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Mono- and Dinuclear Coordination Compounds with Directional Bis(bidentate) Ligands

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The benzene-*o*-dithiol/salicylimine (S-S/N-O) ligands H_3-**1** and H_3-**2** have been synthesized, representing the first examples of a new type of polydentate heterodonor ligands. Schiff-base condensation of salicylaldehyde with an amine linked to a benzene-*o*-dithiol donor group leads to the formation of the ligands. Bis(cyclopentadienyl)titanium dichloride reacts selectively at the S-S donor groups of H_3-**1** and H_3-**2** to yield complexes [Cp_2Ti(H-**1**)] and [Cp_2Ti(H-**2**)], respectively. Ligand H_3-**1** reacts with [Ni(OAc)$_2$]·4H_2O to yield the mononuclear complex $(Bu_4N)_2$[Ni(H-**1**)$_2$] or the dinuclear complex $(Bu_4N)_2$[Ni$_2$(**1**)$_2$] depending on the stoichiometric conditions employed. While $(Bu_4N)_2$[Ni(H-**1**)$_2$] possesses a nickel(II) center with an S_4 coordination environment, the double-stranded dinuclear complex $(Bu_4N)_2$[Ni$_2$(**1**)$_2$] contains two {$Ni^{II}S_2NO$} centers and shows an antiparallel orientation of the ligand strands.

Introduction

Metallosupramolecular chemistry allows for the generation of large and sophisticated molecular structures such as cages,[1] grids,[2] catenanes,[3] and cylinders[4] using noncovalent metal–ligand interactions. To gain a deeper understanding of the self-assembly process and self-organization reactions leading to metallosupramolecular architectures, simple molecules were initially studied. Helicates, in turn, became the model compounds as metallosupramolecular analogues to the perfect, natural example, DNA.[5] Various double- and triple-stranded polynuclear helicates using polydentate catecholato,[6] oligopyridine,[7] imine[8] and, more recently, benzene-*o*-dithiolato[9] ligands have been investigated. The use of directional ligands in dinuclear complexes is of particular interest since they can be manipulated to form regioisomeric complexes with a parallel or antiparallel orientation of the ligand strands.[10] However, investigations into complexes with ligands containing two or more different donor units (i.e. specialized directional ligands) are comparatively rare.[11] Albrecht et al. demonstrated in an impressive example that it is possible to influence the regioselectivity in helicates using a ligand which contains two electronically different binding sites.[12] Reaction of a catechol/aminophenol ligand with either titanium(IV) *or* gallium(III) ions gave triple-stranded homodinuclear helicates with an antiparallel orientation of the ligand strands. Contrary to this, reaction of the catechol/aminophenol ligand with a 1:1 mixture of Ti^{IV} *and* Ga^{III} ions leads to a triple-stranded heterobimetallic helicate featuring the parallel orientation of the ligand strands.

We have studied double- and triple-stranded homo- and heterodinuclear complexes built from mixed benzene-*o*-dithiolato/catecholato ligands.[13] These ligands possess two electronically different, but sterically similar binding sites and form homo- and heterobimetallic helical complexes almost exclusively featuring a parallel orientation of the ligand strands. In fact, mixtures of complexes containing the isomers with the parallel and antiparallel orientation of the ligand strands have only been observed twice and the separation of the isomers proved impossible.[13b]

Herein, we present the synthesis of mixed benzene-*o*-dithiol/salicylimine (S-S/N-O) ligands H_3-**1** and H_3-**2**, which possess two electronically and sterically different bidentate binding sites. The coordination chemistry of these ligands towards titanocene dichloride and nickel acetate has been studied. Nickel(II) is known to adopt a square-planar coordination geometry in complexes with benzene-*o*-dithiolato,[14] salicylimine,[15] and (SNO)[16] ligands. We became interested in the selective metalation of the two binding sites in H_3-**1** and H_3-**2** and in the coordination chemistry of these ligands (parallel vs. antiparallel orientation of the ligands strands) in dinuclear double-stranded nickel(II) complexes.

Results and Discussion

The procedure followed for the preparation of ligands H_3-**1** and H_3-**2** is similar to the method developed for the

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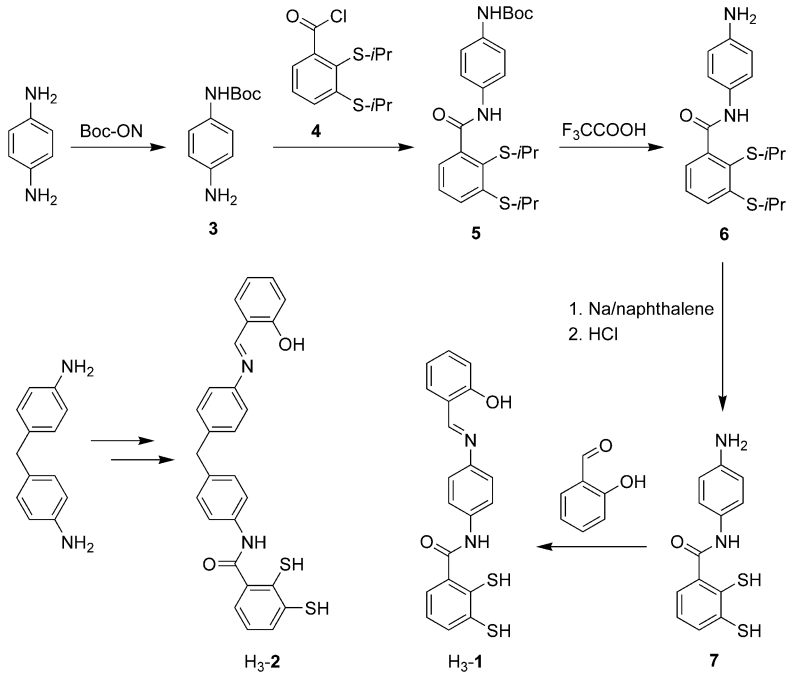
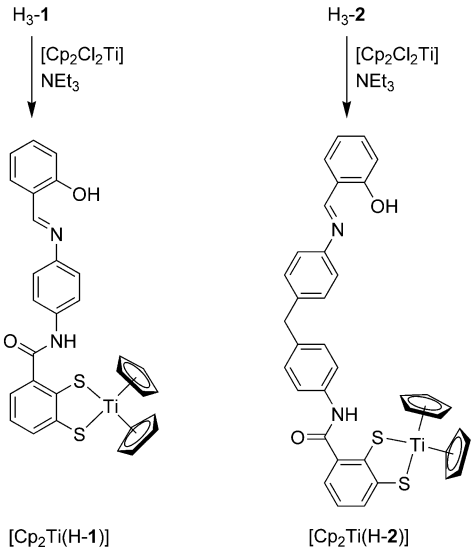


Scheme 1. Preparation of ligands H_3-**1** and H_3-**2**.

synthesis of benzene-*o*-dithiol/catechol ligands.[13a,13b] Scheme 1 shows the preparation of Ligand H_3-**1** in detail. 2,3-Bis(isopropylmercapto)benzoic acid[17] was converted into the acid chloride **4** using oxalyl chloride. Reaction of **4** with the singly protected amine **3**, synthesized from *para*-phenylenediamine and Boc-ON, yields compound **5**. After removal of the Boc group with trifluoroacetic acid, the *S*-isopropyl protection groups are cleaved by reaction with sodium and naphthalene in THF. Treatment with HCl yields the bidentate S-S ligand precursor **7**, which reacts in a Schiff-base condensation with salicylaldehyde to yield H_3-**1**.

In order to prevent reduction of the imine function, it is essential that the reductive cleavage of the S-*i*Pr bonds to give **7** is carried out before the Schiff-base condensation. Ligand H_3-**2** was synthesized using the same procedure, with the only difference being the use of 4,4′-diaminodiphenylmethane in lieu of *para*-phenylenediamine (see Supporting Information).

Following a published procedure, complexes [Cp_2Ti(H-**1**)] and [Cp_2Ti(H-**2**)] were synthesized from stoichiometric amounts of titanocene dichloride and H_3-**1** and H_3-**2**, respectively (Scheme 2).[18] These dark green complexes are stable in air and can be purified by column chromatography (silica gel, dichloromethane/methanol, 20:1, v:v).



Scheme 2. Preparation of complexes [Cp_2Ti(H-**1**)] and [Cp_2Ti(H-**2**)].

Single crystals of [Cp_2Ti(H-**2**)]·EtOH·0.5$CHCl_3$, suitable for an X-ray diffraction analysis, were obtained by layering a chloroform solution of the complex with *n*-pentane. The structure analysis reveals the presence of two essentially identical molecules of [Cp_2Ti(H-**2**)] in the asymmetric unit (Figure 1). Bond lengths and angles in [Cp_2Ti(H-**2**)] resemble those of comparable parameters reported for [Cp_2Ti(bdt)] complexes (bdt^{2-} = benzene-*o*-dithiolato dianion).[18] The five-membered C_2S_2Ti ring is significantly bent along the S-S vector, which is a common feature for [Cp_2Ti(bdt)] and [Ti(bdt)$_3$] complexes[9a,18c,19] but uncommon for bdt^{2-} complexes involving other transition metals.[17a,18b,20] The structure analysis reveals selective binding of the Cp_2Ti fragment to the benzene-*o*-dithiolato donor while the salicylimine donor group remains uncoordinated. This type of discrimination between the potential binding units of an S-S/N-O ligand was initially surprising, since coordination of the hard titanium center to the hard N-O binding would have been expected. Neutralization of the

positive charge at the titanium by the dithiolato donor unit appears as a reasonable explanation for the observed selective binding situation.

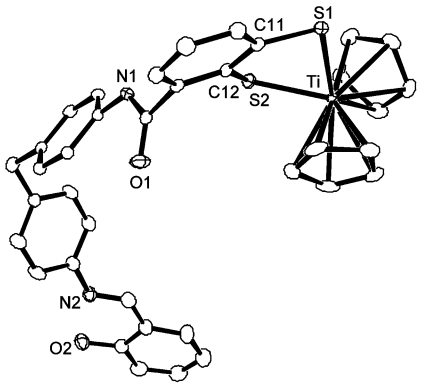
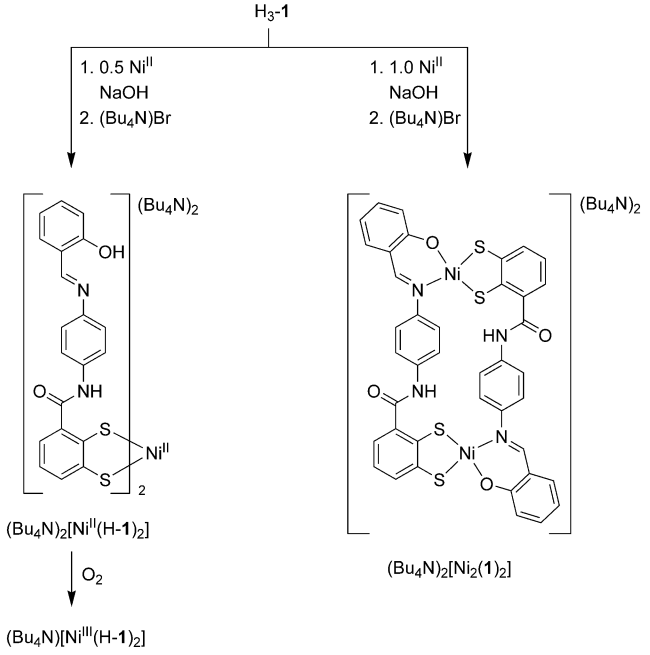


Figure 1. Molecular structure of one of the two molecules of $[Cp_2Ti(H\text{-}\mathbf{2})]$ in the asymmetric unit (hydrogen atoms and solvent molecules have been omitted). Selected bond lengths [Å] and angles [°] for molecule 1 [molecule 2]: Ti–S1 2.4109(12) [2.4074(13)], Ti–S2 2.4194(12) [2.4201(12)], S1–C11 1.757(4) [1.752(4)], S2–C12 1.765(4) [1.761(4)]; S1–Ti–S2 82.05(4) [82.40(4)], Ti–S1–C11 96.63(13) [95.55(14)], Ti–S2–C12 95.37(13) [94.43(13)].

Ligand H_3-**1** is also stepwise metalated by other metal ions. Two equiv. of ligand H_3-**1** react in boiling methanol with one equiv. of nickel acetate in the presence of sodium hydroxide (Scheme 3). The ESI(–) mass spectrum of the brown reaction mixture (Figure 2, **A**) shows the formation of the complex anion $[Ni^{III}(H\text{-}\mathbf{1})_2]^-$ (m/z = 814.0) together with some decomposition products. If exposed to air, the brown color of the solution turned to green within a few minutes. This color change indicates an aerobic oxidation of $[Ni^{II}(H\text{-}\mathbf{1})_2]^{2-}$ to $[Ni^{III}(H\text{-}\mathbf{1})_2]^-$, which is a well known behavior for $\{Ni^{II}S_4\}$ centers.[17a,21] This oxidation process can be followed by time-dependent UV/Vis spectroscopy, wherein the intense band at λ = 464 nm (characteristic for the $\{Ni^{II}S_4\}$ chromophore) disappears within two minutes, while a very intensive absorption at λ = 867 nm and a weak absorption at λ = 352 nm, both characteristic for $\{Ni^{III}S_4\}$ chromophores, appear.[17a,20] Addition of two equiv. of tetrabutylammonium bromide to the brown solution containing $[Ni^{II}(H\text{-}\mathbf{1})_2]^{2-}$ followed by diffusion of diethyl ether into the reaction mixture led to precipitation of brown $(Bu_4N)_2[Ni^{II}(H\text{-}\mathbf{1})_2]$.

A comparison of the IR spectra of ligand H_3-**1** and complex $(Bu_4N)_2[Ni(H\text{-}\mathbf{1})_2]$ supports the exclusive coordination of the benzene-*o*-dithiolate donor groups in $[Ni^{II}(H\text{-}\mathbf{1})_2]^{2-}$. The spectrum of the ligand shows a characteristic S–H vibration at $\tilde{\nu}$ = 2514 cm^{-1}, which is absent in the spectrum of $(Bu_4N)_2[Ni(H\text{-}\mathbf{1})_2]$ indicating coordination of both S-S donor groups. Unfortunately, small quantities of a paramagnetic nickel(III) species, obtained by rapid oxidation of the nickel(II), are present in samples of $(Bu_4N)_2[Ni(H\text{-}\mathbf{1})_2]$ preventing its NMR spectroscopic characterization. Based on ESI MS, UV/Vis, and IR spectra it can be concluded



Scheme 3. Preparation of complexes $(Bu_4N)[Ni(H\text{-}\mathbf{1})_2]$ and $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$.

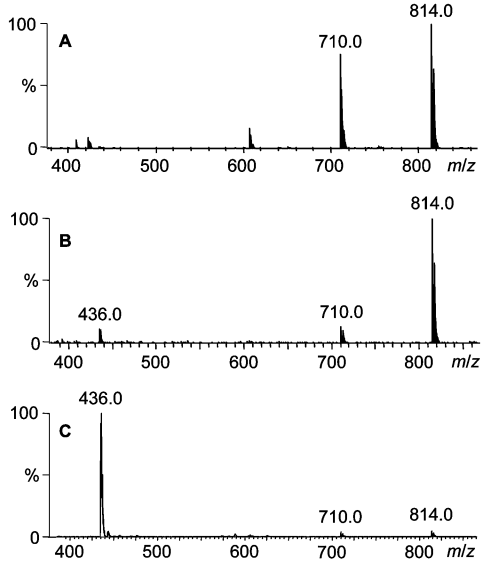


Figure 2. ESI(–) mass spectra of the reaction products obtained in the reaction of ligand H_3-**1** with $[Ni(OAc)_2]$ with different metal/ligand ratios and reaction times (ratio, reaction time, main product): **A**: 1:2, 24 h, $[Ni(H\text{-}\mathbf{1})_2]^-$; **B**: 2:2, 2 h, $[Ni(H\text{-}\mathbf{1})_2]^-$ and $[Ni_2(\mathbf{1})_2]^{2-}$; **C**: 2:2, 24 h, $[Ni_2(\mathbf{1})_2]^{2-}$.

that the nickel atom in $(Bu_4N)_2[Ni(H\text{-}\mathbf{1})_2]$ is coordinated by two benzene-*o*-dithiolato donors, while the salicylimine groups remain uncoordinated.

The reaction of two equiv. of ligand H_3-**1** with two equiv. of nickel(II) ions in methanol, in the presence of sodium hydroxide, initially also leads to a dark brown solution. This solution was heated under reflux for 24 h (Scheme 3). The ESI(–) mass spectrum of the reaction products shows the formation of dianionic double-stranded dinuclear complex

anion $[Ni_2(\mathbf{1})_2]^{2-}$ (Figure 2, **C**). Besides the main product at *m*/*z* = 436.0, traces of the mononuclear complex $[Ni(H\text{-}\mathbf{1})_2]^-$ are also observed (*m*/*z* = 814.0). A comparison of the ESI(–) mass spectra recorded after different reaction times (Figure 2, **B**: 2 h; **C**: 24 h) with the spectrum for $[Ni(H\text{-}\mathbf{1})_2]^-$ (Figure 2, **A**) indicates that the mononuclear complex featuring exclusive coordination of the benzene-*o*-dithiolato binding units appears as a reaction intermediate.

Compound $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ can be isolated in analytically pure form after addition of two equiv. of tetrabutylammonium bromide, followed by gas diffusion of ethyl ether into the crude reaction mixture. The compound crystallized as small reddish-brown needles. The ESI(–) mass spectrum of these needles exhibits exclusively peaks for the dianionic double-stranded dinuclear complex $[Ni_2(\mathbf{1})_2]^{2-}$ at *m*/*z* = 436.0 and for the complex anion with one counterion attached $([(Bu_4N)[Ni_2(\mathbf{1})_2]]^-$ at *m*/*z* = 1114.24 and $[K[Ni_2(\mathbf{1})_2]]^-$ at *m*/*z* = 920.9).

Contrary to the bis(benzene-*o*-dithiolato) complex $(Bu_4N)_2[Ni(H\text{-}\mathbf{1})_2]$, the dinuclear compound $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ is stable in air indicating the absence of $\{Ni(bdt)_2\}$ polyhedra. This assumption is corroborated by the UV/Vis spectrum showing besides the typical π-π* benzene ring absorptions of the ligands at $\lambda \approx 300$ nm two absorptions at λ = 424 and 523 nm. These values are consistent with previously reported data for $\{Ni^{II}S_2NO\}$ centers[16a] and indicate an antiparallel orientation of the ligand strands in anion $[Ni_2(\mathbf{1})_2]^{2-}$.

The ^{1}H NMR spectrum of $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ shows only one set of signals for both ligand strands (Figure 3), indicating that only one of the two possible regioisomers with a parallel or antiparallel orientation of the ligand strands, respectively, is present. Since both a parallel orientation of the ligand strands (C_2-symmetry) and an antiparallel orientation (inversion symmetry) would lead to a highly symmetric complex anion, the NMR spectrum is consistent with both possible orientations of the ligand strands. The resonance for the NH proton (δ = 10.62 ppm) appears at an almost unchanged chemical shift compared to the free ligand H_3-**1** (δ = 10.73 ppm) which was taken as an indication for the presence of only weak intramolecular N–H···S hydrogen bonds. Such hydrogen bonds have been shown to be structure determining in related complexes with catechoylamide ligands[1a,22] but are rarely observed for benzene-*o*-dithiolato complexes.[9,13]

X-ray quality crystals of $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ were obtained by gas diffusion of diethyl ether into a solution of the salt in methanol. The compound crystallizes in the orthorhombic space group *Fdd*2 with *Z* = 8. The complex dianion $[Ni_2(\mathbf{1})_2]^{2-}$, shown in Figure 4, resides on a crystallographic twofold axis which passes through the midpoint of the complex anion. The complex dianion contains two identical *pseudo*-square-planar benzene-*o*-dithiolato/salicylimine nickel(II) complex units, as predicted by UV/Vis spectroscopy. The Ni–S distances [2.156(2) and 2.169(2) Å] are within the typical range for $[Ni^{II}(bdt)_2]$ complexes,[14,17a] while the Ni–O [1.881(4) Å], and Ni–N [1.937(6) Å] bond lengths are comparable to salicylimine nickel(II) complexes.[15] The five-membered C_2S_2Ni and six-membered C_3NONi rings are nearly perfectly planar and coplanar to each other. The amide N–H proton maintains only a weak hydrogen bond to the *o*-sulfur atom of the benzene-*o*-dithiolato unit as predicted by NMR spectroscopy. The weak nature of this interaction is illustrated by the long nitrogen (N1)-sulfur(S2*) distance of 3.04 Å.

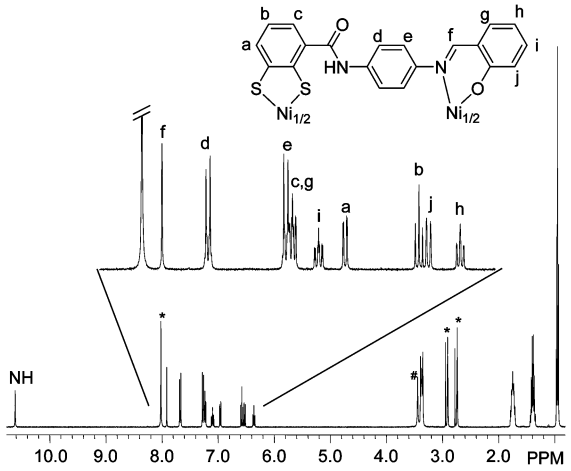


Figure 3. ^{1}H NMR spectrum of complex $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ in $[D_7]$-DMF at room temperature (δ, ppm, * = DMF, # = methanol).

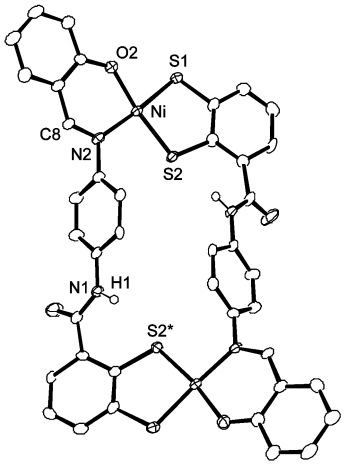


Figure 4. Molecular structure of the $[Ni_2(\mathbf{1})_2]^{2-}$ anion in $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ (the anion resides on a crystallographic twofold axis, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni–S1 2.156(2), Ni–S2 2.169(2), Ni–O2 1.881(4), Ni–N2 1.937(6), C8–N2 1.286(8); S1–Ni–S2 89.31(7), S1–Ni–O2 82.23(15), S1–Ni–N2 176.0(2), S2–Ni–O2 171.54(15), S2–Ni–N2 94.6(2), O2–Ni–N2 93.8(2).

Conclusions

We have prepared new directional ligands with a mixed benzene-*o*-dithiolato/salicylimine (S-S/N-O) donor set. The tetradentate ligands H_3-**1** and H_3-**2** are preferentially metalated by Ti^{IV} and Ni^{II} at the benzene-*o*-dithiolato donor function. This feature can be beneficial in subsequent syn-

theses of heterodinuclear metal complexes. The reactivity of ligand H_3-**1** towards nickel(II) showed that a variation of the metal-to-ligand ratio results in two different coordination motives of the nickel centers. A metal-to-ligand ratio of 1:2 leads to the mononuclear complex $[Ni(H\text{-}\mathbf{1})_2]^{2-}$ with a $\{Ni^{II}(S\text{-}S)_2\}$ coordination polyhedron, while a ratio of 2:2 favours the formation of a double-stranded dinuclear complex with two identical $\{Ni^{II}(S\text{-}S)(N\text{-}O)\}$ coordination polyhedra. Complex anion $[Ni(H\text{-}\mathbf{1})_2]^{2-}$ functions as a reaction intermediate in the formation of the dinuclear complex $[Ni_2(\mathbf{1})_2]^{2-}$. In summary, we have described a new S-S/N-O ligand type which reacts in different stoichiometric amounts with Ni^{II} ions to yield two structurally and electronically different types of metal complexes.

Experimental Section

General: 2,3-Bis(isopropylmercapto)benzoyl chloride **4**[17] and compounds **3**, **5**, and **6** were prepared according to literature procedures.[13b]

4′-[2,3-Bis(mercapto)benzamido]-4-aminobenzene (7): Compound **6** (1.87 g, 5.2 mmol), naphthalene (1.66 g, 13 mmol), and sodium (598 mg, 26 mmol) were suspended in THF (30 mL) and stirred for 12 h at ambient temperature. Subsequently, methanol (15 mL) was added and then all solvents were removed in vacuo. The residue was dissolved in water (20 mL) and the aqueous phase was washed with diethyl ether (3 × 20 mL) and filtered. Addition of hydrochloric acid gave a pale yellow precipitate which was isolated by filtration, washed with water and diethyl ether and dried in vacuo; yield 1.15 g (80.1%). ^{1}H NMR (400 MHz, [D$_7$]DMF, 25 °C): δ = 10.93 (s, 1 H, NH), 8.36 (br. s, 2 H, NH_2), 7.91–7.11 (m, 7 H, Ar-H), 3.80 (br. s, 2 H, SH) ppm. ^{13}C NMR (100 MHz, [D$_7$]DMF, 25 °C): δ = 168.2 (C=O), 138.4, 137.1, 135.5, 132.5, 131.9, 131.6, 126.5, 125.5, 123.1, 121.8 (Ar-C) ppm. $C_{13}H_{12}N_2OS_2$ (276.38): calcd. C 56.49, H 4.38, N 10.14, S 23.20; found C 56.59, H 4.25, N 10.25, S 22.94.

Ligand H_3-1: Compound **7** (1.3 g, 4.7 mmol) was suspended in methanol (10 mL) and salicylaldehyde (0.58 g, 4.7 mmol) in methanol (5 mL) was added. The reaction mixture was stirred for 12 h at ambient temperature. A yellow precipitate formed during this time which was isolated by filtration, washed with methanol and dried in vacuo; yield 1.0 g (55%). ^{1}H NMR (400 MHz, [D$_7$]DMF, 25 °C): δ = 10.73 (s, 1 H, NH), 9.06 (s, 1 H, N=CH), 7.98–6.99 (m, 11 H, Ar-H), 3.55 (br. s, 2 H, SH) ppm. ^{13}C NMR (100 MHz, [D$_7$]-DMF, 25 °C): δ = 166.3 (C=O), 154.65 (N=HC), 140.8, 140.6, 139.9, 130.3, 129.7, 128.5, 128.3, 127.8, 126.1, 124.7, 124.5, 121.8, 121.5, 121.3, 119.7, 115.9 (Ar-C) ppm. IR (KBr): $\tilde{\nu}$ = 3292 (NH), 2514 (SH), 1653 (C=O), 1637 (C=C), 1570 (C=N) cm^{-1}. $C_{20}H_{16}N_2O_2S_2$ (380.48): calcd. C 63.13, H 4.24, N 7.36, S 16.85; found C 63.14, H 4.33, N 7.49, S 16.90.

Ligand H_3-2: Ligand H_3-**2** was synthesized as described for H_3-**1** from *N*-[2,3-bis(mercapto)benzamido]bis(4-aminophenyl) methane (700 mg, 1.9 mmol) and salicylaldehyde (280 mg, 2.3 mmol) in methanol. For the preparation of *N*-[2,3-bis(mercapto)benzamido]-bis(4-aminophenyl) methane and its precursors see Supporting Information; yield 714 mg (80%). ^{1}H NMR (400 MHz, [D$_7$]DMF, 25 °C): δ = 10.48 (s, 1 H, NH), 9.01 (s, 1 H, N=CH), 7.82–6.96 (m, 15 H, Ar-H), 4.76 (br. s, 2 H, SH), 4.03 (s, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, [D$_7$]DMF, 25 °C): δ = 166.0 (C=O), 161.7 (N=CH), 154.6, 146.6, 141.6, 140.8, 138.2, 137.5, 134.0, 133.4, 130.8, 130.5, 129.7, 128.3, 127.8, 126.0, 125.4, 122.1, 121.1, 119.7, 117.3, 115.9 (Ar-C), 41.0 (CH_2) ppm. $C_{27}H_{22}N_2O_2S_2$ (470.11): calcd. C 68.91, H 4.71, N 5.95, S 13.63; found C 68.73, H 5.06, N 5.86, S 13.28.

[Cp_2Ti(H-1)]: Ligand H_3-**1** (100 mg, 0.26 mmol) and bis(cyclopentadienyl)titanium dichloride (70 mg, 0.28 mmol) were suspended in THF (10 mL). After addition of triethylamine (0.3 mL), the mixture was stirred for 12 h at ambient temperature. Subsequently, the solvent was removed in vacuo. The resulting dark green solid was purified by column chromatography (SiO_2, CH_2Cl_2/methanol, 20:1, v:v); yield 61 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.33 (s, 1 H, OH), 9.36 (s, 1 H, NH), 8.65 (s, 1 H, N=CH), 7.87–6.95 (m, 11 H, Ar-H), 6.11 (br. s, 10 H, C_5H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6 (Ar-C-OH), 166.3 (C=O), 159.3 (N=CH), 166.3, 161.1, 152.7, 144.4, 137.4, 135.1, 133.7, 133.0 132.4, 126.7, 124.7, 121.8, 121.0, 119.1, 117.2 (Ar-C), 113.2 (C_5H_5) ppm. $C_{30}H_{24}N_2O_2S_2Ti$ (556.52): calcd. C 64.75, H 4.35, N 5.03, S 11.52; found C 64.48, H 4.16, N 5.26, S 11.46.

[Cp_2Ti(H-2)]: Complex [Cp_2Ti(H-**2**)] was synthesized as described for [Cp_2Ti(H-**1**)] from H_3-**2** (76 mg, 0.16 mmol), [Cp_2TiCl_2] (40 mg, 0.16 mmol) and triethylamine (0.2 mL) in THF; yield 78 mg (75%). Crystals of the solvate [Cp_2Ti(H-**2**)]·EtOH·0.5$CHCl_3$ were obtained at ambient temperature from a chloroform/*n*-pentane solution. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 13.32 (s, 1 H, OH), 9.12 (s, 1 H, NH), 8.62 (s, 1 H, N=CH), 7.84–6.92 (m, 15 H, Ar-H), 6.09 (br. s, 10 H, C_5H_5), 3.99 (s, 2 H, CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 196.7 (Ar-C-OH), 166.3 (C=O), 159.1 (N=CH), 162.0, 161.1, 152.6, 146.5, 140.2, 136.8, 136.5, 135.4, 133.0, 132.2, 129.8, 129.4, 126.4, 124.7, 121.2, 119.8, 119.2, 119.0, 117.2 (Ar-C), 113.2 (C_5H_5), 40.9 (CH_2) ppm. $C_{37}H_{30}N_2O_2S_2Ti$ (646.64): calcd. C 68.72, H 4.68, N 4.33, S 9.92; found C 68.93, H 4.70, N 4.11, S 10.29.

(Bu_4N)$_2$[Ni(H-1)$_2$]: Ligand H_3-**1** (64 mg, 0.17 mmol) and sodium hydroxide (20 mg, 0.5 mmol) were dissolved in methanol (10 mL). After addition of nickel(II) acetate tetrahydrate (23 mg, 0.09 mmol) in methanol (2 mL) the reaction mixture was heated under reflux for 12 h. After cooling to ambient temperature, the mixture was filtered and tetrabutyl ammonium bromide (55 mg, 0.17 mmol) was added to the filtrate. Slow vapour diffusion of diethyl ether into this solution gave a brown precipitate which was collected and dried in vacuo; yield 18 mg (15%). IR (KBr): $\tilde{\nu}$ = 3275 (NH), 2959, 2872 (CH), 1636 (C=O), 1612 (C=C), 1513 (C=N) cm^{-1}. UV/Vis (DMF): λ_{max} (ε) = 313 (28000), 350 (20400) 464 nm (4100 mol^{-1} dm^3 cm^{-1}). MS (ESI, negative ions): *m*/*z* = 814.04 [Ni(H-**1**)$_2$]$^-$, 710.01 [[Ni(H-**1**)$_2$]-C_7H_4O]$^-$. $C_{72}H_{100}N_6NiO_4S_4$ (1300.56): calcd. C 66.49, H 7.75, N 6.46, S 9.86; found C 66.55, H 7.90, N 6.53, S 10.01.

(Bu_4N)$_2$[Ni$_2$(1)$_2$]: Ligand H_3-**1** (31 mg, 0.08 mmol) and sodium hydroxide (10 mg, 0.25 mmol) were dissolved in methanol (10 mL). After addition of nickel acetate tetrahydrate (23 mg, 0.09 mmol) in methanol (2 mL) the reaction mixture was heated under reflux for 12 h. After cooling to ambient temperature, tetrabutyl ammonium bromide (55 mg, 0.18 mmol) was added to the mixture. The mixture was filtered and slow vapour diffusion of diethyl ether into the filtrate gave a red-brown precipitate which was collected and dried in vacuo. X-ray-quality crystals of (Bu_4N)$_2$[Ni_2(**1**)$_2$] were obtained by slow gas diffusion of diethyl ether into a solution of the salt in methanol; yield 11 mg (10%). ^{1}H NMR (400 MHz, [D$_7$]DMF, 25 °C, for assignment of resonances see Figure 3): δ = 10.62 (s, 2 H, NH), 7.92 (s, 2 H, N=CH), 7.67 [d, $^3J_{H,H}$ = 8.4 Hz, 4 H, Ar-H(d)], 7.27 [d, $^3J_{H,H}$ = 8.4 Hz, 4 H, Ar-H(e)], 7.25 [m, 4 H, Ar-H(c, g)], 7.10 [t, $^3J_{H,H}$ = 7.9 Hz, 2 H, Ar-H(i)], 6.96 [d, $^3J_{H,H}$ =

7.5 Hz, 2 H, Ar-H(a)], 6.58 [t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar-H(b)], 6.50 [d, $^3J_{H,H}$ = 7.9 Hz, 2 H, Ar-H(j)], 6.36 [t, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar-H(h)], 3.38 (m, 16 H, NCH_2), 1.75 (m, 16 H, $CH_2CH_2CH_2$), 1.39 (qt, $^3J_{H,H}$ = 7.4 Hz, 16 H, CH_2CH_3), 0.96 (t, $^3J_{H,H}$ = 7.4 Hz, 24 H, CH_3) ppm. ^{13}C NMR (100 MHz, [D$_7$]DMF, 25 °C): δ = 168.1 (C=O), 166.7 (N=CH), 166.9, 165.3, 152.4, 150.1, 146.3, 137.5, 134.6, 134.0, 132.9, 127.9, 124.9, 122.7, 122.2, 121.01, 119.9, 113.6 (Ar-C), 58.9 (NCH_2), 24.2 ($CH_2CH_2CH_2$), 20.2 (CH_2CH_3), 13.8 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3218 (NH), 2958, 2874 (CH), 1684 (C=O), 1654 (C=C), 1609 (C=N) cm^{-1}. UV/Vis (DMF): λ_{max} (ε) = 301 (29000), 424 (6200), 523 nm (1700 mol^{-1} dm^3 cm^{-1}). MS (ESI, negative ions): *m*/*z* = 435.98 $[Ni_2(\mathbf{1})_2]^{2-}$, 920.94 $[K[Ni_2(\mathbf{1})_2]]^-$, 1114.24 $[(Bu_4N)[Ni_2(\mathbf{1})_2]]^-$. $C_{72}H_{98}N_6Ni_2O_4S_4$ (1357.23): calcd. C 63.72, H 7.28, N 6.19, S 9.45; found C 63.88, H 7.39, N 5.91, S 9.24.

X-ray Diffraction Studies: Diffraction data for $[Cp_2Ti(H\text{-}\mathbf{2})]\cdot EtOH\cdot 0.5CHCl_3$ and $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$ were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) for $[Cp_2Ti(H\text{-}\mathbf{2})]\cdot EtOH\cdot 0.5CHCl_3$ or Cu-K_α radiation (λ = 1.54178 Å) for $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$, respectively. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[23] program package. Structure solutions were found with the SHELXS-97[24] package using the heavy-atom method or the direct methods and were refined with SHELXL-97[25] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

CCDC-691379 {for $[Cp_2Ti(H\text{-}\mathbf{2})]\cdot EtOH\cdot 0.5CHCl_3$} and -734840 {for $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./data/request/cif.

Crystal Data for $[Cp_2Ti(H\text{-}2)]\cdot EtOH\cdot 0.5CHCl_3$: $C_{39.5}H_{35.5}N_2Cl_{1.5}O_3S_2Ti$, M = 751.39, μ = 0.510 mm^{-1}, ρ = 1.398 g cm^{-3}, monoclinic, $P2_1/n$, Z = 8, a = 12.1019(4), b = 16.5718(6), c = 35.7715(13) Å, β = 95.6730(10)°, V = 7138.8(4) Å^3, 72140 measured reflections, 17115 unique reflections (R_{int} = 0.0577), R = 0.0754, wR^2 = 0.1940 for 11683 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The asymmetric unit contains two essentially identical molecules of $[Cp_2Ti(H\text{-}\mathbf{1})]$, two molecules of EtOH and one disordered molecule of $CHCl_3$.

Crystal Data for $(Bu_4N)_2[Ni_2(\mathbf{1})_2]$: $C_{72}H_{98}N_6Ni_2O_4S_4$, M = 1357.22, μ = 2.120 mm^{-1}, ρ = 1.251 g cm^{-3}, orthorhombic, $Fdd2$, Z = 8, a = 36.989(2), b = 44.083(3), c = 8.8366(6) Å, V = 14409(2) Å^3, 20469 measured reflections, 6315 unique reflections (R_{int} = 0.1263), R = 0.0773, wR^2 = 0.1536 for 4986 contributing reflections [$I \geq 2\sigma(I)$], refinement against $|F^2|$ with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. The complex anion resides on a crystallographic twofold axis passing through its midpoint. Some residual electron density on and close to the twofold axis was found but could not be refined as solvent molecules (methanol or diethyl ether).

Supporting Information (see also the footnote on the first page of this article): Detailed experimental data for the preparation of H_3-**2**.

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