unit **3** (281 mg, 1.28 mmol) were suspended in MeOH (2 mL) and the mixture was stirred for 24 h at 40 °C. The resulting solution was evaporated to dryness and the oil was purified *via* column chromatography with a Sephadex® LH-20 column (MeOH) yielding the product as a yellow solid (184 mg, 0.178 mmol, 85% yield). ^{1}H NMR (500.25 MHz, $CDCl_3$): δ = 16.4 (br s, OH), 8.68 (m, C11H_2), 7.30 (m, C103*H*), 7.07 (d, *J* = 8 Hz, C105*H*), 6.83 (d, *J* = 8 Hz, C106*H*), 3.72 (m, C13H_2), 2.31 (s, C18H_3), 2.26 (s, C120H_3), 1.47 (s, C15H$_2$), 1.13 (m, C13H_3). ^{13}C NMR (125.80 MHz, $CDCl_3$): δ = 172.3 (s, C17), 162.0 (s, C107), 158.7 (s, C11), 153.9 (s, C2), 133.2 (s, C105), 132.0 (s, C1), 128.1 (s, C103), 125.8 (s, C104), 118.8 (s, C102), 118.3 (s, C106), 62.5 (s, CMe_3), 60.4 (s, C13), 31.5 (s, C13), 24.8 (s, C15), 20.8 (s, C120), 14.8 (s, C18). ESI MS (positive ion mode) *m*/*z* = 1056 $[M + Na]^+$, 1034 $[M + H]^+$, 539 $[M + 2Na]^{2+}$, 517 $[M + 2H]^{2+}$, 528 $[M + H + Na]^{2+}$. HRMS (MALDI) for $C_{60}H_{85}N_6O_3S_3$ $[M + H]^+$ calc.: 1033.58398, found: 1033.58385. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2964s, 2924m, 2897m, 2866m, 1645m, 1622s, 1585m, 1504m, 1471m, 1456m, 1383m, 1364m, 1325w, 1296m, 1163m, 1069w, 822m, 654w.

[(bert^{Me})Ni$_3$]. Trialdehyde **4** (86 mg, 0.165 mmol) and half-unit **3** (220 mg, 1.00 mmol, 6.2 eq.) were dissolved in CH_2Cl_2

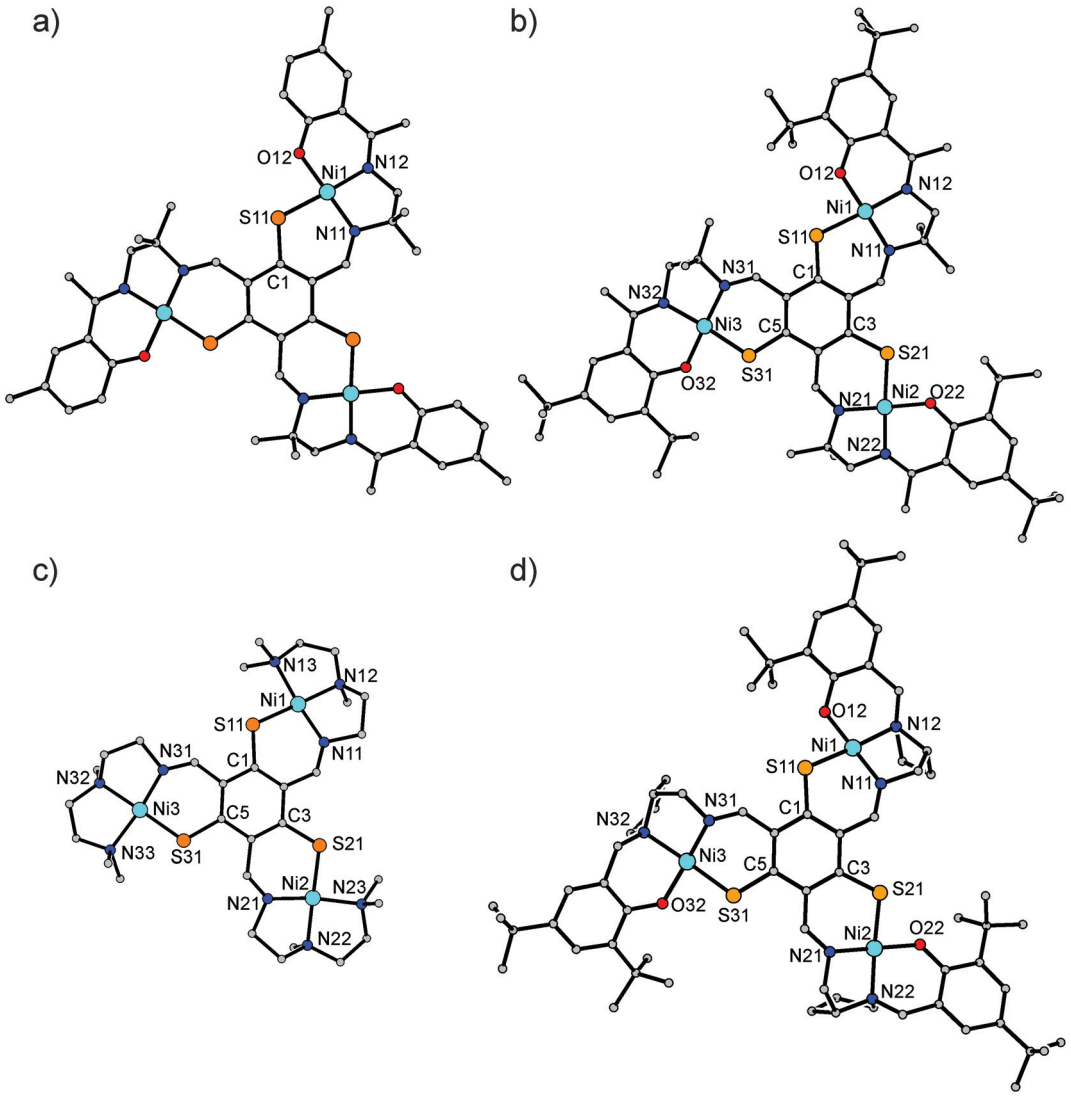


Fig. 1 Molecular structures of (a) [(bert^{Me})Ni$_3$], (b) [(bert$^{t\text{-}Bu_2}$)Ni$_3$], (c) [(bertdien)Ni$_3$]$^{3+}$, and (d) [(habbi)Ni$_3$] (molecule 1) and the numbering schemes used. Hydrogen atoms are omitted for clarity.

(15 mL) and stirred for 6 h. The volatiles were removed under vacuum and the resulting yellow solid was redissolved in EtOH (15 mL). This solution was added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ (258 mg, 1.02 mmol, 6.4 eq.) in EtOH (30 mL) and heated to reflux for 30 min. The precipitating solid was isolated and recrystallized *via* slow evaporation of a mixture of toluene–$CHCl_3$ (80 mg, 0.077 mmol, 47% yield). ^{1}H NMR (500.25 MHz, $C_2D_2Cl_4$): δ = 9.13 (s, C11H), 7.24 (s, C103H), 6.95 (dd, $J_{H.H}$ = 1.5 Hz and $J_{H.H}$ = 8.7, C^{Ar}H), 6.77 (d, $J_{H,H}$ = 8.5 Hz, CH_{ar}), 3.37 (s, C13H_2), 2.38 (s, C18H), 2.22 (s, C120H_3), 1.67 (s, C15H_3 + C16H_3). ^{13}C NMR (125.75 MHz, $C_2D_2Cl_4$): δ = 167.1 (C17), 161.6 (C11), 160.7 (C101), 155.7 (C1), 134.0 (C2), 128.7 (C103), 125.3 (C2), 123.6 (C104), 122.1 (C106), 121.1 (C102), 70.4 (C13), 65.2 (C14), 26.9 (C15 + C16), 20.5 (C120), 18.0 (C18). MALDI MS (positive ion mode) m/z = 1035 [M + H]$^+$. IR (KBr) $\tilde{\nu}$/cm^{-1} = 2965m, 2918w, 2857w, 1616m, 1582s, 1528s, 1458s, 1412s, 1379w, 1325s, 1292m, 1260w, 1234m, 1209w, 1186m, 1153w, 1140w, 1078m, 943w, 824m, 811w. Elemental analysis: Found: C, 56.46; H, 5.56; N, 7.67; S, 8.62. Calc. for [(bert^{Me})Ni$_3$]·0.35toluene ($C_{50.45}H_{56.8}N_6Ni_3O_3S_3$) C, 56.76; H, 5.36; N, 7.87; S, 9.01.

[(bert$^{t\text{-}Bu_2}$)Ni$_3$]. Trialdehyde **4** (73 mg, 0.140 mmol) and half-unit **6** (269 mg, 0.845 mmol, 6 eq.) were dissolved in CH_2Cl_2 (10 mL) and stirred for 6 h. The volatiles were removed under vacuum and the resulting oil was redissolved in EtOH (10 mL). This solution was added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ (209 mg, 0.840 mmol, 6 eq.) and heated to reflux for 75 min. The precipitating crude product was recrystallized *via* slow evaporation of a mixture of the complex in EtOH and CH_2Cl_2 (50 mg, 0.038 mmol, 27%). ^{1}H NMR (500.25 MHz, $CDCl_3$): δ = 9.33 (s, C3H), 7.33 (m, C103H), 7.28 (m, C105H), 3.39 (s, C13H), 2.47 (s, C18H), 1.63 (s, C15H + C16H), 1.34 (s, C111–113H), 1.29 (s, C121–122H). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 167.6 (C17), 162.5 (C11), 160.8 (C101), 156.6 (C1), 141.1 (C106), 135.5 (C104), 127.6 (C105), 125.3 (C2), 122.6 (C104), 120.7 (C102), 70.5 (C14), 65.8 (C13), 35.7 (C110), 34.3

(C120), 31.6 (C121–123), 30.1 (C111–113), 27.3 (C15 + C16), 19.0 (C18). MALDI MS (positive ion mode) m/z = 1328 $[M]^+$. IR (KBr) $\tilde{\nu}/cm^{-1}$ = 2951m, 2905m, 2866w, 1582s, 1524m, 1460s, 1422s, 1383w, 1360w, 1333w, 1292w, 1261w, 1248w, 1223w, 1186w, 1152w, 1084w, 1067w, 943w, 947w, 785w. Elemental analysis: Found: C, 61.23; H, 7.19; N, 6.39. Calc. for [(bert$^{t\text{-Bu}_2}$)-Ni_3]·0.25CH_2Cl_2·0.30H_2O·0.10EtOH ($C_{69.45}H_{97.78}N_6Ni_3O_{3.40}S_3Cl_{0.5}$) C, 61.29; H, 7.24; N, 6.18.

2-2((2-(Dimethylamino)ethyl)(methyl)amino)acetonitrile (10). $Na_2S_2O_5$ (11.891 g, 62.55 mmol) was dissolved in water (30 mL) and cooled to 0 °C. To this cold solution a 37% formaldehyde solution in water (9.590 g, 118.16 mmol) was added and heated under reflux for 10 min. At room temperature *N*,*N*,*N*′-trimethylethylenediamine (15 mL, 12.06 g, 118.03 mmol) was slowly added and the reaction mixture was stirred for 3.5 h at room temperature. To the resulting mixture a solution of NaCN (6.079 g, 124.04 mmol) in water (14 mL) was added and the resulting suspension was stirred overnight. The precipitate and the filtrate were extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. The solvents have been evaporated at 40 °C and 20 mbar yielding the nitrile **10** as a colourless liquid (14.462 g, 102 mmol, 87%). ^{1}H NMR (500.25 MHz, $CDCl_3$): δ = 3.60 (s, CH_2C≡N), 2.54 (t, $^3J_{H,H}$ = 6.3 Hz, CH_2NMe), 2.36 (m, CH_2NMe_2 and NCH_3), 2.21 (s, N(CH_3)$_2$). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 114.6 (s, *C*≡N), 56.9 (s, *C*H_2NMe_2), 52.9 (s, *C*H_2NMe), 45.5 (s, N(*C*H_3)$_2$), 45.2 (s, *C*H_2C≡N), 42.2 (s, NCH_3). ESI MS (positive ion mode) m/z = 142.2 $[M + H]^+$.

***N*′-(2-Aminoethyl)-*N*′,*N*,*N*-trimethylethan-1,2-diamine (9).** $LiAlH_4$ (6.512 g, 172.59 mmol) was suspended in dry thf (90 mL) and cooled to 0 °C. A solution of nitrile **10** (11.015 g, 78.60 mmol) in thf (180 mL) was added slowly over a period of one hour. The resulting suspension was heated under reflux for 3 h and stirred overnight at room temperature. At 0 °C, water (20 mL) has been slowly added and afterwards a solution of KOH (340 g) in water (230 mL). The suspension has been vigorously stirred until all solids dissolved. The solution has been extracted with CH_2Cl_2, the combined organic layers dried over Na_2SO_4 and the volatiles removed at 40 °C and ≥200 mbar. The resulting raw product can be distilled under slight vacuum to yield the product as a colourless liquid (9.511 g, 65.48 mmol, 83%). ^{1}H NMR (500.25 MHz, $CDCl_3$): δ = 2.65 (t, $^3J_{H,H}$ = 6.4 Hz, CH_2NH_2), 2.38–2.27 (m, CH_2), 2.13 (s, CH_3), 1.35 (bs, NH_2). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 60.8 (s, *C*H_2CH$_2$NH_2), 57.3 (s, *C*H_2NMe_2), 55.7 (s, *C*H_2CH$_2$NMe_2), 45.7 (s, N(CH_3)$_2$), 42.4 (s, NCH_3), 39.4 (s, *C*H_2NH_2). ESI MS (positive ion mode) m/z = 146 $[M + H]^+$, 168 $[M + Na]^+$.

[(bertdien)Ni_3][BPh_4)$_3$. Trialdehyde **4** (117 mg, 0.225 mmol) and triamine **9** (240 mg, 1.652 mmol, 7 eq.) were dissolved in CH_2Cl_2 (10 mL) and stirred for 4 h at ambient temperature. The volatiles were removed under vacuum and the resulting oil was redissolved in MeOH (15 mL). This solution was added to a solution of Ni(OAc)$_2$·4H_2O (168 mg, 0.68 mmol, 3 eq.) in MeOH (30 mL) and stirred for 2 h. To the resulting red solution was added a solution of $NaBPh_4$ (231 m, 0.67 mmol, 3 eq.) in MeOH (10 mL). The precipitating solid was isolated, subsequently washed with EtOH and Et_2O and recrystallized *via* slow evaporation of a solution of the complex in CH_3CN (336 mg, 0.900 mmol, 84%). MALDI MS (positive ion mode) m/z = 1131 $[M + BPh_4]^+$. IR (KBr) $\tilde{\nu}/cm^{-1}$ = 3157w, 3119w, 3053m, 3030m, 2997m, 2982m, 2926m, 2872br, 1948w, 1818w, 1818w, 1591m, 1580m, 1466s, 1432s, 1333m, 1290m, 1267w, 124m, 1182w, 1167w, 1138m, 1107m, 1089m, 1045m, 1032m, 941m, 887m, 845m, 788m, 734s, 705s, 611s. Elemental analysis: Found: C, 69.10; H, 6.44; N, 7.82. Calc. for [(bertdien)Ni_3]-(BPh_4)$_3$·CH_3CN ($C_{104}H_{117}N_{10}Ni_3S_3B_3$) C, 68.94; H, 6.51; N, 7.73. To obtain single crystals suitable for X-ray diffraction, [(bertdien)Ni_3](BPh_4)$_3$·CH_3CN has been recrystallized from acetone.

To enhance the solubility in noncoordinating solvents (see the text for details), [(bertdien)Ni_3](BPh_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, $CDCl_3$): δ = 8.97 (d, J = 10 Hz, HC═N), 8.95 (d, J = 11 Hz, HC═N), 7.75 (s, B(Ar^F)$_4^-$), 7.58 (s, B(Ar^F)$_4^-$), 4.08–2.10 (m, CH_2 and CH_3). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 167.4 (s, *C*═N), 167.3 (s, *C*═N), 162.3 (q, $^1J_{BC}$ = 50 Hz, B(Ar^F)$_4^-$), 153.8 (s, C^{Ar}-S), 153.7 (s, C^{Ar}-S), 135.4 (s, B(Ar^F)$_4^-$), 129.5 (q, $^2J_{CF}$ = 32 Hz, B(Ar^F)$_4^-$), 125.8 (m, C^{Ar}C), 125.2 (q, $^1J_{CF}$ = 270 Hz, B(Ar^F)$_4^-$), 118.1 (s, B(Ar^F)$_4^-$), 64.9, 64.3, 64.0, 59.6, 58.5, 51.8, 50.9.

[(bertdien)Ni_3][BF_4)$_3$. Trialdehyde **4** (138 mg, 0.265 mmol) and triamine **9** (305 mg, 2.10 mmol) were dissolved in CH_2Cl_2 (10 mL) and stirred for 4 h at ambient temperature. The volatiles were removed under vacuum and the resulting oil was redissolved in MeOH (15 mL). This solution was added to a solution of Ni(BF_4)$_2$·6H_2O (273 mg, 0.802 mmol) in MeOH (50 mL). The resulting red suspension was heated to reflux for 2 min, the solid dissolved and triethylamine (80 mg, 0.795 mmol) was added. The resulting solution was slowly allowed to cool to ambient temperature during which the product precipitated as a red solid (109 mg, 0.102 mmol, 38%). MALDI MS (positive ion mode) m/z = 810 $[M]^+$. IR (KBr) $\tilde{\nu}/cm^{-1}$ = 2928m, 2884w, 2855w, 2810w, 1593m, 1466s, 1422m, 1343w, 1288w, 1250m, 1084s, 1055s, 968w, 947m, 889m, 789m, 766m, 534m, 523m. Elemental analysis: Found: C, 33.10; H, 5.06; N, 11.35. Calc. for [(bertdien)Ni_3](BF_4)$_3$·H_2O ($C_{30}H_{56}N_9Ni_3S_3B_3F_{12}$) C, 33.01; H, 5.17; N, 11.55.

[(habbi)Ni_3]. A solution of H_6habbi (162 mg, 0.139 mmol) in EtOH (20 mL) was slowly added to a solution of Ni(OAc)$_2$·4H_2O (208 mg, 0.836 mmol) in EtOH (20 mL) and heated to reflux for 40 min. The precipitate has been isolated and recrystallized *via* slow evaporation of a mixture of EtOH and CH_2Cl_2 yielding crystals suitable for single-crystal X-ray diffractions (55 mg, 0.041 mmol, 30%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.86 (s, H3), 7.10 (s, H15), 6.85 (s, H11), 5.71 (m, 1H, H9), 4.32 (m, 1H, H4), 3.48 (m, 1H, H8), 3.03 (m, 2H, H9 + H4), 2.67 (m, 1H, H7), 2.52 (m, 1H, H5), 2.30 (m, 1H, H8), 1.95 (m, 1H, H6), 1.88 (m, 1H, H7), 1.60 (m, 1H, H6), 1.32 (s, H14), 1.30 (s, H18). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 165.5 (C3), 157.8 (C19), 154.5 (C1), 139.5 (C16), 135.0 (C12), 125.2 (C2), 123.4 (C11), 123.3 (C15), 120.2 (C10), 68.2 (C4), 66.6 (C5), 59.7 (C9), 57.0 (C8), 35.4 (C17), 34.1 (C13), 32.1 (C14),

29.9 (C18), 27.5 (C6), 23.5 (C7). MALDI MS (positive ion mode): 1328.7 $[M]^+$. IR (KBr) $\tilde{\nu}/cm^{-1}$ = 2951m, 2903m, 2866m, 1601m, 1462s, 1439s, 1412m, 1358w, 1304m, 1287m, 1240m, 1204w, 1165w, 1128w, 1103w, 1026w, 1005w, 934w, 899w, 874w, 837m, 804w, 766w, 748w, 642w, 550w. $[\alpha]_D^{20}$ = −1255°, C = 0.014 g/100 mL, $CHCl_3$. Elemental analysis: Found: C, 62.36; H, 7.35; N, 6.32. Calc. for [(habbi)Ni_3] ($C_{69}H_{96}N_6S_3O_3Ni_3$) C, 62.32; H, 7.28; N, 6.32.

X-ray crystallography

The single-crystals were coated with oil and measured at low temperature on a Bruker Kappa APEX II diffractometer (four circle goniometer with 4 K CCD detector, Mo-Kα radiation, focussing graphite monochromator; ω- and φ-scans) ([(bert^{Me})-Ni_3]·2toluene, [(bert$^{t\text{-}Bu_2}$)Ni_3]·1.5EtOH·1.5CH_2Cl_2), and a Bruker X8-Prospector diffractometer (three circle goniometer with 4 K CCD detector, Cu-Kα radiation, IμS microfocus source with multilayer optics) ([(bertdien)Ni_3]$(BPh_4)_3$·3acetone, [(habbi)-Ni_3]·CH_2Cl_2·H_2O). Empirical absorption corrections using equivalent reflections were performed using the program SADABS 2008/1.[80] The structures were solved using the program SHELXS-97[81] and refined using SHELXL-97.[81]

In preliminary refinements of [(bertdien)Ni_3]$(BPh_4)_3$ three acetone molecules per formula unit were found to be strongly disordered over approximately five positions. This is in good agreement with the number of electrons and the corresponding void volume was found by SQUEEZE[82,83] after removal of the solvent molecules. Originally 1/3 toluene molecule was found disordered in the asymmetric unit of [(bert^{Me})-Ni_3]·2toluene (one toluene molecule per complex), but it could not be properly refined and was therefore removed from the coordinate set. The SQUEEZE[82,83] electron count can be attributed to *ca.* two toluene molecules per complex. Approximately 1.5 CH_2Cl_2 and 1.5 EtOH molecules were found in the asymmetric unit of [(bert$^{t\text{-}Bu_2}$)Ni_3]·1.5EtOH·1.5CH_2Cl_2 but did not refine properly due to severe disorder. The electron count found by SQUEEZE[82,83] after removal of the solvent corresponds quite closely to 1.5 CH_2Cl_2 and 1.5 EtOH molecules. Approximately 0.6 CH_2Cl_2 and 0.3 H_2O molecules per complex can be found and refined for [(habbi)Ni_3]·CH_2Cl_2·H_2O. Together with the electron density found by SQUEEZE[82,83] in the remaining voids, 1 CH_2Cl_2 and 1 H_2O molecules can be attributed to each complex molecule. The solvent molecules of all structures, determined by the above described procedure, are, however, included in the reported chemical formulae and derived quantities.

The ligands in [(bertdien)Ni_3]$(BPh_4)_3$·3acetone and [(bert^{Me})-Ni_3]·2toluene show partial disorder, which made it necessary to restrain some distances in these ligand areas. Additionally, in [(habbi)Ni_3]·CH_2Cl_2·H_2O the C–Cl distances of the disordered CH_2Cl_2 molecules were restrained.

Crystal data and further details concerning the crystal structure determination are given in Table 1. CCDC 901451 ([bertdien)Ni_3]$(BPh_4)_3$), CCDC 901452 ([bert^{Me})Ni_3]), CCDC 901454 ([(bert$^{t\text{-}Bu_2}$)Ni_3]), and CCDC 901455 ([(habbi)Ni_3]) from the Cambridge Crystallographic Data Center contain the supplementary crystallographic data for this contribution.

Other physical measurements

Infrared spectra (400–4000 cm^{-1}) of solid samples were recorded on a Shimadzu FTIR-8400S spectrometer as KBr

Table 1 Crystallographic data of compounds

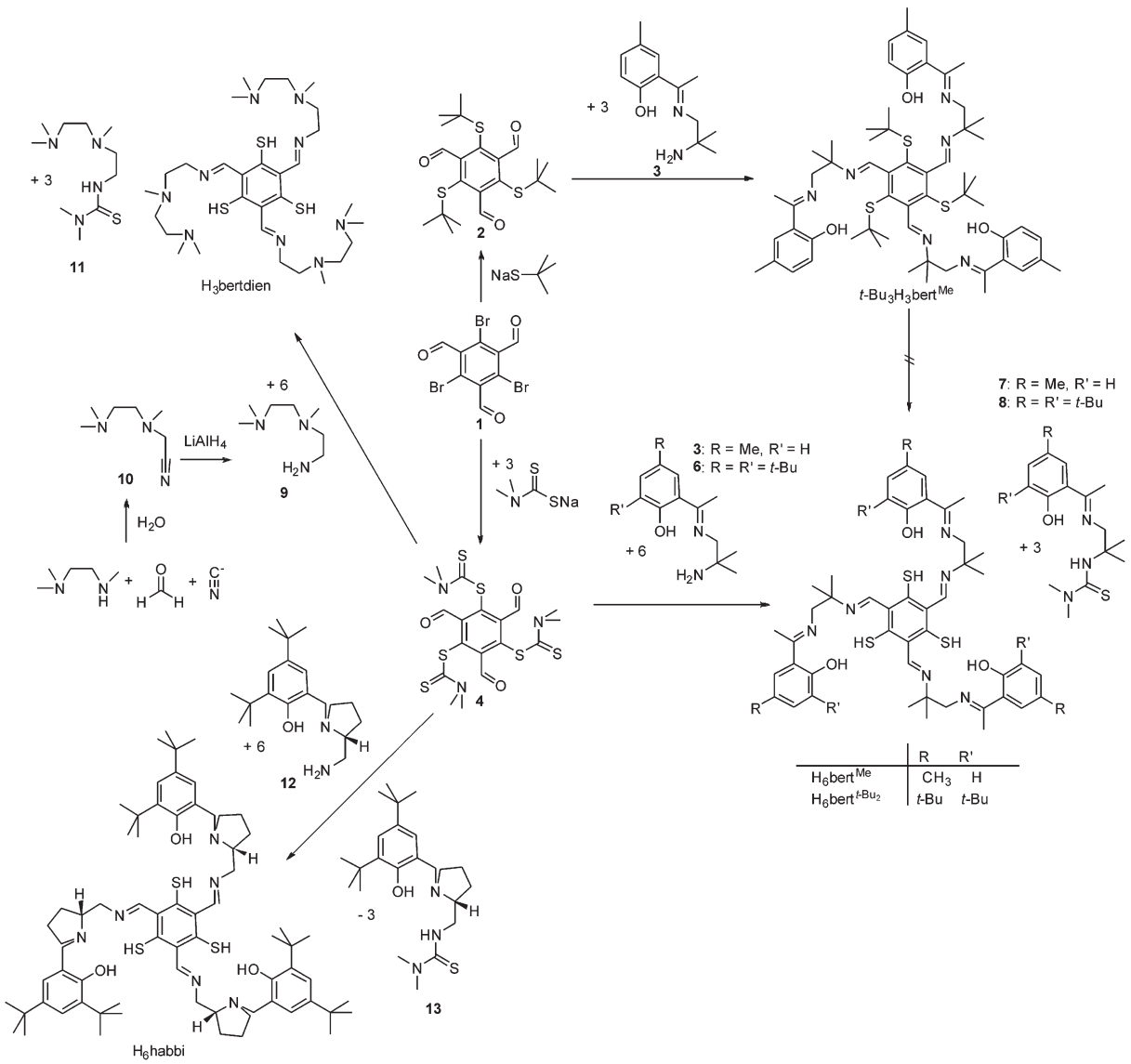
	[(bertdien)Ni_3]$(BPh_4)_3$	[(bert^{Me})Ni_3]	[(bert$^{t\text{-}Bu_2}$)Ni_3]	[(habbi)Ni_3]
Empirical formula	$C_{111}H_{132}B_3N_9Ni_3O_3S_3$	$C_{62}H_{70}N_6Ni_3O_3S_3$	$C_{73.50}H_{108}Cl_3N_6Ni_3O_{4.50}S_3$	$C_{70}H_{100}Cl_2N_6Ni_3O_4S_3$
Formula weight	1945.00	1219.55	1526.32	1432.77
Crystal system	Monoclinic	Trigonal	Triclinic	Trigonal
Space group	$P2_1/c$	$R\bar{3}$	$P\bar{1}$	$R3$
a/Å	17.7065(11)	21.4863(17)	12.1982(12)	24.7936(5)
b/Å	33.162(2)	21.4863(17)	13.1994(15)	24.7936(5)
c/Å	17.0365(10)	27.386(3)	24.094(3)	89.645(3)
α/°	90	90	87.884(4)	90
β/°	90.034(3)	90	83.960(4)	90
γ/°	90	120	88.575(4)	120
V/Å^3	10 003.7(10)	10 949.2(16)	3854.4(7)	47 724(2)
T/K	100(2)	100(2)	100(2)	100(2)
Z	4	6	2	24
Crystal size/mm	0.35 × 0.21 × 0.13	0.23 × 0.17 × 0.14	0.5 × 0.08 × 0.05	0.16 × 0.11 × 0.05
Radiation type	CuKα	MoKα	MoKα	CuKα
μ/mm^{-1}	1.673	0.887	0.961	2.529
ρ/g cm^{-3}	1.291	1.026	1.315	1.196
Θ/range/°	2.50–70.00	2.31–24.98	2.50–25.00	10.80–66.60
Measured refl.	89 035	38 677	37 519	79 261
Unique refl., R_{int}	18 244, 0.0355	4282, 0.0716	13 195, 0.0662	34 119, 0.1052
Observed refl. ($I > 2\sigma(I)$)	15 267	2516	8502	25 902
Data, restraints, parameters	18 244, 11, 1027	4282, 28, 196	13 195, 0, 760	34 119, 45, 2074
R_1, wR_2 ($I > 2\sigma(I)$)	0.0687, 0.1914	0.0690, 0.1849	0.0653, 0.1611	0.0712, 0.1822
R_1, wR_2 (all data)	0.0773, 0.1987	0.1097, 0.2093	0.1005, 0.1770	0.0928, 0.1971
Goodness-of-fit on F^2	1.056	1.046	0.940	1.023
Flack parameter				0.004(16)
CCDC number	901451	901452	901454	901455

disks. ESI mass spectra were recorded on a Bruker Esquire 3000 ion trap mass spectrometer equipped with a standard ESI source. MALDI TOF mass spectra were recorded using a PE Biosystems Voyager™ DE instrument. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX500 or a Bruker Avance III 300 spectrometer using the solvent as an internal standard. Optical rotations were measured using a JASCO DIP-360 polarimeter. 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 counterelectrode was 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 (model 273 A).

Results and discussion

Synthesis of ligands and complexes

The principal problem in the synthesis of the anticipated thiotriplesalen ligand is best illustrated by the fact that several complexes of the parent ligand thiosalen are known,[84–88] but the free thiosalen ligand is unstable since it forms bicyclic dithiocin derivatives.[85,89,90] Thus, a protected ligand precursor is usually used that becomes deprotected during the complex formation. A common route to Ni^{II} thiolate complexes is by the use of *tert*-butyl protected sulfides as the starting material.[91–96] In this respect, we reacted Rubin's aldehyde **1**[77] (Scheme 2) with sodium *tert*-butylmercaptan and obtained the trialdehyde **2**. The reaction of **2** with half-unit **3** afforded the protected thiotriplesalen ligand *t*-$Bu_3H_3bert^{Me}$ as a yellow solid. Unfortunately, employing the reaction conditions that



Scheme 2

have been described for the deprotection in the literature using Lewis acids like Ni^{II} [91–95] or using reductants like Na/NH_3 [97,98] afforded no pure products.

Therefore, we tested other sulfur nucleophiles to introduce the sulfur functionality combined with its facile deprotection. Sodium dithiocarbamate[99] turned out to be the ideal sulfur nucleophile to afford trialdehyde **4**[76] (Scheme 2). We thus reacted trialdehyde **4** with three equivalents of half-unit **3**. However, we could not isolate the expected triimine still having three carbamate protecting groups. Instead, we obtained complicated mixtures of compounds. Using NMR, IR, and MS we could realize that imine condensation and carbamate deprotection resulting in the thiourea byproduct **7** are kinetically competing reactions. Thus, we then used six equivalents of half-unit **3** resulting in the simultaneous nucleophilic cleavage and Schiff-base formation with the formation of H_6bert^{Me} and the thiourea byproduct **7**. Analogously, we obtained the ligand $H_6bert^{t\text{-}Bu_2}$ and the thiourea byproduct **8** starting from the half-unit **6**.

The ligands H_6bert^{Me} and $H_6bert^{t\text{-}Bu_2}$ and their thiourea byproducts exhibit similar solubilities. Moreover, by using column chromatography for separation, the ketimine groups in the ligands H_6bert^{Me} and $H_6bert^{t\text{-}Bu_2}$ proved to be sensitive against cleavage. Therefore, we applied the crude products directly in the reaction with $Ni(OAc)_2{\cdot}4H_2O$ in ethanol to afford the Ni^{II} complexes $[(bert^{t\text{-}Bu_2})Ni^{II}{}_3]$ and $[(bert^{Me})Ni^{II}{}_3]$.

In order to obtain an extended thiophloroglucinol ligand without terminal imine functions, which prevents the chromatographic workup, we synthesized H_3bertdien which requires the triamine **9** (Scheme 2). Different synthetic procedures have been published,[100,101] but the described multi-step procedures only provide unsatisfactory yields. We have thus developed a simple and better yield procedure to afford triamine **9** (Scheme 2). The reaction of trialdehyde **4** with an excess of triamine **9** resulted in the formation of the free ligand H_3bertdien again contaminated with the thiourea byproduct **11**. Although H_3bertdien exhibits no hydrolytically labile terminal imine functions we were not able to find suitable conditions to isolate the free ligand. This might be associated with the quite strong interactions of the nine nitrogen donors with the SiO_2 surface. However, it was again possible to use the crude product without further purification for the reaction with $Ni(OAc)_2{\cdot}4H_2O$ and we obtained after addition of $NaBPh_4$ $[(bertdien)Ni_3](BPh_4)_3$ in good yield. For electrochemical measurements we also prepared the BF_4^- salt $[(bertdien)Ni_3](BF_4)_3$.

In order to obtain an extended thiophloroglucinol ligand, which can be purified using column chromatography, *i.e.* containing neither a hydrolytically labile imine function nor a basic N_3 pendant arm, we employed the chiral saturated salan half-unit **12**[102] in the reaction with **4**. The resulting mixture of the ligand H_6habbi and thiourea **13** can be purified by column chromatography to obtain the free ligand H_6habbi.[76] Reaction of H_6habbi with $Ni(OAc)_2{\cdot}4H_2O$ results in $[(habbi)Ni^{II}{}_3]$.

Structural characterization

The structures of $[(bertdien)Ni^{II}{}_3](BPh_4)_3{\cdot}3$acetone, $[(bert^{Me})Ni^{II}{}_3]{\cdot}2$toluene, $[(bert^{t\text{-}Bu_2})Ni^{II}{}_3]{\cdot}1.5EtOH{\cdot}1.5CH_2Cl_2$, and $[(habbi)Ni^{II}{}_3]{\cdot}CH_2Cl_2{\cdot}H_2O$ were determined by single-crystal X-ray diffraction. The molecular structures are displayed in Fig. 1 (thermal ellipsoid plots are provided in Fig. S1 and S2†) and selected interatomic distances are summarized in Table 2. The structure of $[(bertdien)Ni_3]^{3+}$ exhibits the same disorder phenomenon of one ethylene bridge which has already been observed in the oxygen analog $[(felddien)Ni^{II}{}_3]^{3+}$ (Fig. S3†).[103] The asymmetric unit of $[(habbi)Ni^{II}{}_3]{\cdot}CH_2Cl_2{\cdot}H_2O$ consists of two trinuclear complexes (molecule 1: Ni1, Ni2, Ni3, and molecule 2: Ni4, Ni5, Ni6) and of two times a third of a trinuclear complex (molecule 3: Ni7 and molecule 4: Ni8). The whole

Table 2 Selected interatomic distances [Å]

				[(habbi)Ni_3]			
	$[(bert^{Me})Ni_3]$	$[(bert^{t\text{-}Bu_2})Ni_3]$	$[(bertdien)Ni_3]^{3+}$	Molecule 1	Molecule 2[a]	Molecule 3[a]	Molecule 4[a]
Ni1–S11	2.144(1)	2.146(1)	2.124(1)	2.146(2)	2.147(2)	2.127(2)	2.130(3)
Ni2–S21		2.142(1)	2.130(1)	2.119(2)	2.133(2)		
Ni3–S31		2.140(1)	2.119(1)	2.149(2)	2.136(2)		
Ni1–N11	1.831(4)	1.852(3)	1.844(3)	1.814(5)	1.817(5)	1.818(5)	1.829(8)
Ni2–N21		1.839(4)	1.829(3)	1.825(6)	1.814(6)		
Ni3–N31		1.850(4)	1.842(2)	1.828(6)	1.842(5)		
Ni1–N12	1.883(4)	1.870(4)	1.951(3)	1.933(5)	1.936(5)	1.929(5)	1.963(8)
Ni2–N22		1.873(3)	1.952(3)	1.928(5)	1.942(5)		
Ni3–N32		1.879(3)	1.935(3)	1.957(5)	1.945(6)		
Ni1–O12	1.821(3)	1.822(3)		1.827(4)	1.846(5)	1.831(4)	1.866(6)
Ni2–O22		1.833(3)		1.838(4)	1.837(5)		
Ni3–O32		1.828(3)		1.854(5)	1.851(5)		
Ni1–N13			1.979(3)				
Ni2–N23			1.968(3)				
Ni3–N33			1.975(2)				
S11–C1	1.740(5)	1.729(4)	1.734(3)	1.732(6)	1.723(7)	1.726(6)	1.729(9)
S21–C3		1.731(4)	1.731(3)	1.720(6)	1.711(7)		
S31–C5		1.725(5)	1.732(3)	1.747(7)	1.710(7)		

[a] The labeling scheme has been adapted for molecules 2–4 of [(habbi)Ni_3] to account for analogous atoms.

Table 3 Selected structural properties of the nickel complexes [(felddien)Ni^{II}_3]$(BF_4)_3$,[103] [(talen$^{t\text{-}Bu_2}$)Ni^{II}_3],[9] [(bert^{Me})Ni^{II}_3], [(bert$^{t\text{-}Bu_2}$)Ni^{II}_3], [(bertdien)Ni^{II}_3]$(BPh_4)_3$, and [(habbi)Ni^{II}_3]

						[(habbi)Ni_3]			
		[(felddien)Ni_3]$^{3+}$	[(bertdien)Ni_3]$^{3+}$	[(bert^{Me})Ni_3]	[(bert$^{t\text{-}Bu_2}$)Ni_3]	Molecule 1	Molecule 2	Molecule 3	Molecule 4
d^a [Å]	Ni1	0.43	0.72	0.52	−0.22	1.02	0.92	0.92	0.90
	Ni2	0.07	0.52		0.44	0.54	0.71		
	Ni3	0.13	0.49		−0.40	0.70	0.86		
α^b [°]	Ni1	19.9	19.2	17.2	13.5	35.7	34.3	31.8	31.8
	Ni2	4.4	16.7		13.5	22.1	25.4		
	Ni3	14.1	16.7		19.7	22.2	29.0		
β^c [°]	Ni1			11.9	14.6	36.0	37.4	36.9	35.8
	Ni2				15.0	31.9	18.2		
	Ni3				22.7	30.1	32.4		
γ^d [°]	Ni1			25.0	16.1	20.8	23.7	18.7	22.4
	Ni2				1.8	25.0	32.6		
	Ni3				3.3	17.5	17.2		
$\varphi^{cent\ e}$ [°]	Ni1	13.9	17.3	17.6	21.3	33.2	33.1	29.5	30.0
	Ni2	2.2	16.4		16.5	25.1	25.5		
	Ni3	8.1	20.9		23.6	23.8	26.5		
$\varphi^{term\ f}$ [°]	Ni1			2.4	1.4				
	Ni2				9.2				
	Ni3				12.8				

[a] d is the shortest distance of an Ni^{II} ion from the best plane formed by the six carbon atoms of the central benzene ring of the phloroglucinol backbone. A negative value corresponds to a displacement to the other side of the plane. [b] α is the angle between the best planes of (1) N_2O_2(S) and (2) benzene of the central phloroglucinol backbone. [c] β is the angle between the best planes of (1) N_2O_2(S) and (2) benzene of the terminal phenolate. [d] γ is the angle between the best planes of (1) benzene of the central phloroglucinol backbone and (2) benzene of the terminal phenolate. [e] Bent angle $\varphi^{cent} = 180° - \angle(Ni–X_{NO}{}^{cent}–X_R{}^{cent})$. [f] Bent angle $\varphi^{term} = 180° - \angle(Ni–X_{NO}{}^{term}–X_R{}^{term})$.

trinuclear complexes are generated by C_3 axes. Each structure contains trinuclear complexes in which one ligand coordinates to three Ni^{II} ions. All Ni^{II} ions are four-coordinate in a square-planar coordination environment.

Trinuclear triplesalen complexes are known to exhibit various degrees of ligand folding which results in an overall bowl-shaped molecular structure for the trinuclear Ni^{II} and Cu^{II} complexes of H_6talen$^{t\text{-}Bu_2}$ and we applied several parameters for a quantitative description of the ligand folding[9,12,33] which have also been determined for the complexes within this study (Table 3). The bent angles φ^{cent} and φ^{term} turned out to be a good indicator of the ligand folding. The bent angle φ is defined by $\varphi = 180° - \angle(M–X_{NO}–X_R)$ (X_{NO}: midpoint of adjacent N and O donor atoms; X_R: midpoint of the six-membered chelate ring containing the N and O donor atoms).

The previously reported complex [(felddien)Ni^{II}_3]$^{3+}$ provides an opportunity to investigate the differences in ligand folding by O *vs.* S substitution as it represents the exact O-analog to [(bertdien)Ni^{II}_3]$^{3+}$.[103] The comparison of mean values of φ^{cent} for [(bertdien)Ni^{II}_3]$^{3+}$ (~18°) to [(felddien)Ni^{II}_3]$^{3+}$ (~8°) indicates that the sulfur complex exhibits a more severe ligand folding than its oxygen counterpart. As there is only O *vs.* S substitution and no particular crystal packing effects are evident, the stronger ligand folding in the sulfur complex should be mainly due to electronic effects. Additionally, the longer S–Ni and S–C bonds provide even more space in the sulfur complex so that steric hindrance can be disregarded as the reason for the stronger ligand folding. An even more pronounced central ligand folding is observed in [(habbi)Ni^{II}_3] with $\varphi^{cent} \sim 25–33°$. However, this effect is mainly attributed to the special diamine bridging unit in this complex.

Electrochemical characterization

The electrochemistry of the four new Ni_3 complexes was studied by means of cyclic and square-wave voltammetry. Due to solubility reasons, [(bert$^{t\text{-}Bu_2}$)Ni^{II}_3] and [(habbi)Ni^{II}_3] have been measured in CH_2Cl_2, [(bert^{Me})Ni^{II}_3] in $C_2H_2Cl_4$, and [(bertdien)Ni^{II}_3]$(BF_4)_3$ in CH_3CN solutions. Representative examples of the CVs and of the SWs as well as of [(felddien)-Ni^{II}_3]$(BF_4)_3$ [103] for comparison are provided in Fig. 2 and 3, and redox potentials (all referenced *vs.* Fc^+/Fc) are compiled in Table 4.

The two trinuclear complexes [(felddien)Ni^{II}_3]$(BF_4)_3$ and [(bertdien)Ni^{II}_3]$(BF_4)_3$ both exhibit three reductions, which appear to be more reversible for [(felddien)Ni^{II}_3]$(BF_4)_3$ than for [(bertdien)Ni^{II}_3]$(BF_4)_3$ (Fig. 2). These may be assigned to the known reductions of Ni^{II} ions to Ni^{I} ions in related coordination environments.[104,105] Comparing the potentials for these processes (Table 4), it is interesting to note that the sulfur complex [(bertdien)Ni^{II}_3]$^{3+}$ is by 0.26–0.28 V easier to reduce than the oxygen analog [(felddien)Ni^{II}_3]$^{3+}$. This reflects some flexibility of thiolate ligands in charge donation compared to their oxygen analogs so that the Ni^{I} ions are less destabilized.[106] In the oxidative region, only irreversible, less resolved electron transfer processes are observed.

Interestingly, the complexes with terminal phenolate ligands exhibit no reductive electrochemistry but a rich oxidative electrochemistry (Fig. 3). This reflects the stronger electron density donation by σ and π donation of the terminal

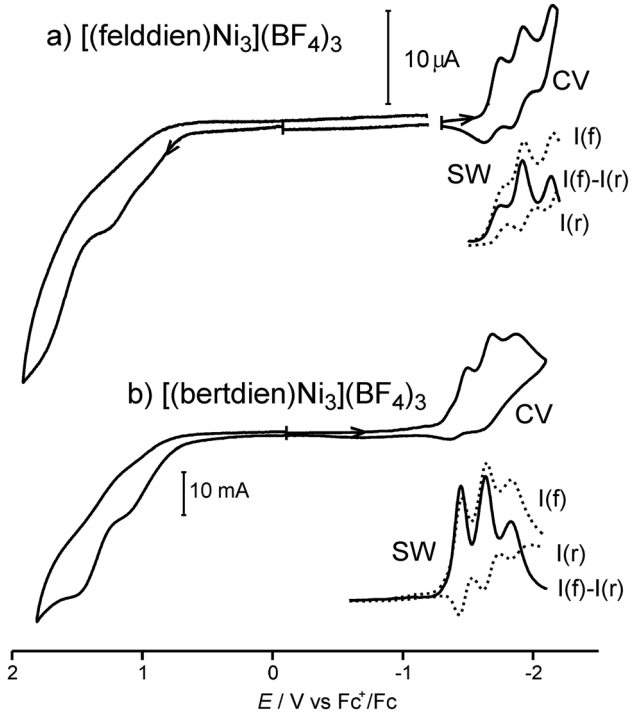


Fig. 2 CV and SW of (a) [(felddien)Ni_3]$(BF_4)_3$ [103] and (b) [(bertdien)Ni_3]-$(BF_4)_3$ measured in CH_3CN solution at 20 °C recorded at a platinum working electrode. Scan rate 200 mV s^{-1}.

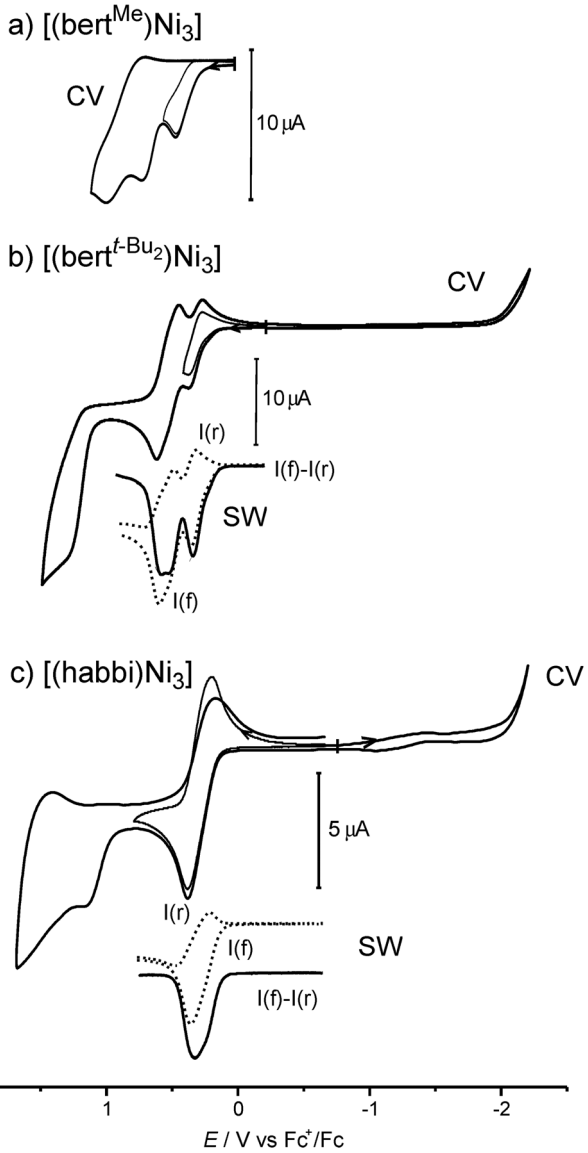


Fig. 3 CV and SW of (a) [(bert^{Me})Ni_3] measured in $C_2H_2Cl_4$ (solvent decomposition of $C_2H_2Cl_4$ limits measurements to positive potential), (b) [(bert$^{t\text{-}Bu_2}$)Ni_3] and (c) [(habbi)Ni_3] all measured in CH_2Cl_2 solution at 20 °C recorded at a platinum working electrode. Scan rate 200 mV s^{-1}.

phenolates *vs.* pure σ donation of the terminal amines. The triplesalen complex [(talen$^{t\text{-}Bu_2}$)Ni^{II}_3] exhibits three reversible oxidative waves with the second wave being a not yet resolved two-electron oxidation. Spectro-electrochemical measurements revealed a complicated temperature-dependent equilibrium between a metal-centered oxidation leading to a Ni^{III} species and a phenolate-centered oxidation leading to a coordinated phenoxyl radical. However, the assignment of the oxidation to the terminal or the central phenolate units was only tentative at that stage.[9]

The sulfur complex [(bert$^{t\text{-}Bu_2}$)Ni^{II}_3] exhibits quite an analogous electrochemical behavior as its oxygen analog [(talen$^{t\text{-}Bu_2}$)-Ni^{II}_3]. The second oxidation is partially resolved in the SW, which manifests its two-electron nature. Furthermore, these oxidations in [(bert$^{t\text{-}Bu_2}$)Ni^{II}_3] are at only slightly higher potentials than in [(talen$^{t\text{-}Bu_2}$)Ni^{II}_3]. These closely related redox processes indicate that these oxidations are not centered at the central phloroglucinol backbone but at the terminal Ni–phenolate parts. A further argument for the assignment to the oxidation of the terminal Ni–phenolate units arises from the

Table 4 Electrochemical properties of the Ni^{II} complexes ($E_{1/2}$ for processes exhibiting peaks in the forward and back scans, peak potentials for processes, exhibiting no peak for the back scan (irr), presented in V *vs.* Fc^+/Fc)

	Oxidation					Reduction			Ref.
[(felddien)Ni_3]$(BF_4)_3$		$+1.27^{irr}$				−1.69	−1.88	−2.10	103
[(bertdien)Ni_3]$(BF_4)_3$	$+1.53^{irr}$	$+1.10^{irr}$				−1.42	−1.62	−1.82	This work
[(talen$^{t\text{-}Bu_2}$)Ni_3]		+1.00		$+0.55^{a}$	+0.22				9
[(bert^{Me})Ni_3]			$+0.85^{irr}$	$+0.61^{irr}$	$+0.39^{irr}$				This work
[(bert$^{t\text{-}Bu_2}$)Ni_3]		$+1.29^{irr}$		$+0.56/+0.51^{b}$	+0.33				This work
[(habbi)Ni_3]		$+1.16^{irr}$			+0.30				This work

[a] Presumable 2 electron process which is not resolved. [b] Separation of two one-electron processes detected by SW.

irreversibility of these redox waves in [(bert^{Me})Ni$^{II}_3$] as it is well established that coordinated phenolates with *tert*-butyl groups in *ortho* and *para* positions can be reversibly oxidized, while a methyl protection is not sufficient for the stabilization of the oxidized phenoxyl radical resulting in irreversible electron transfer processes.[107–110] The complex [(habbi)Ni$^{II}_3$] exhibits a reversible oxidation at 0.30 V. As three terminal phenolate units are available, this electron transfer wave might even be a three-electron oxidation without the splitting observed in [(talen$^{t\text{-}Bu_2}$)Ni$^{II}_3$] and [(bert$^{t\text{-}Bu_2}$)Ni$^{II}_3$], indicative of less electronic communications. The shape of the SW voltammogram provides a further indication of a non-one-electron step.

Considering all data provided in Table 4 indicate that the triplesalen complexes with terminal phenolates can be oxidized in the 0.2 to 0.6 V region, which is assigned to the terminal phenolates, while in the range above 1 V irreversible oxidative waves are observed for all compounds, implying that the central backbone is oxidized. While all these processes are irreversible in the Ni complexes, it should be emphasized that [(felddien)Cu$^{II}_3$]$^{3+}$ exhibits a reversible one-electron oxidation at 0.80 V.[103] Spectroelectrochemistry provided an increase of absorption intensity around 26 800 cm^{-1}, which is characteristic of the formation of phenoxyl radicals.[107–110] This comparison indicates that the potential and the reversibility for the oxidation of the central phloroglucinol backbone are metal-dependent.

Conclusions

We have established a versatile procedure for the synthesis of extended thiophloroglucinol ligands in general and thiotriplesalen ligands in particular. Rubin's aldehyde **1** is nucleophilically substituted by three equivalents of dithiocarbamate to obtain the tris(dithiocarbamate)trialdehyde **4**. This can be reacted with six equivalents of a primary amine resulting in a simultaneous three-fold Schiff-base formation and three-fold deprotection of the dithiocarbamate to obtain the free trithiols, which are contaminated with three equivalents of a thiourea derivative as the deprotection byproduct. This thiourea byproduct could be removed for H$_6$habbi, but not for H$_3$bertdien, H$_6$bert^{Me}, and H$_6$bert$^{t\text{-}Bu_2}$. However, reaction of the pure ligand H$_6$habbi or the mixtures of H$_3$bertdien, H$_6$bert^{Me}, and H$_6$bert$^{t\text{-}Bu_2}$ with Ni^{II} salts resulted in the formation of the trinuclear Ni$^{II}_3$ complexes [(bertdien)Ni$^{II}_3$](X)$_3$ (X = BPh$_4^-$, BF$_4^-$) [(bert^{Me})Ni$^{II}_3$], [(bert$^{t\text{-}Bu_2}$)Ni$^{II}_3$], and [(habbi)Ni$^{II}_3$] as evidenced by single-crystal X-ray diffraction. The molecular structures consist of square-plane coordinated Ni^{II} ions that are bridged by a central thiophloroglucinol backbone.

Comparison of the molecular structures to those of their oxygen analog phloroglucinol-bridged complexes reveals a stronger ligand folding at the central Ni–S bond. The electrochemical analysis in conjunction with the oxygen-analogs allows one to assign the reversible oxidations in the nickel complexes of triplesalen and thiotriplesalen ligands to include the terminal phenolate units and not the central backbone.

Having the desired thiotriplesalen ligands in hand, we will evaluate their potential to optimize the SMM behavior of sulfur analogs of $[M^t_6M^c]^{n+}$ complexes. Furthermore, we will analyze in detail the differences in electronic structures of the ligands and the complexes by the O–S substitution as well as their potential for a more efficient spin-polarization contribution to the exchange interactions.

Acknowledgements

This work was supported by the DFG (FOR945 'Nanomagnets: from Synthesis *via* Interactions with Surfaces to Function'), the Fonds der Chemischen Industrie, and Bielefeld University. We would like to thank Dr Andreas Mix (Bielefeld University) for fruitful discussions on NMR spectroscopy.

References

1 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143.
2 G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bull.*, 2000, **25**, 66–71.
3 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, 2006.
4 M. Urdampilleta, S. Klyatskaya, J.-P. Cleuziou, M. Ruben and W. Wernsdorfer, *Nat. Mater.*, 2011, **10**, 502–506.
5 R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer and F. Balestro, *Nature*, 2012, **488**, 357–360.
6 M. N. Leuenberger and D. Loss, *Nature*, 2001, **410**, 789–793.
7 C. J. Wedge, G. A. Timco, E. T. Spielberg, R. E. George, F. Tuna, S. Rigby, E. J. L. McInnes, R. E. P. Winpenny, S. J. Blundell and A. Ardavan, *Phys. Rev. Lett.*, 2012, **108**, 107204–107209.
8 T. Glaser, M. Heidemeier and T. Lügger, *Dalton Trans.*, 2003, 2381–2383.
9 T. Glaser, M. Heidemeier, R. Fröhlich, P. Hildebrandt, E. Bothe and E. Bill, *Inorg. Chem.*, 2005, **44**, 5467–5482.
10 T. Glaser, *Chem. Commun.*, 2011, **47**, 116–130.
11 Please note that the general formulation of triplesalen as provided in Scheme 1a has not been accessible yet due to synthetic constraints but must contain specific substituents.
12 T. Glaser, M. Heidemeier, J. B. H. Strautmann, H. Bögge, A. Stammler, E. Krickemeyer, R. Huenerbein, S. Grimme, E. Bothe and E. Bill, *Chem.–Eur. J.*, 2007, **13**, 9191–9206.
13 T. Glaser, M. Heidemeier, S. Grimme and E. Bill, *Inorg. Chem.*, 2004, **43**, 5192–5194.
14 H. Theil, C.-G. Freiherr von Richthofen, A. Stammler, H. Bögge and T. Glaser, *Inorg. Chim. Acta*, 2008, **361**, 916–924.
15 H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179–253.

16 I. Fernández, R. Ruiz, J. Faus, M. Julve, F. Lloret, J. Cano, X. Ottenwaelder, Y. Journaux and C. Munoz, *Angew. Chem., Int. Ed.*, 2001, **40**, 3039–3042.
17 T. Glaser, M. Gerenkamp and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2002, **41**, 3823–3825.
18 H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265–274.
19 J. Cano, E. Ruiz, S. Alvarez and M. Verdaguer, *Commun. Inorg. Chem.*, 1998, **20**, 27–56.
20 D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88–94.
21 V. A. Ung, A. Thompson, D. A. Bardwell, D. Gatteschi, J. C. Jeffery, J. A. McCleverty, F. Totti and M. D. Ward, *Inorg. Chem.*, 1997, **36**, 3447–3454.
22 J. A. McCleverty and M. D. Ward, *Acc. Chem. Res.*, 1998, **31**, 842–851.
23 T. Glaser, M. Heidemeier, T. Weyhermüller, R.-D. Hoffmann, H. Rupp and P. Müller, *Angew. Chem., Int. Ed.*, 2006, **45**, 6033–6037.
24 T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill and J. Schnack, *Inorg. Chem.*, 2009, **48**, 607–620.
25 E. Krickemeyer, V. Hoeke, A. Stammler, H. Bögge, J. Schnack and T. Glaser, *Z. Naturforsch.*, 2010, **65b**, 295–303.
26 V. Hoeke, M. Heidemeier, E. Krickemeyer, A. Stammler, H. Bögge, J. Schnack, A. Postnikov and T. Glaser, *Inorg. Chem.*, 2012, **51**, 10929–10954.
27 V. Hoeke, K. Gieb, P. Müller, L. Ungur, L. Chibotaru, M. Heidemeier, E. Krickemeyer, A. Stammler, H. Bögge, C. Schröder, J. Schnack and T. Glaser, *Chem. Sci.*, 2012, **3**, 2868–2882.
28 V. Hoeke, M. Heidemeier, E. Krickemeyer, A. Stammler, H. Bögge, J. Schnack and T. Glaser, *Dalton Trans.*, 2012, **41**, 12942–12959.
29 V. Hoeke, E. Krickemeyer, M. Heidemeier, H. Theil, A. Stammler, H. Boegge, T. Weyhermueller, J. Schnack and T. Glaser, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4398–4409.
30 T. Glaser, M. Heidemeier, H. Theil, A. Stammler, H. Bögge and J. Schnack, *Dalton Trans.*, 2010, **39**, 192–199.
31 T. Glaser, M. Heidemeier and R. Fröhlich, *Compt. Rend. Chim.*, 2007, **10**, 71–78.
32 B. Feldscher, E. Krickemeyer, M. Moselage, H. Theil, V. Hoeke, Y. Kaiser, A. Stammler, H. Bögge and T. Glaser, *Sci. China, Ser. B: Chem.*, 2012, **55**, 951–966.
33 C. Mukherjee, A. Stammler, H. Bögge and T. Glaser, *Chem.–Eur. J.*, 2010, **16**, 10137–10149.
34 C. R. Kemnitz, R. R. Squires and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 6564–6574.
35 L. A. Hammad and P. G. Wenthold, *J. Am. Chem. Soc.*, 2001, **123**, 12311.
36 A. Rajca, *Chem.–Eur. J.*, 2002, **8**, 4834–4841.
37 I. Ratera and J. Veciana, *Chem. Soc. Rev.*, 2012, **41**, 303–349.
38 R. C. Fort, S. J. Getty, D. A. Hrovat, P. M. Lahti and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 7549–7552.
39 S. Kato, K. Morokuma, D. Feller, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1983, **105**, 1791–1795.
40 P. G. Wenthold, J. B. Kim and W. C. Lineberger, *J. Am. Chem. Soc.*, 1997, **119**, 1354–1359.
41 T. Glaser, H. Theil and M. Heidemeier, *C. R. Chim.*, 2008, **11**, 1121–1136.
42 T. Glaser, *Coord. Chem. Rev.*, 2013, **257**, 140–152.
43 A. M. W. Cargill Thompson, D. Gatteschi, J. A. McCleverty, J. A. Navas, E. Rentschler and M. D. Ward, *Inorg. Chem.*, 1996, **35**, 2701–2703.
44 V. A. Ung, S. M. Couchman, J. C. Jeffery, J. A. McCleverty, M. D. Ward, F. Totti and D. Gatteschi, *Inorg. Chem.*, 1999, **38**, 365–369.
45 S. R. Bayly, J. A. McCleverty, M. D. Ward, D. Gatteschi and F. Totti, *Inorg. Chem.*, 2000, **39**, 1288–1293.
46 S. R. Bayly, E. R. Humphrey, H. de Chair, C. G. Paredes, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, F. Totti, D. Gatteschi, S. Courric, B. R. Steele and C. G. Screttas, *J. Chem. Soc., Dalton Trans.*, 2001, 1401–1414.
47 X. Ottenwaelder, J. Cano, Y. Journaux, E. Riviere, C. Brennan, M. Nierlich and R. Ruiz-Garcia, *Angew. Chem., Int. Ed.*, 2004, **43**, 850–852.
48 M.-C. Dul, X. Ottenwaelder, E. Pardo, R. Lescouezec, Y. Journaux, L. M. Chamoreau, R. Ruiz-Garcia, J. Cano, M. Julve and F. Lloret, *Inorg. Chem.*, 2009, **48**, 5244–5249.
49 E. Pardo, J. Ferrando-Soria, M.-C. Dul, R. Lescouëzec, Y. Journaux, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, L. Cañadillas-Delgado, J. Pasán and C. Ruiz-Pérez, *Chem.–Eur. J.*, 2010, **16**, 12838–12851.
50 M.-C. Dul, E. Pardo, R. Lescouëzec, Y. Journaux, J. Ferrando-Soria, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, D. Cangussu, C. L. M. Pereira, H. O. Stumpf, J. Pasán and C. Ruiz-Pérez, *Coord. Chem. Rev.*, 2010, **254**, 2281–2296.
51 E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouezec, Y. Journaux, F. Lloret and M. Julve, *Dalton Trans.*, 2008, 2780–2805.
52 S. P. Foxon, G. R. Torres, O. Walter, J. Z. Pedersen, H. Toftlund, M. Hüber, K. Falk, W. Haase, J. Cano, F. Lloret, M. Julve and S. Schindler, *Eur. J. Inorg. Chem.*, 2004, 335–343.
53 S. Turba, O. Walter, S. Schindler, L. P. Nielsen, A. Hazell, C. J. McKenzie, F. Lloret, J. Cano and M. Julve, *Inorg. Chem.*, 2008, **47**, 9612–9623.
54 A. R. Paital, T. Mitra, D. Ray, W. T. Wong, J. Ribas-Ariño, J. J. Novoa, J. Ribas and G. Aromi, *Chem. Commun.*, 2005, 5172–5174.
55 C. Yuste, J. Ferrando-Soria, D. Cangussu, O. Fabelo, C. Ruiz-Pérez, N. Marino, G. D. Munno, S.-E. Stiriba, R. Ruiz-García, J. Cano, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2010, **363**, 1984–1994.
56 D. Plaul and W. Plass, *Inorg. Chim. Acta*, 2011, **374**, 341–349.
57 D. Plaul, D. Geibig, H. Görls and W. Plass, *Polyhedron*, 2009, **28**, 1982–1990.
58 W. Plass, *Chemie in unserer Zeit*, 1998, **32**, 323–333.

59 A. A. Ovchinnikov, *Theor. Chim. Acta*, 1978, **47**, 297–304.
60 M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Book Company, New York, 1969.
61 E. I. Solomon, D. W. Randall and T. Glaser, *Coord. Chem. Rev.*, 2000, **200–202**, 595–632.
62 H. B. Gray and J. R. Winkler, *Annu. Rev. Biochem.*, 1996, **65**, 537–561.
63 H. Beinert, R. H. Holm and E. Münck, *Science*, 1997, **277**, 653–659.
64 R. P. Houser, J. A. Halfen, V. G. Young Jr., N. J. Blackburn and W. B. Tolman, *J. Am. Chem. Soc.*, 1995, **117**, 10745–10746.
65 R. P. Houser, V. G. J. Young and W. B. Tolman, *J. Am. Chem. Soc.*, 1996, **118**, 2101–2102.
66 P. L. Holland and W. B. Tolman, *J. Am. Chem. Soc.*, 1999, **121**, 7270–7271.
67 L. Noodleman and D. A. Case, *Adv. Inorg. Chem.*, 1992, **38**, 423–470.
68 M. Moore, K. Feghali and S. Gambarotta, *Inorg. Chem.*, 1997, **36**, 2191–2194.
69 O. Kahn and J.-J. Girerd, *Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmosphere and Technology*, Elsevier, Amsterdam, 1984.
70 T. Glaser, T. Beissel, E. Bill, T. Weyhermüller, V. Schünemann, W. Meyer-Klaucke, A. X. Trautwein and K. Wieghardt, *J. Am. Chem. Soc.*, 1999, **121**, 2193–2208.
71 K. Rose, E. S. Shadle, T. Glaser, S. d. Vries, A. Cherepanow, G. W. Canters, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 1999, **121**, 2353–2363.
72 H. Kwart and E. R. Evans, *J. Org. Chem.*, 1966, **31**, 410–413.
73 M. S. Newman and H. A. Karnes, *J. Org. Chem.*, 1966, **31**, 3980–3984.
74 S. Brooker, G. B. Caygill, P. D. Croucher, T. C. Davidson, D. L. J. Clive, S. R. Magnuson, S. P. Cramer and C. Y. Ralston, *J. Chem. Soc., Dalton Trans.*, 2000, 3113–3121.
75 H. Theil, R. Fröhlich and T. Glaser, *Z. Naturforsch.*, 2009, **64b**, 1633–1638.
76 B. Feldscher, H. Theil, A. Stammler, H. Bögge and T. Glaser, *Inorg. Chem.*, 2012, **51**, 8652–8654.
77 D. Bruns, M. Hirokazu and K. P. C. Vollhardt, *Org. Lett.*, 2003, **5**, 549–552.
78 T. J. Dunn, C. F. Ramogida, C. Simmonds, A. Paterson, E. W. Y. Wong, L. Chiang, Y. Shimazaki and T. Storr, *Inorg. Chem.*, 2011, **50**, 6746–6755.
79 J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Org. Lett.*, 2003, **5**, 3823–3826.
80 G. M. Sheldrick, *SADABS*, 2008, University of Göttingen, Göttingen, Germany.
81 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.
82 A. L. Spek, *PLATON/SQUEEZE*, Bijvoet Center for Biomolecular Research, Utrecht University, Utrecht, The Netherlands.
83 A. L. Spek, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 194.
84 P. A. Stenson, A. Marin-Becerra, C. Wilson, A. J. Blake, J. McMaster and M. Schröder, *Chem. Commun.*, 2006, 317–319.
85 P. J. Marini, K. S. Murray and B. O. West, *J. Chem. Soc., Dalton Trans.*, 1983, 143–151.
86 N. Goswami and D. M. Eichhorn, *Inorg. Chem.*, 1999, **38**, 4329–4333.
87 N. Goswami and D. M. Eichhorn, *Inorg. Chim. Acta*, 2000, **303**, 271–276.
88 J. C. Dutton, G. D. Fallon and K. S. Murray, *Inorg. Chem.*, 1988, **27**, 34–38.
89 M. F. Corrigan and B. O. West, *Aust. J. Chem.*, 1976, **29**, 1413–1427.
90 M. F. Corrigan, I. D. Rae and B. O. West, *Aust. J. Chem.*, 1978, **31**, 587–594.
91 E. Bouwman, R. K. Henderson, A. K. Powell, J. Reedijk, W. J. J. Smeets, A. L. Spek, N. Veldman and S. Wocadlo, *J. Chem. Soc., Dalton Trans.*, 1998, 3495–3499.
92 J. Becher, C. E. Stidsen, H. Toftlund and F. M. Asaad, *Inorg. Chim. Acta*, 1986, **121**, 23–26.
93 J. Becher, H. Toftlund and P. H. Olesen, *J. Chem. Soc., Chem. Commun.*, 1983, 740–742.
94 P. K. Bharadwaj, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc.*, 1986, **108**, 1351–1352.
95 E. Bouwman, R. K. Henderson, J. Reedijk, N. Veldman and A. L. Spek, *Inorg. Chim. Acta*, 1999, **287**, 105–108.
96 S. Brooker, *Coord. Chem. Rev.*, 2001, **222**, 33–56.
97 T. Fritz, G. Steinfeld, S. Käss and B. Kersting, *Dalton Trans.*, 2006, 3812–3821.
98 B. Kersting, G. Steinfeld, T. Fritz and J. Hausmann, *Eur. J. Inorg. Chem.*, 1999, 2167–2172.
99 M. Kulka, *Can. J. Chem.*, 1956, **34**, 1093–1100.
100 H. Ford, C.-H. Chang and E. J. Behrmann, *J. Am. Chem. Soc.*, 1981, **103**, 7773–7779.
101 E. D. Dziadulewicz, T. J. Ritchie, A. Hallet, C. R. Snell, S. Y. Ko, R. Wrigglesworth, G. A. Hughes, A. R. Dunstan, G. C. Bloomfield, G. S. Drake, M. C. Brown, W. Lee, G. M. Burgees, C. Davis, M. Yaqoob, M. N. Perkins, E. A. Campbell, A. J. Davis and H. P. Rang, *J. Med. Chem.*, 2000, **43**, 769–771.
102 K. Matsumoto, T. Oguma and T. Katsuki, *Angew. Chem., Int. Ed.*, 2009, **48**, 7432–7435.
103 B. Feldscher, A. Stammler, H. Bögge and T. Glaser, *Polyhedron*, 2011, **30**, 3038–3047.
104 S. Brooker, P. D. Croucher, T. C. Davidson and P. D. Smith, *Polyhedron*, 2000, **19**, 1887–1894.
105 S. Brooker, P. D. Croucher, T. C. Davidson, G. S. Dunbar, C. U. Beck and S. Subramanian, *Eur. J. Inorg. Chem.*, 2000, 169–179.
106 T. Beissel, F. Birkelbach, E. Bill, T. Glaser, F. Kesting, C. Krebs, T. Weyhermüller, K. Wieghardt, C. Butzlaff and A. X. Trautwein, *J. Am. Chem. Soc.*, 1996, **118**, 12376–12390.

107 B. Adam, E. Bill, E. Bothe, B. Goerdt, G. Haselhorst, K. Hildenbrand, A. Sokolowski, S. Steenken, T. Weyhermüller and K. Wieghardt, *Chem.–Eur. J.*, 1997, **3**, 308–319.
108 J. B. H. Strautmann, S. Walleck, H. Bögge, A. Stammler and T. Glaser, *Chem. Commun.*, 2011, **47**, 695–697.
109 J. B. H. Strautmann, C.-G. Freiherr von Richthofen, S. DeBeer George, E. Bothe, E. Bill and T. Glaser, *Chem. Commun.*, 2009, 2637–2639.
110 J. B. H. Strautmann, S. DeBeer George, E. Bothe, E. Bill, T. Weyhermüller, A. Stammler, H. Bögge and T. Glaser, *Inorg. Chem.*, 2008, **47**, 6804–6824.