Dinuclear Complexes with Bis(benzenedithiolate) Ligands

Han Vinh Huynh,[a] Christian Schulze-Isfort,[a] Wolfram W. Seidel,[a] Thomas Lügger,[a] Roland Fröhlich,[b] Olga Kataeva,[b] and F. Ekkehardt Hahn*[a]

Dedicated to Professor Kenneth N. Raymond on the occasion of his 60th birthday

Abstract: As a part of a broader study directed towards helical coordination compounds with benzenedithiolate donors, we have synthesized the bis(benzenedithiol) ligands 1,2-bis(2,3-dimercaptobenzamido)ethane (H_4-**1**) and 1,2-bis(2,3-dimercaptophenyl)ethane (H_4-**2**). Both ligands form dinuclear complexes with Ni^{II}, Ni^{III} and, after air-oxidation, Co^{III} ions under equilibrium conditions. Complexes $(NEt_4)_4[Ni^{II}_2(\mathbf{1})_2]$ (**11b**), $(NEt_4)_2[Ni^{III}_2(\mathbf{1})_2]$ (**13**), and $Na_4[Ni^{II}_2(\mathbf{2})_2]$ (**14**) were characterized by X-ray diffraction. In all complexes, two square-planar $[Ni(S_2C_6H_3R)_2]$ units are linked in a double-stranded fashion by the carbon backbone and they assume a coplanar arrangement in a stairlike manner. Cyclic voltammetric investigations show a strong dependence of the redox potential on the type of the ligand. The substitution of $\mathbf{1}^{4-}$ for $\mathbf{2}^{4-}$ on nickel (−785 mV for **11b** versus −1130 mV for **14**, relative to ferrocene) affects the redox potential to a similar degree as the substitution of nickel for cobalt (−1160 mV for $[Co_2(\mathbf{1})_2]^{2-}/[Co_2(\mathbf{1})_2]^{4-}$, relative to ferrocene). The redox waves display a markedly less reversible behavior for complexes with the shorter bridged ligand $\mathbf{2}^{4-}$ compared to those of $\mathbf{1}^{4-}$.

Keywords: cobalt · cyclic voltammetry · helicates · nickel · S ligands

Introduction

The ability of polydentate ligands to form helical coordination compounds by self-assembly with metal ions is an intriguing field of modern metal-based supramolecular chemistry. The first triple-stranded helical complex $[Fe_2(RA)_3]$ (RA = rhodothurulic acid), was isolated and characterized as early as 1978 by Raymond et al.,[1] almost 10 years before Lehn et al.[2] introduced the term helicate. Although $[Fe_2(RA)_3]$ contained only oxygen donors (three hydroxamate groups for each Fe^{III}), the early helicate chemistry was dominated by nitrogen donor ligands.[3] Later, Raymond et al.,[4] Albrecht and Kotila,[5] and Stack et al.[6] developed triple-stranded helicates based on di(catechol) ligands. Today, a large number of helicates that are based on di(catechol) ligands have been reported[7] and even supramolecular clusters different from helicates can be obtained with such ligands.[8] Even helicates containing binding groups with two different donor atoms (e.g. aminophenoles) have been described;[9] however, surprisingly, no helicates with thiolate donor functions are known so far. This phenomenon can be rationalized in terms of the obstacles encountered during the ligand synthesis, such as the air sensitivity of benzene-1,2-dithiols and the often discouraging search for suitable equilibrium conditions for the complex synthesis.

We have launched a systematic investigation aimed at the incorporation of benzenedithiolate binding units into ligands to result in helicate formation. Our interest was not only triggered by the novelty of such ligands, but also by the remarkable electronic and magnetic properties of benzene-1,2-dithiolate complexes in general. A triple-stranded helicate with nitrogen or oxygen donors, for example Fe_2L_3 where L = bis(catecholate) ligand, usually contains two chiral metal atoms that are coordinated in an octahedral fashion. This does not hold for tris(benzenedithiolate) complexes in which the benzenedithiolate binding units can be coordinated in an octahedral or trigonal-prismatic fashion depending on the metal oxidation state.[10] This unique behavior of benzenedithiolate complexes reveals the intriguing opportunity to develop dinuclear coordination compounds in which the helicity might be switched on or off by electron transfer that causes a change in the coordination geometry at the metal center from achiral D_{3h} to chiral O_h. Similar arguments hold for bis(benzenedithiolate) complexes that can adopt a square-

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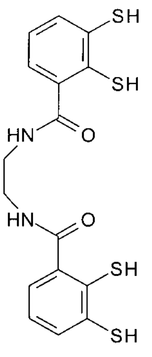
[a] Prof. Dr. F. E. Hahn, Dipl.-Chem. H. V. Huynh,
Dipl.-Chem. C. Schulze-Isfort, Dr. W. W. Seidel, Dr. T. Lügger
Anorganisch-chemisches Institut
Westfälische Wilhelms-Universität Münster
Wilhelm-Klemm-Strasse 8, 48149 Münster (Germany)
Fax: (+49) 251-8333108
E-mail: fehahn@uni-muenster.de

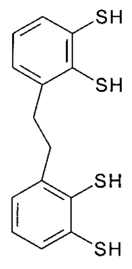
[b] Dr. R. Fröhlich, O. Kataeva
Organisch-chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)

pyramidal or tetrahedral coordination geometry, depending on the oxidation state of the metal atom. This has already been demonstrated with Mn^{III} and Mn^{II} complexes.[11]

We have recently reported the synthesis of chelate complexes with tripodal tris(benzenedithiolate) and bis(benzenedithiolate) ligands based on 2,3-dimercaptobenzoic acid.[12] To obtain dinuclear complexes, these ligands had to be substituted with shorter bridging units between the benzene-1,2-dithiol units to disable chelate formation. This led to the synthesis of the ligands H$_4$-**1** and H$_4$-**2** in which the benzenedithiol units are linked by a short diamide bridge or an alkyl chain, respectively. The difference in the type of bridge causes not only steric differences, but we also hoped it would cause electronic consequences at the donor centers.



H$_4$-**1**



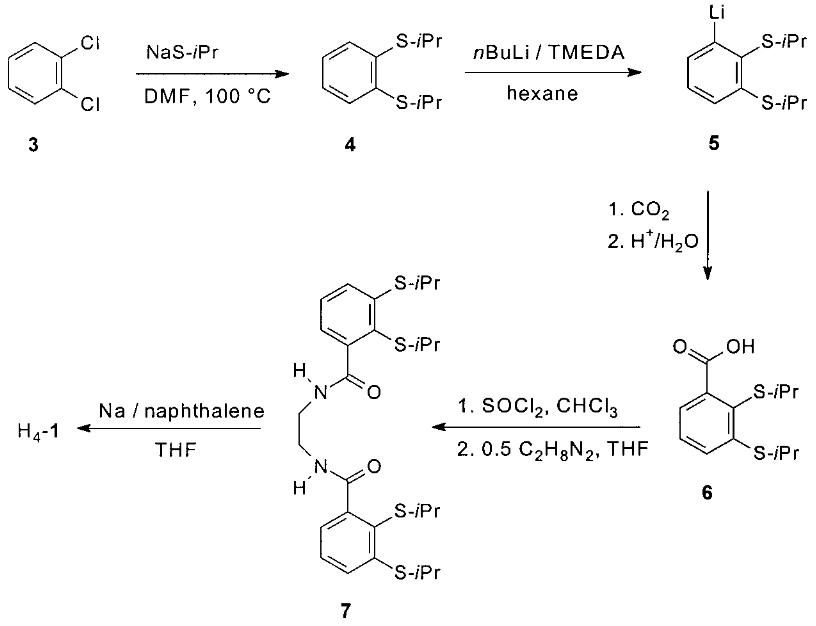
H$_4$-**2**

Herein, we report on the synthesis of the ligands H$_4$-**1** and H$_4$-**2** as well as an improved method for the preparation of 2,3-bis(isopropylmercapto)benzoic acid (**6**).[12a] An initial study of the coordination chemistry of **1**$^{4-}$ and **2**$^{4-}$ with Ni^{II}, Ni^{III}, and Co^{III} ions is presented. Nickel[13] and cobalt[14] are known to adopt a square-planar coordination geometry in bis(benzenedithiolate) complexes in the +2 and +3 oxidation states, respectively. Therefore, no helical triple-stranded complexes M$_2$L$_3$ (L = bis(benzenedithiolate)) were expected. Instead it was assumed, that the ligands **1**$^{4-}$ and **2**$^{4-}$ form double-stranded dinuclear complexes with Ni^{II}, Ni^{III}, and Co^{III}. In addition we wished to study the effect of the different bridging units in **1**$^{4-}$ and **2**$^{4-}$ on the properties of the resulting complexes.

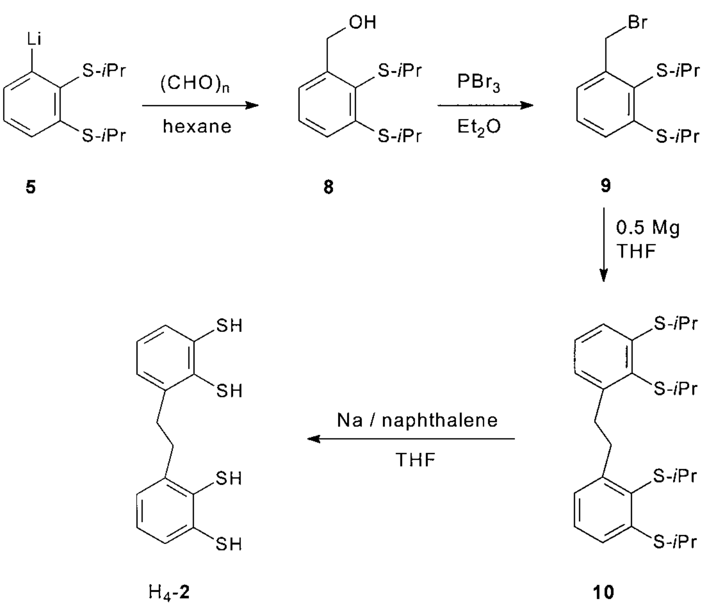
Results and Discussion

Preparation of the ligands: The key step in the synthesis of diamide compounds of type H$_4$-**1** is the preparation of 2,3-bis(isopropylmercapto)benzoic acid (**6**) (Scheme 1). Published syntheses for **6**, which involve multiple lithiation of benzene-1,2-dithiol followed by reaction with CO$_2$ and S-alkylation,[12b, 15] suffer from the use of expensive *n*-butyllithium as well as low yields. In our search for a more efficient route to **6**, we found lithium 2,3-bis(isopropylmercapto)benzene (**5**) to be an excellent precursor for the synthesis of **6**. Compound **5** can be prepared by *ortho*-lithiation of 1,2-di(isopropylmercapto)benzene (**4**)[16] with one equivalent *n*-butyllithium in the presence of TMEDA.[17] Compound **4** was obtained from *o*-dichlorobenzene and sodium isopropylmercaptane in DMF. Reaction of **5** with dry CO$_2$ followed by hydrolysis gave nearly quantitatively the desired product **6**, which can be readily purified by recrystallization from diethyl ether/hexane. The bridging of two molecules **6** by standard methods[12b] with 1,2-ethylenediamine under formation of two stable amide bonds gave 1,2-bis[2,3-di(isopropylmercapto)benzamido]ethane (**7**). Cleavage of the four S–alkyl bonds in **7** with sodium/naphthalene[12b] and hydrolysis finally afforded the bis(benzenedithiol) H$_4$-**1** as an off-white powder.

The poor solubility in most organic solvents of bis(benzenedithiol) ligands with a diamide bridge, such as H$_4$-**1**, is a limiting factor for the study of their coordination chemistry. To overcome this limitation, we designed and synthesized ligand H$_4$-**2**, the first example of an alkyl-bridged bis(benzenedithiol) ligand (Scheme 2). The synthesis of such ligands is similar to the method employed by Albrecht et al. for the preparation of alkyl-bridged bis(catechol) ligands.[5b] The key step in the synthesis of H$_4$-**2** is the reaction of the lithiated species **5** with paraformaldehyde to afford the benzyl alcohol **8**. Treatment of **8** with PBr$_3$ leads to the benzyl bromide **9**, which can undergo a Wurtz-type coupling reaction to give **10**. Finally, formation of H$_4$-**2** is accomplished by reductive cleavage of the four S–isopropyl bonds with sodium/naphthalene as described.[12b] As expected, and in contrast to diamide-bridged H$_4$-**1**, H$_4$-**2** is highly soluble in most common organic solvents, such as tetrahydrofuran, dichloromethane, chloroform, and methanol.



Scheme 1. Synthesis of ligand H$_4$-**1**.

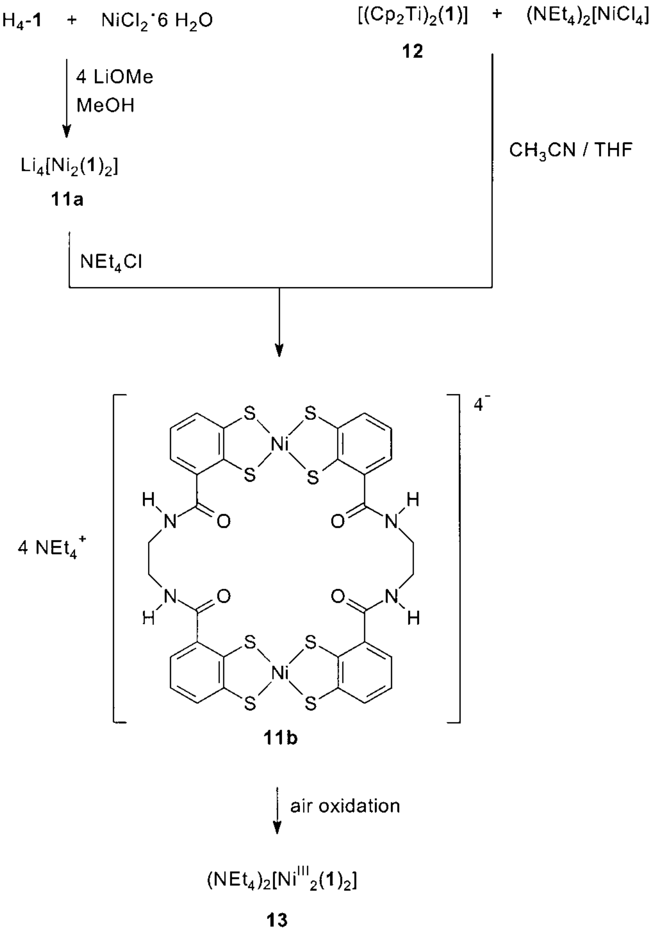


Scheme 2. Synthesis of ligand H_4-**2**.

Preparation of the complexes: Usually, benzenedithiolato complexes are prepared by a simple metathesis reaction of highly reactive alkali metal benzenedithiolates and metal halides by salt elimination. However, the topology of the ligands $\mathbf{1}^{4-}$ and $\mathbf{2}^{4-}$ also allows the formation of oligonuclear species or even complex polymers. Therefore, a fast complex formation reaction under kinetic control is undesirable. An alternative to the use of alkali metal benzenedithiolates turned out to be the ligand-transfer reaction between titanocene benzenedithiolato complexes and tetrachlorometalates.[12b, 18] We have recently described the synthesis of mononuclear bis(benzenedithiolato) cobaltate(III) complexes by means of this reaction.[12b,c] During our efforts to optimize the reaction pathway to dinuclear double-stranded bis(benzenedithiolato) nickelate complexes we found that both the use of alkali benzenedithiolates as well as the ligand-transfer reaction lead to the desired complexes when elevated reaction temperatures and long reaction times are employed.

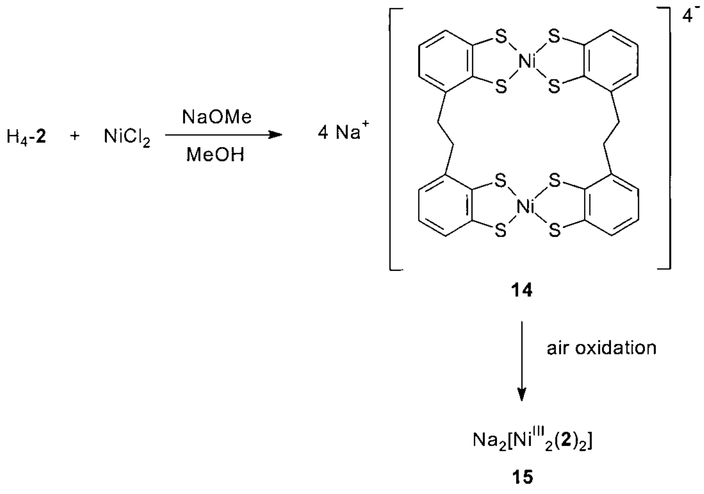
Treatment of $NiCl_2$ or $NiCl_2 \cdot 6H_2O$ with H_4-**1** in a 1:1 stoichiometry in the presence of four equivalents of LiOMe in methanol under reflux conditions afforded a brown solution of $Li_4[Ni_2(\mathbf{1})_2]$ (**11a**). Complex $(NEt_4)_4[Ni_2(\mathbf{1})_2]$ (**11b**) was isolated after metathesis with NEt_4Cl as a brown air-sensitive microcrystalline salt (Scheme 3). Complex **11b** can also be prepared by a ligand-transfer reaction between the neutral dinuclear bis(titanocene) complex $[(Cp_2Ti)_2(\mathbf{1})]$ (**12**) and $(NEt_4)_2[NiCl_4]$ in an acetonitrile/tetrahydrofuran solvent mixture under reflux conditions. The reaction can be monitored visually: the color change of the reaction mixture from dark green (**12**) to dark brown indicated the formation of **11b**.

Aerial oxidation of **11b**, as indicated by a color change from dark brown to intense green, led to the Ni^{III} complex $(NEt_4)_2[Ni_2(\mathbf{1})_2]$ (**13**). Complexes **11b** and **13** are only soluble in *N,N*-dimethylformamide or *N,N*-dimethylacetamide, respectively. Both compounds can be crystallized by vapor diffusion of benzene (**11b**) and diethyl ether (**13**) in a concentrated *N,N*-dimethylformamide solution.



Scheme 3. Preparation of complexes **11a**, **11b**, and **13**.

The dark red nickel(II) complex $Na_4[Ni_2(\mathbf{2})_2]$ (**14**) was prepared from Na_4-**2** and $NiCl_2$ in methanol by salt elimination, as described for **11a** (Scheme 4). Upon mixing of both reagents, a dark red precipitate was observed which dissolved again when the reaction mixture was heated to reflux. This behavior again proves the necessity to ensure equilibrium conditions during complex synthesis. Exposure of a methanol



Scheme 4. Preparation of complexes **14** and **15**.

solution of **14** to air resulted in a color change to green, which indicated the formation of the Ni^{III}/Ni^{III} complex **15**. Complexes with the alkyl-bridged ligand $\mathbf{2}^{4-}$ are more soluble than their analogues with $\mathbf{1}^{4-}$. For example, complex **14** is freely soluble in methanol, *N*,*N*-dimethylformamide, and acetone, and slightly soluble in tetrahydrofuran. Red-brown crystals of **14** were grown from a concentrated acetone solution over a period of three weeks at room temperature. Finally, the intensely blue cobalt complex $(NEt_4)_2[Co^{III}_2(\mathbf{1})_2]$ (**16**) was prepared from **12** and $(NEt_4)_2[CoCl_4]$ in an acetonitrile/THF solution followed by aerial oxidation.

Crystal structures: Complex **11b** crystallized from a DMF/benzene solution as solvate $\mathbf{11b}\cdot C_6H_6\cdot HC(O)N(CH_3)_2$. Complex **13** crystallized as a diethyl ether solvate. However, the NEt_4^+ ions as well the diethyl ether solvent molecules are highly disordered in crystals of **13**. The disorder of the solvent molecules could not be resolved. The diffraction data were therefore refined against a model without solvent molecules that accepted poor *R* indices. The diffraction data for **13** and the derived molecular structure can therefore only be used to establish the identity of the molecule and the overall geometry (see the Experimental Section, crystal structure determination). Crystals of **14** were obtained as an acetone/water solvate $\mathbf{14}\cdot 4\,CH_3C(O)CH_3\cdot 3\,H_2O$. Figure 1 shows the molecular structures of the nickelate anions with the diamide-bridged ligand $\mathbf{1}^{4-}$ (**11b** and **13**). The anion of compound **14** and the stairlike arrangement of the NiS_4 planes in this anion are depicted in Figure 2.

The structure analyses of all three complexes revealed discrete dinuclear bis(benzenedithiolato) nickelate complex anions along with NEt_4^+ ions for **11b** and **13** and Na^+ ions for **14**. Each complex anion contains two square-planar $[Ni(S_2C_6H_3R)_2]$ units with the nickel centers coordinated by two benzenedithiolate units in a square-planar fashion. The structural parameters of the $[Ni(S_2C_6H_3R)_2]$ moieties are unexceptional. The average Ni–S bond lengths in the nickelate(II) complexes **11b** (2.166 Å) and **14** (2.175 Å) are slightly longer than those in the oxidized nickelate(III) complex **13** (2.152 Å) and are in good agreement with the values for the recently reported complexes $[Ni(S_2C_6H_2tBu_2)_2]^{-2/-1}$.[19]

The amide N–H group in catecholamide complexes is normally involved in a hydrogen bond to the *o*-oxygen atom of the catechol.[4, 6] A similar behavior was observed in the anion of **11b** in which all amide N–H groups point to the *o*-sulfur atom of the benzenedithiolate. However, only two (O1 ··· S2, O1* ··· S2*) of these hydrogen bonds was observed in the anion of **13**. In any case, the N–H ··· S hydrogen bonds are weak and packing effects in the crystal structure might be more important for the conformation of the ligand than the formation of hydrogen bonds.

We were particularly interested to find out whether the dinuclear anions in **11b**, **13**, and **14** adopt a double-stranded helical molecular structure. Such a double-stranded helicate would result if the two planar NiS_4 units in each nickelate anion were not arranged in a coplanar fashion. The structure analyses, however, showed a stairlike arrangement of the NiS_4 planes in all three complexes. This is illustrated in Figure 2 for complex **14**. It can be seen that the two $[Ni(S_2C_6H_3R)_2]$ entities are arranged in a stairlike manner and with exactly coplanar NiS_4 planes. The coplanarity of the NiS_4 planes in the anion of **14** in the solid state is enforced by a crystallographic inversion center in the center of the complex anion.

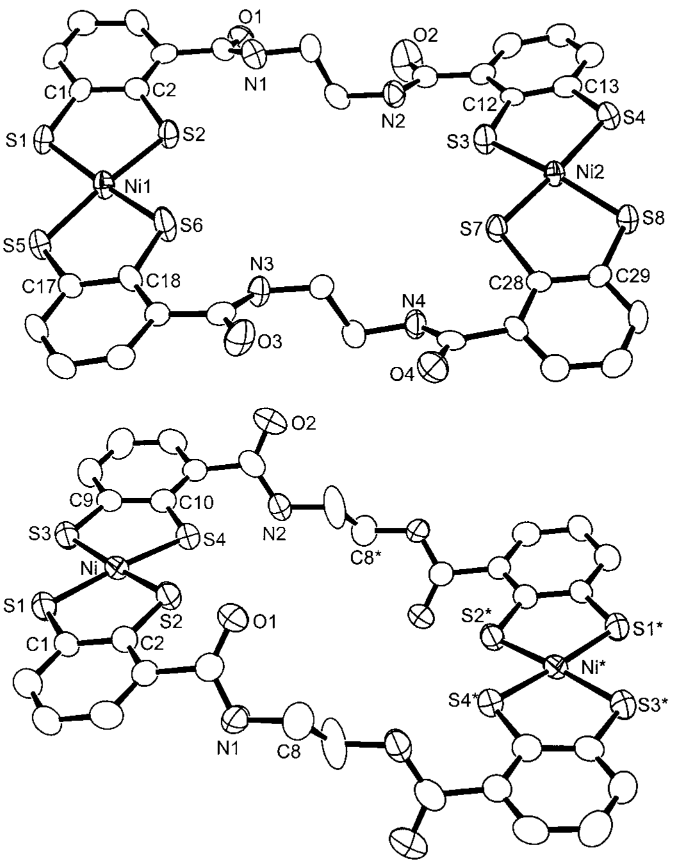


Figure 1. Molecular structures of the nickelate anions in complexes **11b** (top) and **13** (bottom) with the crystallographic numbering scheme. Hydrogen atoms, solvent molecules, and cations have been omitted. Starred atoms in the anion of **13** are related to their corresponding atom by a crystallographic inversion center. Selected bond lengths [Å] and angles [°]: **11b** Ni1–S1 2.167(2), Ni1–S2 2.161(2), Ni1–S5 2.170(2), Ni1–S6 2.161(2), Ni2–S3 2.162(2), Ni2–S4 2.171(2), Ni2–S7 2.171(2), Ni2–S8 2.167(2), S1–C1 1.768(8), S2–C2 1.743(8), S3–C12 1.767(7), S4–C13 1.766(8), S5–C17 1.742(7), S6–C18 1.753(8), S7–C28 1.765(7), S8–C29 1.749(8); S1-Ni1-S2 91.31(8), S1-Ni1-S5 90.45(8), S1-Ni1-S6 172.34(11), S2-Ni1-S5 174.10(9), S2-Ni1-S6 88.88(8), S5-Ni1-S6 90.13(8), S3-Ni2-S4 89.86(8), S3-Ni2-S7 89.49(8), S3-Ni2-S8 171.44(10), S4-Ni2-S7 174.84(9), S4-Ni2-S8 90.74(8), S7-Ni2-S8 90.67(8), C1-S1-Ni1 105.2(3), C2-S2-Ni1 106.3(3), C12-S3-Ni2 106.8(3), C13-S4-Ni2 105.5(3), C17-S5-Ni1 105.3(3), C18-S6-Ni1 108.4(3), C28-S7-Ni2 106.9(2), C29-S8-Ni2 105.3(3); **13**: Ni–S1 2.140(3), Ni–S2 2.155(3), Ni–S3 2.151(3), Ni–S4 2.162(3), S1–C1 1.730(9), S2–C2 1.742(9), S3–C9 1.736(10), S4–C10 1.756(10); S1-Ni-S3 88.52(10), S1-Ni-S2 91.51(10), S1-Ni-S4 175.24(12), S2-Ni-S3 174.84(12), S2-Ni-S4 89.00(10), S3-Ni-S4 91.39(10), C1-S1-Ni 105.1(3), C2-S2-Ni 105.5(3), C9-S3-Ni 105.3(4), C10-S4-Ni 105.4(3).

The distance between the two NiS_4 units in the anions of **11b** and **13** is longer than in **14** owing to the longer ethylenediamide bridges. In addition, the rigid amide functions decrease the flexibility of the ligand. However, these features were insufficient for a distortion of the NiS_4 planes away from coplanarity. Thus, both **11b** and **13** exhibit a stair-type structure similar to **14**. The distance between the two nickel atoms in **14** amounts to 6.72 Å compared to 10.89 Å for **11b** and 10.96 Å for **13**.

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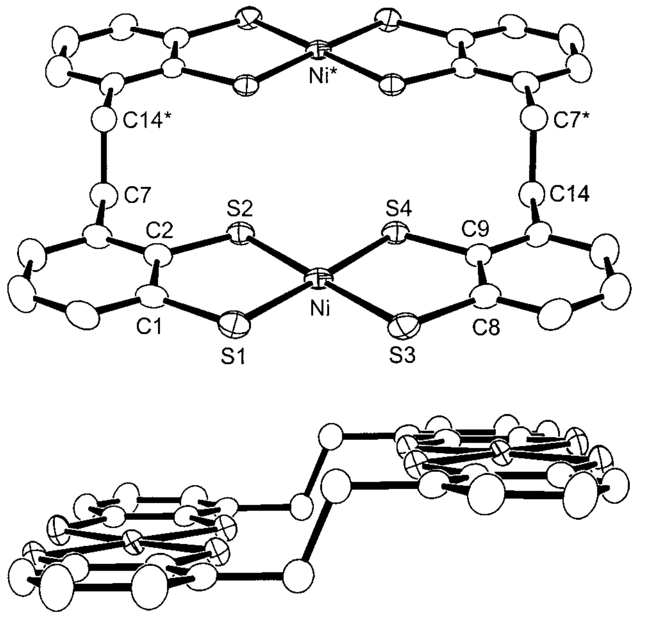

Figure 2. Molecular structure of the nickelate anion in complex **14** (top) and of the stair-type conformation of the nickelate anion (bottom) with the crystallographic numbering scheme. Hydrogen atoms, solvent molecules, and cations have been omitted. Starred atoms are related to their corresponding atom by a crystallographic inversion center. Selected bond lengths [Å] and angels [°]: Ni–S1 2.1712(12), Ni–S2 2.1825(11), Ni–S3 2.1752(12), Ni–S4 2.1727(12), S1–C1 1.766(4), S2–C2 1.756(4), S3–C8 1.768(4), S4–C9 1.757(4); S1-Ni-S2 90.77(4), S1-Ni-S3 90.25(4), S1-Ni-S4 178.03(5), S2-Ni-S3 178.96(5), S2-Ni-S4 87.92(4), S3-Ni-S4 91.06(4), C1-S1-Ni 105.94(14), C2-S2-Ni 105.92(14), C8-S3-Ni 105.41(14), C9-S4-Ni 105.97(14).

The deep blue crystals of **16** were also investigated by X-ray diffraction. The diffraction data obtained were insufficient for a satisfactory refinement of the structural parameters since the majority of the diffraction data were of very low intensity. However, the data were sufficient to show that complex **16** has a molecular structure similar to the nickel complexes **11**, **13**, and **14**. Complex **16** contains two slightly distorted square-planar [$Co^{III}S_4$] units, which are bridged in a double-stranded fashion. This coordination geometry is typical for Co^{III} benzenedithiolates and has also been reported for the mononuclear Co^{III} complex with the ligand 1,7-bis(dimercaptobenzamido)heptane.[12c]

Even dinuclear bis(benzenedithiolate) complexes with square-planar coordination geometry are able to form helical structures. For such a helicity in a dinuclear complex, it would be required that the MS_4 planes are arranged in a non-coplanar fashion and are twisted around the metal–metal vector. While no such helicity was found for double-stranded dinuclear nickelate anions with bis(benzenedithiolate) ligands, complexes **11b**, **13**, and **14** are still the first examples of dinuclear bis(benzenedithiolato) complexes in which the two tetracoordinated metals are linked in a double-stranded fashion by a carbon backbone.

Electronic properties of the complexes: Cyclic voltammetric and UV/Vis studies were carried out to investigate how the bridging itself and how the type of bridge in the ligands influences the electronic properties of the metal centers. Figure 3 depicts the cyclic voltammograms (CV) for the $[Ni_2(\mathbf{1})_2]^{2-}/[Ni_2(\mathbf{1})_2]^{4-}$ and $[Ni_2(\mathbf{2})_2]^{2-}/[Ni_2(\mathbf{2})_2]^{4-}$ couples in *N*,*N*-dimethylformamide. Both species show quasi-reversible two-electron transfer waves. The anodic peak potentials versus $[Cp_2Fe]^0/[Cp_2Fe]^+$ were recorded at −785 mV and −1130 mV, respectively. The difference correlates well with the electronic structure of the bridging unit. Ligand $\mathbf{2}^{4-}$, which contains an electron-donating alkyl bridge, creates a more electron-rich environment than $\mathbf{1}^{4-}$, which has an electron-withdrawing diamide bridge. Thus, complexes with $\mathbf{2}^{4-}$ show a more negative reduction potential.

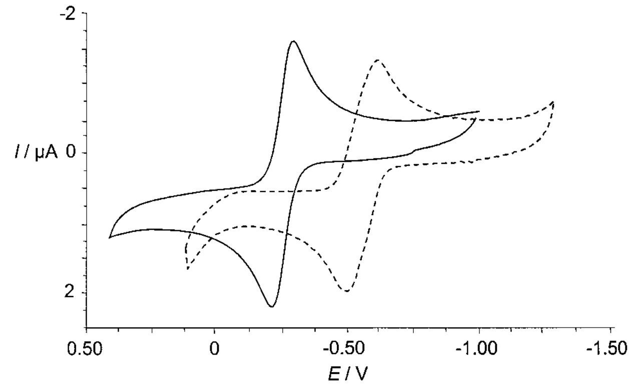

Figure 3. Cyclic voltammograms of **11b** (——) and **14** (- - - -) in DMF.

The substitution of a diamide bridge for an alkyl bridge in the nickelate complex anions leads to a potential shift of approximately −350 mV. The anodic peak potential of the cobalt complex $[Co_2(\mathbf{1})_2]^{2-}/[Co_2(\mathbf{1})_2]^{4-}$ was found at −1160 mV. The change of the metal center in isostructural complexes from nickel to cobalt again leads to a potential shift of −375 mV. Thus, the change from the diamide-linked ligand $\mathbf{1}^{4-}$ to the alkyl linked ligand $\mathbf{2}^{4-}$ affects the Ni^{II}/Ni^{III} potential in a comparable way to the substitution of the metal center from nickel to cobalt in complexes of $\mathbf{1}^{4-}$. These results corroborate the proposal[20] that the SOMO in bis(enedithiolate) complexes carries both metal and ligand character. The Ni^{III}/Ni^{IV} redox couple, reported by Sellmann et al.,[19] was not observed. The ligands $\mathbf{1}^{4-}$ and $\mathbf{2}^{4-}$ generate a much less electron-rich environment than the alkyl-substituted benzenedithiolates used by Sellmann. The oxidation to Ni^{IV} was expected at potentials $\approx +1.0$ V (vs. NHE). However, no reversible redox reactions were observed in this region. We assume that ligand oxidation occurs at potentials above 0.8 V (vs. NHE).

The fact that each species exhibits only one redox wave leads to the assumption that no strong intramolecular interaction of the nickel centers exist in the dinuclear complexes. Consequently, no mixed-valence species were observed. However, a thorough analysis of the cyclic voltammograms discloses slight differences between the couple **11b**/**13** with the longer diamide bridge and the couple **14**/**15** with the shorter ethylene bridge. The difference of the peak potentials, ΔE, is close to ideal reversibility for **11b**/**13** (70 mV). The nickel centers behave as independent mononuclear complexes. In contrast, ΔE for **14**/**15** amounts to 162 mV, which might indicate a slight nickel–nickel interaction in complexes **14** and **15**.

The UV/Vis spectra of the nickel(II/III) complexes with ligand $\mathbf{1}^{4-}$ and $\mathbf{2}^{4-}$ data are depicted in Figure 4. The spectra of the Ni^{II} complexes **11b** and **14** are similar to each other and show the typical $\pi-\pi^*$ benzene ring absorptions of the ligand at ≈300 nm. Both nickel(II) complexes also show intense bands at $\lambda = 465$ nm (**11b**) and 385 nm (**14**). The spectra of the oxidized nickel complexes **13** and **15** are also very similar to each other and show, in addition to $\pi-\pi^*$ benzene ring absorptions ≈300 nm, an additional very intense band at $\lambda =$ 860 nm for **13** and 875 nm for **15**, respectively. This absorption is typical for bis(benzenedithiolate) complexes in their oxidized form. However, its assignment is discussed controversially.[19, 21] The smaller energy gap of **15** compared to that of **13** for this transition is interestingly correlated with the shift to a more negative redox potential from **11b**/**13** to **14**/**15**.

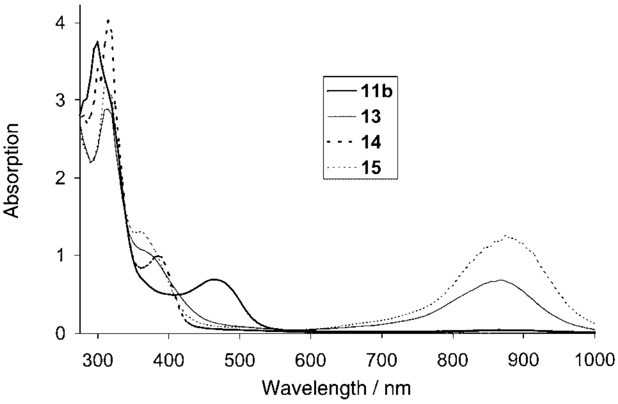

Figure 4. UV/Vis spectra of complexes **11b**, **13**, **14**, and **15** in DMF.

The UV/Vis data for complex **16** are typical for square-planar Co(benzenedithiolate) complexes. Spectra of similar complexes have been reported.[12c, 22]

Experimental Section

Materials and methods: If not stated otherwise, all manipulations were performed in an atmosphere of dry argon by means of standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was purified by vacuum distillation from Na/benzophenone. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 NMR spectrometer. Elemental analyses (C,H,N,S) were performed at the Westfälische Wilhelms-Universität Münster on a Vario EL III CHNS elemental analyzer. Mass spectra were obtained with a Varian MAT212 (EI), Micromass Quattro LC-Z (ESI), and DANI 8521/Finnigan MAT IDT800 (GC-MS) spectrometers. IR spectra were recorded on a Bruker Vektor22 spectrometer. UV/Vis spectra were measured on a Varian Cary 50 spectrometer. Cyclic voltammetric data were acquired on a ECO/Metrohm PGSTAT30 potentiometer with a platinum working electrode, an Ag/AgCl double-junction electrode (3 M KCl solution) as the reference electrode, and NBu_4BF_4 as the supporting electrolyte. The complex salts $(NEt_4)_2[NiCl_4]$[23] and $(NEt_4)_2[CoCl_4]$[24] were prepared as published.

1,2-Bis(isopropylmercapto)benzene (4): This compound was prepared similarly to a previously reported method.[16] 1,2-Dichlorobenzene (10.72 g, 8 mL, 71.00 mmol) was added dropwise to a suspension of sodium isopropylmercaptane (35 g, 356 mmol) in *N,N*-dimethylformamide (200 mL). The mixture was stirred for three days at 100 °C and was then allowed to cool to ambient temperature. It was then poured into water (500 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Evaporation of the solvent and vacuum distillation yielded **4** as a colorless oil (15.27 g, 67.45 mmol, 95% based on 1,2-dichlorobenzene). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.33$ (dd, 2H; Ar–H), 7.14 (dd, 2H; Ar–H), 3.48 (m, $^3J = 6.4$ Hz, 2H; SCH), 1.33 (d, $^3J = 6.4$ Hz, 12H; CH_3); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 137.5$, 130.6, 126.3 (Ar–C), 36.8 (SCH), 22.8 (CH_3) cm^{-1}; MS (70 eV, EI): *m/z* (%): 226 (60) $[M]^+$, 184 (25) $[M - C_3H_6]^+$, 142 (100) $[M - 2C_3H_7]^+$, 108 (10) $[M - 2C_3H_7 - H_2S]^+$, 97 (16) $[C_5H_5S]^+$, 78 (46) $[C_6H_6]^+$, 41 (81) $[C_3H_5]^+$; elemental analysis calcd (%) for $C_{12}H_{18}S_2$ (226.39): C 63.66, H 8.01, S 28.32; found: C 63.92, H 7.91, S 28.26.

Lithium 2,3-bis(isopropylmercapto)benzene (5): A sample of *n*-butyllithium (8.8 mL of a 2.5 M solution in hexane, 22 mmol) was added dropwise to a solution of TMEDA (3.3 mL, 22 mmol) and 1,2-bis(isopropylmercapto)benzene (**4**) (5.0 g, 22 mmol) in hexane (200 mL) at 0 °C. After 30 min, the ice bath was removed and the stirring was continued at ambient temperature for 3 h to result in the formation of an off-white slurry. The lithium salt was used directly without further purification for the synthesis of **6**.

2,3-Bis(isopropylmercapto)benzoic acid (6): Dry CO_2 was bubbled through a slurry of **5** (22 mmol) in hexane at 0 °C for 2 h. After evaporation of the solvent, the residue was dissolved in water and acidified with hydrochloric acid (37%) to pH 2. The aqueous solution was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$. Volatiles were removed in vacuo to afford a yellow solid. The product was recrystallized from diethyl ether/hexane to yield an off-white powder (5.65 g, 20.90 mmol, 95% based on **4**). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 12.24$ (brs, 1H; CO_2H), 7.66 (dd, $^3J = 3.6$ Hz, $^3J = 2.4$ Hz, 1H; Ar–H), 7.33–7.43 (m, 2H; Ar–H), 3.54 (m, 2H; SCH), 1.38 (d, $^3J = 6.6$ Hz, 6H; CH_3), 1.27 (d, $^3J = 6.6$ Hz, 6H; CH_3); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 171.3$ (CO_2H), 146.1, 137.8, 129.9, 129.4, 128.8, 126.1 (Ar–C), 40.4 (SCH), 36.1 (SCH), 22.8 (CH_3), 22.4 (CH_3); IR (KBr pellet): $\tilde{\nu} = 2658$, 2561 (br, O–H), 1701 (s, C=O) cm^{-1}; MS (70 eV, EI): *m/z* (%): 270 (100) $[M]^+$, 228 (9) $[M - C_3H_6]^+$, 209 (21) $[M - H_2O - C_3H_7]^+$; elemental analysis calcd (%) for $C_{13}H_{18}O_2S_2$ (270.40): C 57.74, H 6.71, S 23.71; found: C 58.00, H 6.73, S 23.24.

1,2-Bis[2,3-di(isopropylmercapto)benzamido]ethane (7): The preparation of this compound by bridging of two molecules of **6** was carried out as previously described[12] from **6** (1.0 g, 3.70 mmol) and 1,2-ethylenediamine (0.106 g, 1.77 mmol). The product was isolated as a white powder (887 mg, 1.57 mmol, 85% based on 1,2-ethylenediamine). ^1H NMR ([D$_6$]DMSO, 200 MHz, 25 °C): $\delta = 8.21$ (brs, 2H; CONH), 7.36 (d, 4H; Ar–H), 7.10 (m, 2H; Ar–H), 3.60 (m, $^3J = 6.3$ Hz, 2H; SCH), 3.38 (m, $^3J = 6.5$ Hz, 2H; SCH), 3.34 (s, 4H; CH_2), 1.30 (d, $^3J = 6.5$ Hz, 12H; $CH(CH_3)_2$), 1.11 (d, $^3J = 6.3$ Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR ([D$_6$]DMSO, 50.32 MHz, 25 °C): $\delta =$ 168.2 (CONH), 145.5, 144.6, 128.8, 127.8, 126.4, 123.2 (Ar–C), 34.7 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$), 22.3 ($CH(CH_3)_2$), one of the CH(CH3)$_2$ signals and the CH_2 signal are hidden by the solvent peaks; IR (KBr pellet): $\tilde{\nu} = 3355$, 3257 (s, N–H), 2960, 2923, 2863 (m, SC–H), 1677 (s, C=O), 1550 (s, N–H), 1638, 1571, 1519 (m, Ar–C=C), 1442 (m, CH_2) cm^{-1}; MS (70 eV, EI): *m/z* (%): 564 (46) $[M]^+$, 521 (100) $[M - i\text{Pr}]^+$, 253 (21), 211 (29), 43 (3); elemental analysis calcd (%) for $C_{28}H_{40}N_2O_2S_4$ (564.87): C 59.54, H 7.14, N 4.96, S 22.70; found: C 59.35, H 7.00, N 4.81, S 22.73.

1,2-Bis(2,3-dimercaptobenzamido)ethane (H$_4$-1): Compound **7** (1.094 g, 1.94 mmol) and naphthalene (1.242 g, 9.70 mmol) were dissolved in tetrahydrofuran (60 mL) and pieces of sodium (450 mg, 19.57 mmol) were added. The mixture was stirred for 12 h at ambient temperature and then methanol (10 mL) was added dropwise. After 10 min, the solvent was removed in vacuo, the residue was dissolved in degassed water (20 mL), and the mixture was filtered. The aqueous filtrate was washed with diethyl ether (3 × 10 mL) and acidified with hydrochloric acid (37%) to afford a white solid. The precipitate was filtered off and washed with water (2 × 20 mL) and diethyl ether (2 × 10 mL). Drying in vacuo yielded H$_4$-**1** as an off-white powder (462 mg, 1.16 mmol, 60% based on **7**). ^1H NMR ([D$_7$]DMF, 200 MHz, 25 °C): $\delta = 8.00$ (brs, 2H; CONH), 6.83 (dd, 2H; Ar–H), 6.71 (dd, 2H; Ar–H), 6.32 (t, 2H; Ar–H), 5.17 (brs, 4H; SH), 2.87 (m, 4H; CH_2); ^{13}C NMR ([D$_7$]DMF, 50.32 MHz, 25 °C): $\delta = 170.0$ (CONH), 135.1, 134.0, 132.0, 126.3, 125.4 (Ar–C), 40.0 (CH_2); IR (KBr pellet): $\tilde{\nu} =$ 3285 (s, N–H), 3057, 2945 (w, Ar–H), 2528 (m, S–H), 1633 (s, C=O), 1572 (s, N–H), 1536 (s, Ar–C=C), 1442 (m, CH_2) cm^{-1}; MS (70 eV, EI): *m/z* (%): 396 (31) $[M]^+$, 364 (3) $[M - SH]^+$, 228 (100), 199 (45), 168 (87), 78 (9), 34 (87); elemental analysis calcd (%) for $C_{16}H_{16}N_2O_2S_4$ (396.55): C 48.46, H 4.07, N 7.06, S 32.34; found: C 48.43, H 4.37, N 6.80, S 31.96.

2,3-Di(isopropylmercapto)benzyl alcohol (8): Dry paraformaldehyde (663 mg, 22.1 mmol) was added slowly to an off-white slurry of **5** (22 mmol) in hexane. The mixture was stirred for two days and carefully quenched with water (30 mL) at 0 °C. After acidification with hydrochloric acid (37 %), the aqueous layer was separated and extracted with diethyl ether (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, and after removal of the solvent and column chromatography (SiO_2, Et_2O/petrol ether, 1:3), **8** was obtained as a colorless oil (2.82 g, 11 mmol, 50 % based on **4**). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.17-7.28$ (m, 3H; Ar–H), 4.83 (s, 2H; CH_2), 3.50 (m, 2H; SCH), 2.92 (s, 1H; OH), 1.37 (d, $^3J = 7.2$ Hz, 6H; CH_3), 1.22 (d, $^3J = 7.2$ Hz, 6H; CH_3); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 146.2$, 144.9, 130.4, 129.9, 125.8, 124.4 (Ar–C), 64.3 (CH_2), 38.9 (SCH), 35.8 (SCH), 23.0 (CH_3), 22.6 (CH_3); IR (KBr pellet): $\tilde{\nu} = 3606$, 3473 (s, O–H), 3048 (w, Ar–H), 2965, 2927, 2867 (m, SC–H), 1560 (w, Ar–C=C), 782 (m, Ar–H) cm^{-1}; MS (70 eV, EI): m/z (%): 256 (81) $[M]^+$, 239 (47) $[M - OH]^+$, 213 (27) $[M - C_3H_7]^+$, 181 (52) $[M - SC_3H_7]^+$, 153 (100) $[M - SC_3H_7 - CO]^+$; elemental analysis calcd (%) for $C_{13}H_{20}OS_2$ (256.42): C 60.89, H 7.86, S 25.01; found: C 60.47, H 7.86, S 24.66.

2,3-Di(isopropylmercapto)benzyl bromide (9): PBr_3 (0.66 g, 2.44 mmol, 230 µL) was added dropwise to a solution of **8** (1.242 g, 4.84 mmol) in diethyl ether (10 mL) at 0 °C. The solution was stirred for 15 min at ambient temperature and methanol (700 µL) was added. The mixture was diluted with diethyl ether (60 mL) and water (50 mL). The organic layer was separated, washed with aqueous $NaHCO_3$ (5 % solution), saturated aqueous NaCl, and dried over $MgSO_4$. After removal of the solvent, **9** was obtained as a pale yellow oil (1.3 g, 4.07 mmol, 84 %). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.15-7.28$ (m, 3H; Ar–H), 4.87 (s, 2H; CH_2), 3.52 (m, 2H; SCH), 1.38 (d, $^3J = 6.4$ Hz, 6H; CH_3), 1.24 (d, $^3J = 7.0$ Hz, 6H; CH_3); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 145.7$, 143.1, 131.8, 129.0, 126.8, 126.3 (Ar–C), 38.8 (SCH), 35.8 (SCH), 33.0 (CH_2), 23.1 (CH_3), 22.6 (CH_3); IR (KBr pellet): $\tilde{\nu} = 3050$ (w, Ar–H), 2967, 2927, 2867 (m, SC–H), 1559 (w, Ar–C=C), 594 (m, Ar–H) cm^{-1}; MS (70 eV, EI): m/z (%): (42) $[M]^+$, 239 (7) $[M - Br]^+$, 197 (36) $[M - Br - C_3H_6]^+$, 153 (73) $[M - Br - 2C_3H_7]^+$, 91 (45) $[C_7H_7]^+$, 41 (100); elemental analysis calcd (%) for $C_{13}H_{19}BrS_2$ (319.31): C 48.90, H 6.00, S 20.08; found: C 48.84, H 5.93, S 19.93.

1,2-Bis[2,3-di(isopropylmercapto)phenyl]ethane (10): A solution of **9** (1.2 g, 3.8 mmol) in tetrahydrofuran (5 mL) was added to magnesium (46 mg, 1.9 mmol). The mixture was stirred for 30 min at ambient temperature and then heated to reflux until almost all of the magnesium had dissolved (≈2 h). Volatiles were removed in vacuo and the residue was redissolved in dichloromethane (30 mL). The solution was washed with saturated aqueous NaCl and dried over $MgSO_4$. Removal of the solvent and column chromatography (SiO_2, Et_2O/petroleum ether 1:2) gave **10** as an off-white solid (790 mg, 1.65 mmol, 87 %). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.07-7.21$ (m, 3H; Ar–H), 3.47 (m, 4H; SCH), 3.16 (s, 4H; CH_2), 1.39 (d, $^3J = 6.8$ Hz, 12H; CH_3), 1.23 (d, $^3J = 6.8$ Hz, 12H; CH_3); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 147.7$, 144.9, 131.2, 128.6, 125.7, 123.9, (Ar–C), 38.9 (SCH), 37.0 (CH_2), 35.6 (SCH), 23.0 (CH_3), 22.6 (CH_3); IR (KBr pellet): $\tilde{\nu} = 3051$ (w, Ar–H), 2958, 2923, 2863 (m, SC–H), 1557 (m, Ar–C=C), 1444 (s, CH_2), 788 (m, Ar–H) cm^{-1}; MS (70 eV, EI): m/z (%): 478 (100) $[M]^+$, 435 (63) $[M - C_3H_7]^+$, 393 (89) $[M - C_3H_7 - C_3H_6]^+$, 351 (48) $[M - C_3H_7 - 2C_3H_6]^+$, 309 (37) $[M - SC_3H_7 - 3C_3H_6]^+$, 275 (23) $[M - SC_3H_7 - 3C_3H_6 - H_2S]^+$, 241 (11) $[M - SC_3H_7 - 3C_3H_6 - 2H_2S]^+$, 91 (37) $[C_7H_7]$; elemental analysis calcd (%) for $C_{26}H_{38}S_4$ (478.82): C 65.22, H 8.00, S 26.78; found: C 64.93, H 8.01, S 27.06.

1,2-Bis(2,3-dimercaptophenyl)ethane (H_4-2): A solution of **10** (840 mg, 1.75 mmol) and naphthalene (1.12 g, 8.75 mmol) in tetrahydrofuran was treated with sodium pieces (405 mg, 17.6 mmol). The mixture was stirred for 12 h at ambient temperature. The resulting reddish brown reaction mixture was cooled in an ice bath and carefully quenched with methanol (2 mL). After the mixture had been stirred for 10 min, all solvents were removed in vacuo and the residue was redissolved in water (20 mL). The aqueous solution was washed with diethyl ether (3 × 20 mL) and acidified with hydrochloric acid (37 %) causing the formation of a white solid which was extracted with dichloromethane (3 × 20 mL). The combined pale yellow organic layers were dried over $MgSO_4$. Removal of the solvent yielded H_4-**2** as an off-white solid (530 mg, 1.70 mmol, 97 %). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.29$ (dd, $^3J = 4.0$ Hz, $^3J = 5.3$ Hz, 2H; Ar–H), 6.99–7.01 (m, 4H; Ar–H), 3.93 (s, 2H; SH), 3.78 (s, 2H; SH), 3.04 (s, 4H; CH_2); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 141.7$, 132.5, 130.3, 129.1, 127.6, 126.2 (Ar–C), 35.9 (CH_2); IR (KBr pellet): $\tilde{\nu} = 3048$, 3036 (w, Ar–C–H), 2943, 2926, 2855 (m, C–H), 2549 (m, S–H), 1440, 717 (C–H) cm^{-1}; MS (70 eV, EI): m/z (%): 310 (100) $[M]^+$, 276 (6) $[M - H_2S]^+$, 138 (5), 69 (9), 43 (3); elemental analysis calcd (%) for $C_{14}H_{14}S_4$ (310.50): C 54.15, H 4.54, S 41.30; found: C 54.35, H 4.46, S 41.37.

$[(Cp_2Ti)_2(1)]$ (12): The complex was prepared by a published method[12b,c] from H_4-**1** (400 mg, 1.01 mmol) and $[Cp_2TiCl_2]$ (500 mg, 2.01 mmol). The compound was isolated as a dark green powder (530 mg, 0.71 mmol, 71 %). ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 7.51$ (m, 2H; Ar–H), 7.34 (brs, 2H; CONH), 7.24 (d, $^3J = 7.6$ Hz, 2H; Ar–H), 7.17 (d, $^3J = 7.6$ Hz, 2H; Ar–H), 5.96 (s, 20H; C_5H_5), 3.74 (d, $^3J = 5.0$ Hz, 4H; CH_2); ^{13}C NMR ($CDCl_3$, 50.32 MHz, 25 °C): $\delta = 169.0$ (CONH), 158.6, 152.5, 136.1, 131.6, 125.1, 124.6 (Ar–C), 113.3 (C_5H_5), 39.5 (CH_2); IR (KBr pellet): $\tilde{\nu} = 3107$ (m, N–H), 1637, 1518 (s, C=O), 815 (s, C_5H_5), 728 (m, Ar–H) cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{32}N_2O_2S_4Ti_2$ (748.66): C 57.76, H 4.31, N 3.74, S 17.13; found: C 57.66, H 4.28, N 3.52, S 16.81.

Complexes $X_4[Ni_2(1)_2]$ (11a, $X = Li^+$) and (11b, $X = NEt_4^+$): A solution of H_4-**1** (580 mg, 1.46 mmol) and $LiOCH_3$ (6 mmol, 6 mL of a 1 M solution in MeOH) in MeOH (15 mL) was added dropwise to a solution of $NiCl_2$ (190 mg, 1.46 mmol) in MeOH (15 mL). The mixture was heated to reflux for 2 h. After the mixture had been cooled to ambient temperature, the solvent was removed in vacuo. The brown residue was washed with diethyl ether (2 × 10 mL) and dried under vacuum to give complex **11a** (yield: 605 mg, 0.65 mmol, 89 % based on H_4-**1**). Complex **11a** was dissolved in *N,N*-dimethylformamide and NEt_4Cl (950 mg) was added. Vapor diffusion of benzene into this concentrated solution yielded crystals of $(NEt_4)_4[Ni_2(1)_2] \cdot C_6H_6 \cdot DMF$ (**11b** $\cdot C_6H_6 \cdot$ DMF), which were suitable for X-ray diffraction studies. ^1H NMR for solvent-free **11a** ([D$_7$]DMF, 200 MHz, 25 °C): $\delta = 10.09$ (brs, 4H; CONH), 7.38 (d, $^3J = 7.3$ Hz, 4H; Ar–H), 7.07 (d, $^3J = 7.3$ Hz, 4H; Ar–H), 6.47 (t, $^3J = 7.3$ Hz, 4H; Ar–H), 3.25 (s, 8H; CH_2); ^{13}C NMR for solvent-free **11a** ([D$_7$]DMF, 50.32 MHz, 25 °C): $\delta = 169.7$ (CONH), 157.5, 151.5, 131.6, 128.5, 122.2, 118.8 (Ar–C), 39.7 (CH_2); IR (KBr pellet): $\tilde{\nu} = 3203$ (s, N–H), 1623 (s, C=O) cm^{-1}; elemental analysis calcd (%) for the solvent-free powder $C_{32}H_{24}Li_4N_4Ni_2O_4S_8$ (930.19): C 41.32, H 2.60, N 6.02, S 27.57; found: C 41.66, H 2.54, N 5.97, S 27.80.

$(NEt_4)_2[Ni_2(1)_2]$ (13): A solution of complex **12** (200 mg, 0.27 mmol) in tetrahydrofuran (100 mL) was added to a solution of $(NEt_4)_2[NiCl_4]$ (125 mg, 0.27 mmol) in acetonitrile (100 mL). Initially the reaction mixture was green (both **12** and the nickel salt are green in solution). While refluxing the mixture for 12 h, the color slowly changed from green to brown (planar $Ni^{II}S_4$ complexes are brown and $[Cp_2TiCl_2]$ is red). Aerial oxidation of the reaction mixture resulted in a further color change to green again. Volatile materials were removed under vacuum and the residue was washed with tetrahydrofuran (2 × 20 mL) in order to remove $[Cp_2TiCl_2]$. After drying in a vacuum, complex **13** was isolated as a dark green solid (81 mg, 0.07 mmol, 52 %). Vapor diffusion of diethyl ether into a concentrated *N,N*-dimethylformamide solution yielded crystals of a diethyl ether solvate (see X-ray crystallography section) suitable for X-ray diffraction studies. MS (ESI): m/z: 451 $[M - 2NEt_4]^{2-}$; elemental analysis calcd (%) for solvent-free powder $C_{48}H_{64}N_6Ni_2O_4S_8$ (1162.93): C 49.58, H 5.55, N 7.23, S 22.05; found: C 49.80, H 5.41, N 7.44, S 21.70.

$Na_4[Ni_2(2)_2]$ (14): A solution of H_4-**2** (793 mg, 2.55 mmol) and $NaOCH_3$ (11 mmol, 11 mL of a 1 M solution in MeOH) in MeOH (10 mL) was added dropwise to a solution of $NiCl_2$ (338 mg, 2.6 mmol) in MeOH (40 mL). The mixture was stirred overnight and was then heated to reflux for 3 h. After cooling to ambient temperature, the mixture was filtered and the filtrate was dried in a vacuum. The residue was dissolved in acetone (40 mL) and filtered again. The filtrate was concentrated to 20 mL and stored at ambient temperature. After three weeks, red-brown needles had formed which were collected by filtration. Further concentration of the filtrate led to the precipitation of a second crop of crystals of **14** $\cdot 4CH_3C(O)CH_3 \cdot 3H_2O$. These crystals were dried in vacuo to yield 535 mg, 0.65 mmol, 51 % of solvent-free **14**. ^1H NMR of solvent-free **14** ([D$_7$]DMF, 200 MHz, 25 °C): $\delta = 7.22$ (dd, 4H; Ar–H), 6.62-6.52 (m, 8H; Ar–H), 3.16 (s, 8H; CH_2); ^{13}C NMR of solvent-free **14** ([D$_7$]DMF, 50.32 MHz, 25 °C): $\delta = 155.3$, 149.8, 144.4, 139.6, 125.0, 124.5 (Ar–C), 38.0 (CH_2); elemental analysis calcd (%) for solvent-free $C_{28}H_{20}Na_4Ni_2S_8$ (822.28): C 40.90, H 2.45, S 31.19; found: C 41.22, H 2.32, S 30.97.

$Na_2[Ni_2(2)_2]$ (15): This complex was synthesized by aerial oxidation of a methanol solution of **14** (isolated yield 56 %). MS (ESI): m/z: 365 $[M -$

$2 Na]^{2-}$; elemental analysis calcd (%) for $C_{28}H_{20}Na_2Ni_2S_8$ (776.30): C 43.32, H 2.60, S 33.04; found: C 43.40, H 2.55, S 33.87.

$(NEt_4)_2[Co_2(1)_2]$ (16): Complex **16** was synthesized by the same method as described for **13** but with $(NEt_4)_2[CoCl_4]$ (185 mg, 0.40 mmol) and complex **12** (300 mg, 0.40 mmol) followed by aerial oxidation. An intense blue solid (105 mg, 0.09 mmol, 45%) was obtained. MS (ESI): *m*/*z*: 451 $[M - 2 NEt_4]^{2-}$; UV/Vis (DMF): λ_{max} (ε) = 660 (19700), 365 (26900), 320 (19700 $mol^{-1} dm^3 cm^{-1}$); elemental analysis calcd (%) for $C_{48}H_{64}Co_2N_6O_4S_8$ (1163.41): C 49.55, H 5.54, N 7.22, S 22.05; found: C 49.40, H 5.45, N 7.01, S 33.87.

X-ray crystallography: X-ray diffraction data were collected at −75°C (**11b** and **13**) on a Enraf-Nonius KappaCCD or at −120°C (**14**) on a Bruker AXS APEX diffractometer both equipped with a rotating anode and with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). An empirical absorption correction with SORTAV[26] was applied to the raw data for **11b** ($0.81 \leq T \leq 0.87$) and **13** ($0.79 \leq T \leq 0.97$). An absorption correction with the program SADABS[26] was applied to the data for **14** ($0.71 \leq T \leq 1.00$). The structure solution was achieved in all cases with SHELXS[27] and the refinement was carried out with SHELXL[28] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions and were refined as riding atoms (**11b** and **13**) or were unrefined (**14**), respectively. ORTEP[29] was used for all drawings of molecular structures. Additional data collection and refinement details are listed in Table 1. The quality of the crystals of **13** was poor. Complex **13** crystallizes as a diethyl ether solvate. The solvent molecules are disordered. Because of this disorder, the number of diethyl ether solvent molecules could not be determined. Microanalytical data also gave different results as the crystals rapidly loose their solvent molecules. Therefore, no attempt was made to resolve the disorder and the solvent molecules were not included in the refinement; this left some electron density unaccounted for and thus led to a relatively large residual electron density and poor *R* indices. However, the identity of complex **13** could be established unequivocally. Complexes **13** and **14** reside on an inversion center in the unit cell, the asymmetric unit contains half of the molecule.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-171296 (**11b**), CCDC-171297 (**13**), and CCDC-171298 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.ac.uk).

Table 1. Selected crystal and data collection details for **11b**, **13**, and **14**.

	11b · C_6H_6 · DMF	**13**[a]	**14** · 4 $CH_3C(O)CH_3$ · 3 H_2O
formula	$C_{73}H_{117}N_9Ni_2O_5S_8$	$C_{48}H_{64}N_6Ni_2O_4S_8$	$C_{40}H_{50}Na_4Ni_2O_7S_8$
fw [amu]	1574.66	1162.95	1108.66
a [Å]	16.893(1)	16.740(1)	7.2375(8)
b [Å]	9.918(1)	17.436(1)	13.0760(15)
c [Å	24.295(1)	9.889(1)	13.2871(15)
α [°]	90.0	90.0	98.962(2)
β [°]	99.37(1)	96.02(1)	103.842(2)
γ [°]	90.0	90.0	100.532(2)
V [Å^3]	4016.2(5)	2870.5(4)	1173.9(2)
ρ_{calcd} [g cm^{-1}]	1.302	1.346	1.568
space group	*Pc*	$P2_1/c$	$P\bar{1}$
Z	2	2	1
μ [m^{-1}]	0.729	0.992	1.242
unique data	14024	6503	3060
observed data $\{I > 2\sigma(I)\}$	9164	3996	2368
*R*1 (obs. data)	0.0686	0.1281	0.0433
*wR*1	0.147	0.354	0.1092
*R*2 (all data)	0.1201	0.1787	0.0568
*wR*2	0.1717	0.3861	0.1162
GOF	1.018	1.058	0.987
no. of variables	844	266	277
res. electron density [e Å^3]	0.926/ − 0.480	1.915/ − 0.960	0.692/ − 0.450

[a] See the Experimental Section for an explanation of high residual electron density and poor *R* indices.

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