# Novel Synthesis of Macrocyclic Amine-Thiophenolate Ligands: X-ray Crystal Structure of a $Ni_4$ Complex of an $N_8S_4$ Ligand

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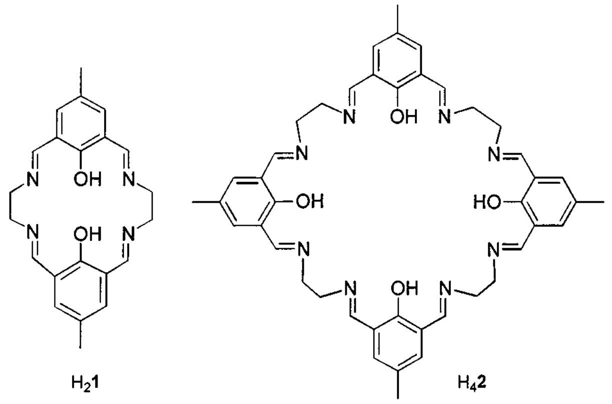
**Keywords:** Macrocyclic compounds / Amine-Thiolate Donors / Polynuclear Complexes / Nickel / Condensation reactions

A novel route to macrocyclic amine-thiophenolate ligands is described. The new, air-stable thiophenolate precursor 1,2-bis(4-*tert*-butyl-2,6-diformyl-phenylsulfanyl)ethane (**4**) is readily condensed with two equivalents of 1,2-ethanediamine or 1,3-propanediamine under medium to high dilution conditions to give 2 × 4 condensation products. The smaller 1 × 2 macrocyclic compounds are not produced under these conditions. Subsequent reduction with $NaBH_4$ (reduction of imine groups) and $Na/NH_3$ (reductive cleavage of aryl-alkylsulfides) provides the 36- and 40-membered amine-thiophenolate ligands $H_4$**6a** and $H_4$**6b**. The macrocyclic compounds are versatile ligands for the preparation of polynuclear transition metal complexes. With divalent nickel $H_4$**6a** forms the di- and tetranuclear complexes $[Ni_2(\mathbf{6a})]$ (**7**) and $[Ni_4(\mathbf{6a})][ClO_4]_4$ (**8**). Reaction of **8** with four equivalents of $NH_4SCN$ yields the novel isothiocyanate complex $[Ni_4^{II}(\mathbf{6a})(NCS)_4]\cdot 10MeCN$ (**9**). The structure consists of well-separated molecules of the tetranuclear complex $[Ni^{II}_4(\mathbf{6a})(NCS)_4]$ ($C_i$ symmetry). Two symmetry-related binuclear $[N_2Ni(\mu_2\text{-}SR)_2NiN_4]$ fragments composed of thiolate-bridged distorted planar $\{N_2S_2Ni\}$- and distorted *cis*-octahedral $\{(SCN)_2N_2S_2Ni\}$ units reside within the cavity of the macrocycle. The intramolecular distance between the two binuclear units is 6.144(1) Å.

## Introduction

One of the most efficient syntheses of macrocyclic amine phenolate ligands such as $H_2$**1** (Scheme 1) involves a Schiff base condensation of 2,6-diformyl-4-methyl-phenol with an aliphatic α,ω-diamine in the presence of a labile first-row transition metal ion. Since its discovery by Robson and coworkers in 1970,[1] this reaction has been applied to a large variety of such ligands because they are ideally suited to prepare homo- and heterodinuclear and mixed-valence complexes.[2–7] Higher condensation products,[8][9] such as the 36-membered amine-phenolate ligand $H_4$**2**,[10] can also be obtained by this method.



Scheme 1. Macrocyclic N/O-Donor Ligands $H_2$**1**[1] and $H_4$**2**[10a]

In contrast to the large number of macrocyclic amine-phenolate ligands, there exist only a few examples of the corresponding imino- and aminothiophenolates.[11][12] This is true in particular for larger macrocyclic $N_xS_y$ compounds.[13] To the best of our knowledge, all the macrocyclic $N_xS_y$ compounds described to date have been obtained by metal template condensations using the air-sensitive compound 2,6-diformyl-4-methyl-thiophenol as starting material.[14]

We describe here an alternative route to macrocyclic amine-thiophenolate ligands by employing the air-stable thiophenolate precursor, 1,2-bis(4-*tert*-butyl-2,6-diformylphenylsulfanyl)ethane (**4**). The tetraaldehyde is readily condensed with aliphatic α,ω-diamines, and subsequent reduction of the intermediate thioether/imine compounds provides the 36- and 40-membered ligands $H_4$**6a**,**b**. This is demonstrated by the solid-state structure of $[Ni_4(\mathbf{6a})(NCS)_4]\cdot 10MeCN$.

## Results and Discussion

### Ligand Syntheses

The synthesis of the new octaamine-tetrathiophenol compounds $H_4$**6a**,**b**·8HCl was accomplished in three steps employing 4-*tert*-butyl-2,6-diformylbromobenzene **3** as starting reagent (Scheme 2). In the first step, compound **3** was reacted with dipotassium 1,2-ethanedithiolate in DMF in a 2:1 stoichiometric ratio to give the tetraaldehyde **4** in nearly quantitative yield. Condensation of **4** with two equivalents of 1,2-ethanediamine in a $CH_2Cl_2$/MeOH mixed solvent system under high-dilution conditions, followed by sodium borohydride reduction of the intermediate imine-thioether product, gave the amine-thioether compound **5a** in yields greater than 80%. The smaller 1 × 2−condensation product, i.e. the 18-membered $N_4S_2$ macrocycle, is not formed

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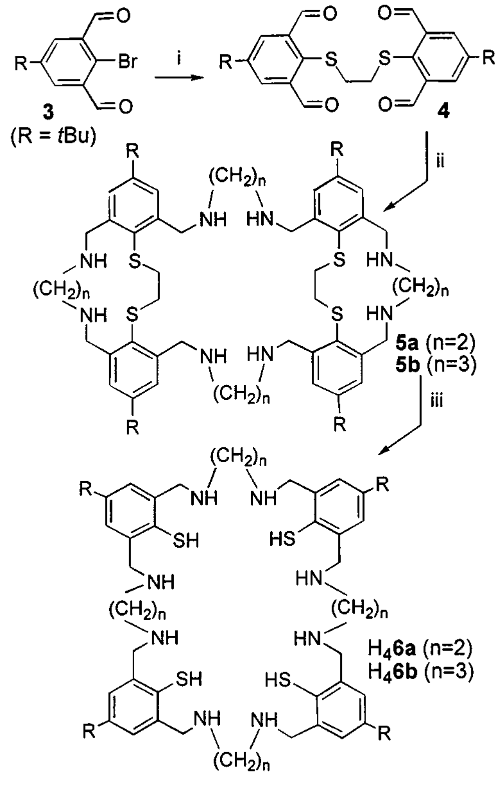
under these conditions. Attempts to obtain this compound by using more dilute solutions (and longer reaction times) were unsuccessful, but instead resulted in higher yields of **5a**. In the last step, compound **5a** was reduced with sodium in liquid ammonia (reductive cleavage of the ArS−$CH_2$-$CH_2$−SAr bonds) to give, after hydrolysis with hydrochloric acid, the hydrochloride salt of the amine-thiolate ligand, $H_4$**6a**·8HCl. A similar reaction sequence was employed to prepare the 40-membered amine-thiolate ligand $H_4$**6b**·8HCl. Both ligands were stored as their hydrochloride salts under an atmosphere of dry nitrogen. The compounds $H_4$**6a**,**b**·8HCl are only slightly soluble in water, although the ligands dissolve in methanol in the presence of a base such as $NEt_3$.



Scheme 2. Preparation of macrocyclic amine-thiophenolate ligands $H_4$**6a**,**b**: (i). $HSCH_2CH_2SH$, $K_2CO_3$, DMF, 25°C; (ii). 2 equiv. $NH_2(CH_2)_nNH_2$, 10%MeOH/$CH_2Cl_2$; $NaBH_4$; (iii). Na/$NH_3$, HCl

The new compounds **4**, **5a**,**b**, and $H_4$**6a**,**b**·8HCl were characterized by $^1$H NMR, $^{13}$C NMR and IR spectroscopy. In the IR spectra of $H_4$**6a**,**b**·8HCl the N−H and S−Hstretching vibrations appear as broad bands at 2750 and 2400 cm$^{-1}$, respectively. The relatively low value for ν(S−H) is presumably due to intramolecular hydrogen bonding interactions with adjacent NH protons. According to the $^1$H and $^{13}$C NMR spectra, compounds $H_4$**6a**,**b**·8HCl exhibit fourfold symmetry in solution. Compound $H_4$**6a**·8HCl, for example, displays only four resonances at $\delta$ = 7.42, 4.34, 3.44, and 1.19 for the Ar*H*, ArC*H*$_2$N, NC*H*$_2$C*H*$_2$N, and C(C*H*$_3$)$_3$ protons, respectively. Due to fast H/D exchange, the S*H* and N*H* protons are not observed under these conditions. As expected, the $^{13}$C NMR spectrum of $H_4$**6a**·8HCl displays eight signals for the 56 carbon atoms. The macrocyclic structure of $H_4$**6a**·8HCl was confirmed by an X-ray structure determination of one of its metal complexes (see below).

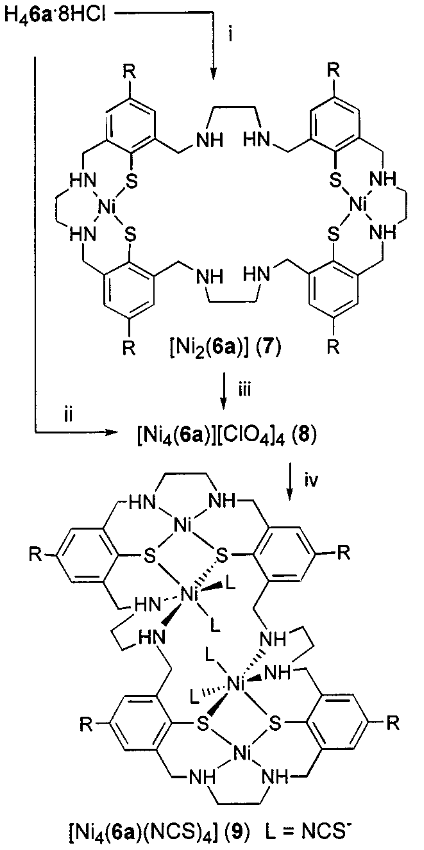
The strategy for the synthesis of the macrocyclic amine-thiophenolate ligands presented in this study differs from those employed by other groups for related amine-thiophenolate ligands. Such compounds have been prepared almost exclusively by metal-templated condensations between 2,6-diformyl-4-methyl-thiophenol and certain α,ω-diamines, followed by sodium borohydride reduction of the imine-thiolate complexes and hydrolysis of the resulting amine-thiolate complexes. The latter route has also been employed in the synthesis of the phenolate analogue of $H_4$**6a**.[10c] Our approach makes use of the air-stable tetraaldehyde/dithioether compound **4** which can be condensed with aliphatic diamines in the absence of metal ions. Since the 2 × 4 condensation products are almost exclusively formed under these conditions, it is likely that the bridging thioether unit serves as the template for macrocycle formation. However, the cyclization reactions still demand medium to high-dilution conditions (final concentration ≈ 0.01 M), since otherwise only polymeric material is obtained. It also appears that the yield of cyclization product (**5a**: > 92%, **5b**: 56%) decreases with increasing chain length of the diamine.

## Synthesis and Characterization of Nickel Complexes 7−9

The preparation of nickel(II) complexes of $H_4$**6a**·8HCl was accomplished by reaction with nickel(II) salts in methanol or acetonitrile in the presence of a base such as triethylamine. Depending on the metal-to-ligand ratio the metalations of $H_4$**6a**·8HCl afforded di- or tetranuclear nickel(II) complexes (see Scheme 3). The reaction of $H_4$**6a**·8HCl with two equivalents of $NiCl_2·6H_2O$ produced a purple, microcrystalline solid of composition [$Ni_2$(**6a**)]·MeOH (**7**), whereas the reaction with four equivalents of $Ni(ClO_4)_2·6H_2O$ yielded the red-brown complex [$Ni_4$(**6a**)]-[$ClO_4$]$_4$ (**8**). Complex **8** could also be obtained by metalation of **7** with two equivalents of $Ni(ClO_4)_2·6H_2O$.

Complex **7** is diamagnetic and exhibits good solubility in most common organic solvents. Its UV/Vis spectrum in acetonitrile (Figure 1) is very similar to other planar $N_2S_2Ni$ complexes,[15][16] indicating that both nickel ions exhibit planar $N_2S_2$ coordination environments in the solution state. On the basis of the $^1$H NMR spectroscopic data (see Experimental Section) we propose a structure as shown in Scheme 3 with the two nickel ions occupying diagonally opposite sides of the macrocycle.

The metalation of **7** with nickel(II) perchlorate to form **8** is accompanied by distinct spectral changes. Isobestic points occurred at 544 and 680 nm. These spectral changes were clearly discernible until the ratio of concentrations of **7** and $Ni^{2+}$ was 1:2 (see Figure 1). At higher $Ni^{2+}$ concentrations the spectrum remained essentially unchanged, implying that $H_4$**6a** coordinates no more than four $Ni^{2+}$ ions. The IR spectrum of **8** reveals three very strong and sharp



Scheme 3. Preparation of dinuclear and tetranuclear nickel complexes of $H_4$**6a**: (i). 2.0 equiv. $NiCl_2\cdot 6H_2O$, $NEt_3$/MeOH; (ii). 4.0 equiv. $Ni(ClO_4)_2\cdot 6H_2O$, $NEt_3$/MeOH; (iii). 2 equiv. $Ni(ClO_4)_2\cdot 6H_2O$, $CH_3CN$; (iv). 4 equiv. $NH_4SCN$, $CH_3CN$

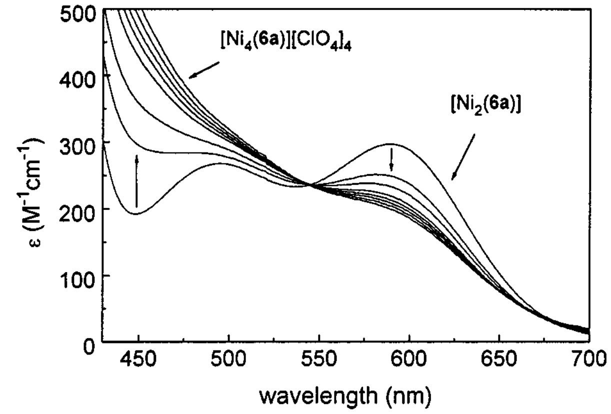


Figure 1. Titration of $[Ni_2($**6a**$)]\cdot$MeOH (**7**) ([**7**] = 1 × $10^{-3}$ M) with $10^{-3}$ M $Ni(ClO_4)_2\cdot 6H_2O$ in MeCN (0.0–4.0 added equiv) at 295 K followed by UV/Vis spectroscopy

absorptions for ν(ClO) at 1150, 1115, and 1089 $cm^{-1}$ consistent with the presence of the $ClO_4^-$ ions. It was not possible to grow single crystals of this product, although the reaction of **8** with $NH_4SCN$ in $CH_3CN$ yielded single crystals of $[Ni_4($**6a**$)(NCS)_4]\cdot 10CH_3CN$ (**9**) suitable for an X-ray crystal structure determination.

## X-ray Crystal Structure of $[Ni_4(6a)(NCS)_4]\cdot 10CH_3CN$ (9)

The X-ray crystal structure determination of **9** revealed the structure to consist of well-separated molecules of the tetranuclear isothiocyanate complex and acetonitrile molecules of crystallization. Figure 2 shows the molecular structure of the neutral, centrosymmetric complex $[Ni_4($**6-a**$)(NCS)_4]$. Selected bond lengths and angles are collected in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] in $[Ni_4($**6-a**$)(NCS)_4]\cdot 10CH_3CN$ (**9**)[a]

| Bond lengths | | | |
|---|---|---|---|
| Ni(1)−S(1) | 2.463(2) | Ni(2a)−S(1) | 2.212(2) |
| Ni(1)−S(2a) | 2.503(2) | Ni(2a)−S(2a) | 2.179(2) |
| Ni(1)−N(2) | 2.091(5) | Ni(2a)−N(1) | 1.943(5) |
| Ni(1)−N(3) | 2.167(4) | Ni(2a)−N(4a) | 1.935(5) |
| Ni(1)−N(5) | 2.060(5) | | |
| Ni(1)−N(6) | 2.071(5) | | |
| N(5)−C(29) | 1.124(8) | S(5)−C(29) | 1.658(7) |
| N(6)−C(30) | 1.175(8) | S(6)−C(30) | 1.633(6) |
| Ni(1)···Ni(2a) | 3.147(1) | | |
| Bond angles | | | |
| S(1)−Ni(1)−S(2a) | 74.63(6) | S(1)−Ni(2a)−S(2a) | 86.54(6) |
| S(1)−Ni(1)−N(2) | 92.80(13) | S(1)−Ni(2a)−N(1) | 95.7(2) |
| S(1)−Ni(1)−N(3) | 95.38(13) | S(1)−Ni(2a)−N(4a) | 178.6(2) |
| S(1)−Ni(1)−N(5) | 172.2(2) | S(2a)−Ni(2a)−N(1) | 177.5(2) |
| S(1)−Ni(1)−N(6) | 88.62(15) | S(2a)−Ni(2a)−N(4a) | 92.74(15) |
| S(2a)−Ni(1)−N(2) | 166.71(13) | N(1)−Ni(2a)−N(4a) | 85.0(2) |
| S(2a)−Ni(1)−N(3) | 94.05(13) | | |
| S(2a)−Ni(1)−N(5) | 97.6(2) | Ni(1)−N(5)−C(29) | 170.7(5) |
| S(2a)−Ni(1)−N(6) | 92.3(2) | N(5)−C(29)−S(5) | 179.8(6) |
| N(2)−Ni(1)−N(3) | 82.6(2) | Ni(1)−N(6)−C(30) | 165.1(5) |
| N(2)−Ni(1)−N(5) | 95.0(2) | N(6)−C(30)−S(6) | 177.4(7) |
| N(2)−Ni(1)−N(6) | 91.7(2) | | |
| N(3)−Ni(1)−N(5) | 86.0(2) | | |
| N(3)−Ni(1)−N(5) | 173.2(2) | | |
| N(5)−Ni(1)−N(6) | 90.8(2) | | |

[a] Symmetry transformations used to generate equivalent atoms: Ni(2a), S(2a), N(4a): 1−x, 2−y, 1−z.

All donor atoms of the 36-membered macrocycle are involved in coordination to the four nickel atoms to give two four-coordinate $N_2S_2Ni$ and two six-coordinate $N_4S_2Ni$ coordination units. Each Ni atom forms a five-membered chelate ring with one of the four ethanediamine moieties of the ligand. These $N_2Ni$ units are bridged by two thiophenolate sulfur atoms to give two symmetry-related binuclear $[N_2Ni(\mu_2\text{-}SR)_2NiN_2(NCS)_2]$ units. The average Ni−N and Ni−S bond lengths within these binuclear units compare well with those of other $N_2S_2Ni^{II}$ and $N_4S_2Ni^{II}$ complexes, although the bond length Ni(1)−N(3) at 2.167(4) Å is quite long for an octahedral $N_4S_2Ni^{II}$ complex.[17] The intramolecular distance between the two distorted *cis*-octahedral and the two distorted planar nickel atoms at 6.144(1) Å and 9.005(1) Å, respectively, may be used to describe the distance between the two binuclear subunits.

An interesting feature to note is the fact that the isothiocyanate ions within each binuclear unit occupy *cis* positions at the six-coordinate nickel atom {SCN−Ni(1)−NCS at 90.8(2)°}. It is assumed that this coordination mode is enforced by the short $C_2$ alkyl chain which links the 2,6-

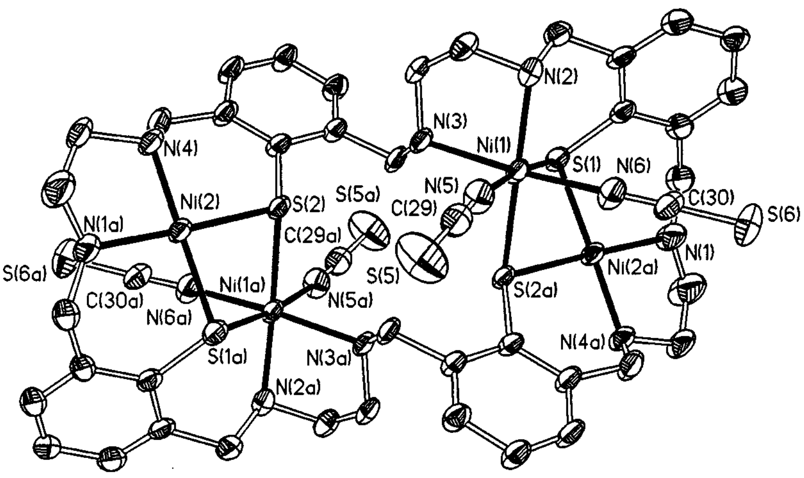


Figure 2. Perspective view of the molecular structure of the tetranuclear isothiocyanate complex [$Ni_4$(**6a**)$(NCS)_4$] in **9**. Hydrogen atoms and *tert*-butyl groups are omitted for reasons of clarity

bis(aminomethyl)-4-*tert*-butylthiophenolate moieties. This is in marked contrast to coordinatively unsaturated $N_2Ni(\mu_2\text{-}SR)_2NiN_2$ complexes in which the thiophenolate moieties are connected via a $C_3$ alkyl chain. Here the exogenous ligands are coordinated in *trans*-axial positions (see Scheme 4).[18][19]

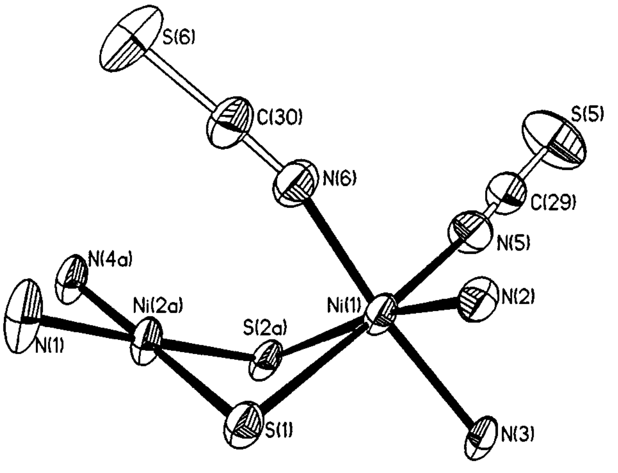
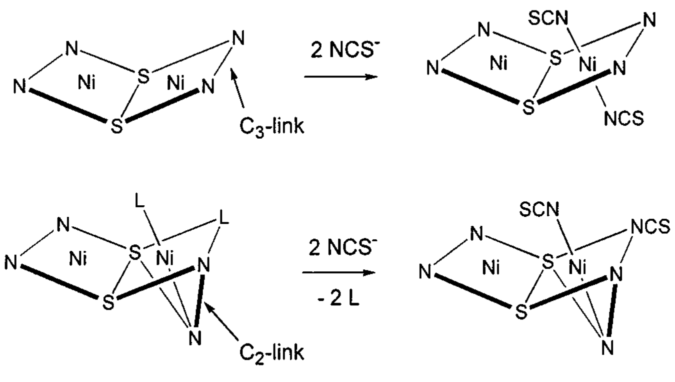


Figure 3. Coordination units in the central $[N_2Ni(\mu_2\text{-}SR)_2\text{-}NiN_2(NCS)_2]$ core in **9** showing 50% thermal ellipsoids



Scheme 4. Stereochemical courses of reactions of coordinatively unsaturated nickel complexes containing a $[N_2Ni(\mu_2\text{-}SR)_2NiN_2]$ core structure: influence of the bridging alkyl chain

## Conclusion

A new synthetic route to macrocyclic amine-thiolate ligands has been developed. The air-stable thiophenolate precursor 1,2-bis(4-*tert*-butyl-2,6-diformylphenylsulfanyl)ethane can be condensed with aliphatic α,ω-diamines $\{NH_2(CH_2)_nNH_2\}$ to give the 2 × 4 macrocyclic compounds {4·(7 + n) ring-atoms} in the absence of metal ions. By varying the building blocks it should be possible to obtain a wide range of polydentate amine-thiolate ligands which could be useful for the preparation of new polynuclear transition metal thiolate complexes

## Experimental Section

**General:** $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE DPX 200 spectrometer. All chemical shifts are quoted on the δ scale with TMS or the solvent as internal standard. Coupling constants are expressed in Hz. Melting points were determined in capillaries and are uncorrected. CHN-Analyses were determined with a Perkin−Elmer Elemental Analyzer 240. IR spectra were recorded on a Bruker VECTOR 22 FT-IR-spectrophotometer as KBr pellets. Absorption spectra were recorded on a Jasco V-570 UV/VIS/NIR spectrometer. Compound **3**[20] was prepared as described in the literature. All other chemicals were of reagent grade and used without further purification. Solvents were predried over molecular sieves and freshly distilled from appropriate drying agents.

**Compound 4:** To a suspension of 1,2-ethanedithiol (2.50 g, 26.5 mmol) and $K_2CO_3$ (8.29 g, 60.0 mmol) in DMF (80 mL) was added solid **3** (14.3 g, 53.0 mmol), and the reaction mixture was stirred for 12 h. Water (200 mL) was then added dropwise with stirring. The resulting precipitate was isolated by filtration, washed with water (3 × 50 mL), and dried in air. The solid was purified by recrystallization from dichloromethane/cyclohexane to give 11.5 g (92%) of **4** as pale yellow crystals. M.p. 178° C. − IR (KBr): $\tilde{\nu}$ = 2872m (CH), 1687s $cm^{-1}$ (CO). − $^1H$ NMR ($CDCl_3$): δ = 10.67 (s, 4 H, C*H*O), 8.11 (s, 4 H, Ar*H*), 2.96 (s, 4 H, C$H_2$), 1.31 (s, 18 H, C$H_3$). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 191.0 (*C*HO), 153.9, 138.3, 136.9, 131.3, 38.5, 35.2, 30.9.

**Compound 5a:** A solution of 1,2-ethanediamine (493 mg, 8.20 mmol) in 10% $MeOH/CH_2Cl_2$ (100 mL) and a solution of **3**

(2.05 g, 4.36 mmol) in $CH_2Cl_2$ (100 mL) were simultaneously added within 3 h to 300 mL of $CH_2Cl_2$ with stirring. After the reaction mixture was stirred for further 12 h at room temperature, the solvents were removed at reduced pressure to obtain a white solid. The solid was dissolved in MeOH/$CH_2Cl_2$ (100 mL, 1:1), a solution of $NaBH_4$ (1.20 g, 31.7 mmol) in 50 mL of MeOH was added, and the resulting homogeneous reaction mixture was stirred for further 2 h. After the excess reducing agent was destroyed by acidification with 1M HCl, the pH was readjusted to 11 by addition of 2M NaOH solution, and the aqueous phase extracted with $CH_2Cl_2$ (3 × 200 mL). The combined organic phases were dried over $K_2CO_3$, filtered, and the solvent removed under reduced pressure. The pale-yellow residue was purified by column chromatography ($SiO_2$) using MeOH/$NEt_3$/$CH_2Cl_2$ (10:5:85) as eluting solvent to give 2.12 g (92%) of the product as a white foam. − IR (KBr): $\tilde{\nu}$ = 3310w cm$^{-1}$ (NH). − $^1$H NMR ($CDCl_3$): δ = 7.34 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 7.24 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 4.02 (s, 8 H, BzC$H_2$), 3.97 (s, 8 H, BzC$H_2$), 3.25 (s, 8 H, SC$H_2$), 2.91 (s, 8 H, NHC$H_2$), 2.81 (s, 8 H, NHC$H_2$), 1.90 (s br, 8 H, NH), 1.30 (s, 36 H, C$H_3$). − $^{13}$C NMR ($CDCl_3$): δ = 151.7, 144.3, 144.0, 130.3, 127.0, 126.4, 53.9, 53.3, 48.7, 37.4, 34.4, 31.1.

**Compound 5b:** Analogously to the preparation of **5a**, compound **5b** was prepared from **3** (2.05 g, 4.36 mmol) and 1,3-propanediamine (608 mg, 8.20 mmol). Yield: 1.35 g (56%). − IR (KBr): $\tilde{\nu}$ = 3295w cm$^{-1}$ (NH). − $^1$H NMR ($CDCl_3$): δ = 7.25 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 7.14 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 3.95 (s, 8 H, BzC$H_2$), 3.85 (s, 8 H, BzC$H_2$), 3.03 (s, 8 H, SC$H_2$), 2.73 (m, 16 H, NHC$H_2$), 1.72 (m, 8 H, NHC$H_2$), 1.23 (s, 36 H, C$H_3$). − $^{13}$C NMR ($D_2O$/2%DCl): δ = 155.9, 136.9, 136.6, 131.9, 130.8, 126.3, 50.7, 49.9, 45.4, 44.6, 37.8, 34.9, 30.5, 23.0, 20.9.

**Compound $H_4$6a·8HCl:** To a solution of sodium (1.00 g, 43.0 mmol) in liquid ammonia (100 mL) was added a solution of **5a** (2.00 g, 1.90 mmol) in THF (30 mL) and the deep-blue reaction mixture was stirred for 1 h. After the excess reducing equivalents were destroyed by careful addition of $NH_4Cl$, the suspension was evaporated to dryness, and the resulting pale yellow residue was taken up in water (40 mL). The yellow solution was cooled to 0° C, and the pH of the solution adjusted to 1 by addition of 12M hydrochloric acid. The pale yellow solid was collected by filtration and recrystallized from 1M HCl to give $H_4$**6a**·8HCl (1.79 g, 73%) as white crystals. − IR (KBr): $\tilde{\nu}$ = 3423, 2750br (N−H), 2400br cm$^{-1}$ (S−H). − $^1$H NMR ($D_2O$): δ = 7.41 (s, 8 H, Ar*H*), 4.36 (s, 16 H, BzC$H_2$N), 3.45 (s, 16 H, NC$H_2$), 1.23 (s, 36 H, C$H_3$). − $^{13}$C NMR ($D_2O$): δ = 152.0, 133.9, 131.9 (CH), 130.7, 51.5, 43.0, 34.5, 30.7.

**Compound $H_4$6b·8HCl:** Analogously to the preparation of $H_4$**6a**·8HCl, this compound was prepared by reduction of **5b** (2.11 g, 1.90 mmol) with sodium (1.00 g, 43.0 mmol) in liquid ammonia (100 mL). Recrystallization from 1M HCl afforded $H_4$**6b**·8HCl (1.56 g, 61%) as white crystals. − $^1$H NMR ($D_2O$): δ = 7.47 (s, 8 H, Ar*H*), 4.38 (s, 16 H, BzC$H_2$N), 3.12 (t, $^3J$ = 7.5 Hz, 16 H, NC$H_2$), 2.17 (qnt, $^3J$ = 7.5 Hz, 8 H, C$H_2$), 1.16 (s, 36 H, C$H_3$). − $^{13}$C NMR ($CD_3OD$): δ = 154.1, 136.6, 131.8 (CH), 129.3, 51.5, 45.8, 35.8, 31.4, 23.9.

**[$Ni_2$(6a)]·MeOH (7):** To a solution of $H_4$**6a**·8HCl (129 mg, 0.100 mmol) in MeOH (3 mL) was added $NiCl_2·6H_2O$ (47 mg, 0.200 mmol) in MeOH (1 mL) and $NEt_3$ (121 mg, 1.20 mmol). The purple solution was stirred overnight, during which time a purple, microcrystalline precipitate of **7** deposited. The crystals were filtered, washed with cold MeOH (1 mL), and dried in vacuum. Yield: 58 mg (51%). − IR (KBr): $\tilde{\nu}$ = 3129w cm$^{-1}$ (NH). − UV/Vis (MeCN): $\lambda_{max}$ ($\varepsilon_M$) = 495 (270), 588 nm (298 M$^{-1}$cm$^{-1}$). − $^1$H NMR (200 MHz, $CDCl_3$/$CD_3OD$, 1:1): δ = 7.22 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 6.90 (d, $^4J$ = 2.0 Hz, 4 H, Ar*H*), 4.42 (d, $^2J$ = 12.0 Hz, 4 H, C$H_2$), 3.90 (d, $^2J$ = 12.0 Hz, 4 H, C$H_2$), 3.27 (d, $^2J$ = 12.0 Hz, 4 H, C$H_2$), 3.04 (m, 8 H, C$H_2$), 2.95 (m, 4 H, C$H_2$), 2.50 (m, 8 H, C$H_2$), 1.26 (s, 36 H, C$H_3$). − $C_{56}H_{84}N_8Ni_2S_4·CH_3OH$ (1147.00): calcd. C 59.69, H 7.73, N 9.77; found C 59.42, H 7.33, N, 9.52.

**[$Ni_4$(6a)][$ClO_4$]$_4$·3MeOH (8):** To a solution of **7** (115 mg, 0.100 mmol) in MeOH (3 mL) was added $Ni(ClO_4)_2·6H_2O$ (76 mg, 0.20 mmol) in MeOH (1 mL). The brown solution was stirred for 12 h, during which time a microcrystalline precipitate of **8** deposited. The crystals were filtered, washed with cold MeOH (1 mL), and dried in air. Yield: 128 mg (74%). − IR (KBr): $\tilde{\nu}$ = 3200w (NH), 1142, 1113, 1087vs cm$^{-1}$ [$ClO_4^-$, $\nu_3(F_2)$]. − UV/Vis (MeCN): $\lambda_{max}$ (ε) = 586 (204), 1017 nm (10 M$^{-1}$cm$^{-1}$). − $C_{56}H_{84}N_8Ni_4S_4·Cl_4O_{16}·3CH_3OH$ (1726.27): calcd. C 41.05, H 5.61, N 6.49; found C 41.32, H 5.45, N 6.36.

**[$Ni_4$(6a)(NCS)$_4$]·10$CH_3CN$ (9):** To a solution of **8** (36 mg, 0.021 mmol) in MeCN (5 mL) was added a solution of $NH_4SCN$ (6.5 mg, 0.085 mmol) in MeOH (1 mL). The brown solution was filtered and kept at room temp. for 12 h, during which time the tetranuclear isothiocyanate complex **9** deposited as brown-red crystals. Yield: 25 mg (63%). Crystals of **9** quickly lose the MeCN molecules of crystallization upon storage in air at 298 K. − IR (KBr): $\tilde{\nu}$ = 3200w (NH), 2075vs cm$^{-1}$ (CN). − UV/Vis (DMF): $\lambda_{max}$ (ε) = 520sh (317), 975 nm (65 M$^{-1}$cm$^{-1}$). − $C_{60}H_{84}N_{12}Ni_4S_8$ (1464.65): C 49.20, H 5.78, N 11.48; found C 48.93, H 5.31, N 11.01.

**X-ray Crystal Structure Determination:** Single crystals of complex **9** were obtained by the procedure described above. A red-brown crystal of [$Ni_4$(**6a**)(NCS)$_4$]·10MeCN measuring 0.42 × 0.35 × 0.09 mm was mounted with some mother-liquor in a glass capillary. Intensity data were collected at −60°C using a STOE IPDS diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied. Of 8518 unique reflections 5890 measured $F_o > 4\sigma(F_o)$. Structure solution (direct methods) and refinements were carried out with SHELXS-86 and SHELXL-93 software,[21] respectively. The complex [$Ni_4$(**6a**)(NCS)$_4$]·10MeCN crystallizes in the triclinic space

Table 2. Crystal data and structure refinement for [$Ni_4$(**6a**)(NCS)$_4$]·10$CH_3CN$

| | |
|---|---|
| empirical formula | $C_{80}H_{114}N_{22}Ni_4S_8$ |
| formula weight | 1875.26 |
| crystal size, mm$^3$ | 0.42 × 0.35 × 0.09 |
| *T*,°C | −60 |
| space group | $P\bar{1}$ |
| *a*, Å | 11.217(2) |
| *b*, Å | 14.862(3) |
| *c*, Å | 15.342(3) |
| *α*, deg | 78.26(3) |
| *β*, deg | 70.90(3) |
| *γ*, deg | 85.35(3) |
| *V*, Å$^3$ | 2366.0(8) |
| *Z* | 1 |
| density, g·cm$^{-3}$ | 1.316 |
| *μ*(Mo K*α*), mm$^{-1}$ | 1.013 |
| *θ* range, deg | 4.48−25.92 |
| reflections collected | 18381 |
| unique reflections | 8518 ($R_{int}$ = 0.1403) |
| observed reflections | 5890 ($F_o > 4\sigma(F_o)$) |
| *R*1, *wR*2 [$F_o > 4\sigma(F_o)$] | 0.0817, 0.1975[a] |
| *R*1, *wR*2 (all data) | 0.1144, 0.2246[a] |
| goodness-of-fit on $F^2$ | 1.095 |
| resid. elect. density, eÅ$^{-3}$ | 0.903/−0.696 |

[a] $w = 1/[\sigma^2(F_o^2) + (0.1182P)^2 + 2.7688P]$, $P = (F_o^2 + 2F_c^2)/3$.

group $P\bar{1}$. The asymmetric unit contains one half of the atoms of the formula unit ($Z = 1$). The disordered *tert*-butyl methyl carbon atoms and C- and N-atoms of the MeCN solvates were refined isotropically. All other non-hydrogen atoms were refined anisotropically. An isotropic split-atom model was applied for the disordered *tert*-butyl methyl carbon atoms. The multiplicities of the respective orientations C(20a)–C(21a)–C(22a): 0.68, C(20b)–C(21b)–C(22b): 0.32 were refined. In the final stages of anisotropic refinement, hydrogen atoms were included at calculated positions and refined by using a riding model. The final difference Fourier maps showed no unusual features. Final $R$ factors are given in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-128515. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft. The author thanks Prof. Dr. H. Vahrenkamp for his generous support. Financial support from the Wissenschaftliche Gesellschaft Freiburg and the Graduiertenkolleg "Ungepaarte Elektronen" is also gratefully acknowledged. We also thank Prof. Dr. B. Krebs (University of Münster) for providing facilities for X-ray crystallographic measurements and are indebted to S. Höck for help in collecting the X-ray data.

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Received June 2, 1999
[I99242]