

# Preparation and Characterization of Mononuclear Ni Complexes of Tetradentate Amine-thioether and Amine-thiolate Ligands

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*Z. Naturforsch.* **2007**, 62b, 508–518; received October 24, 2006

A short route for the preparation of tetradentate amine-thioether and amine-thiolate ligands derived from thiosalen is reported. The ligating properties of several of the synthesized ligands towards Ni(II) has been examined. The diamine-dithiophenolate ligands ( $L^6$ )<sup>2-</sup> [ $H_2L^6 = N,N'$ -dimethyl- $N,N'$ -di(2-mercaptobenzyl)-ethane-1,2-diamine] and ( $L^7$ )<sup>2-</sup> [ $H_2L^7 = N,N'$ -di(2-mercaptobenzyl)-piperazine] support the formation of four-coordinate  $Ni^{II}N_2S_2$  complexes [ $Ni^{II}(L^6)$ ] (**10**) and [ $Ni^{II}(L^7)$ ] (**11**). By contrast, the amine-thioethers **2** [ $N',N''$ -bis(2-*tert*-butylthio)benzyl)ethane-1,2-diamine],  $L^2$  [8,11-diaza-5,13-dibenzo-1,4-dithia-cyclotetradecane] and its *N*-methylated derivative  $L^{2,Me}$  were found to produce the six-coordinate Ni(II) complexes [ $Ni^{II}Cl_2(2)_2$ ] (**9**), [ $Ni^{II}_2(\mu-Cl)_2(L^2)_2$ ][ClO<sub>4</sub>]<sub>2</sub> (**12**), [ $Ni^{II}(NCS)_2(L^2)$ ] (**13**), and [ $Ni^{II}Cl_2(L^{2,Me})$ ] (**14**). The results of IR, NMR and UV/vis spectroscopy and the crystal structures of complexes **9**–**13** are reported.

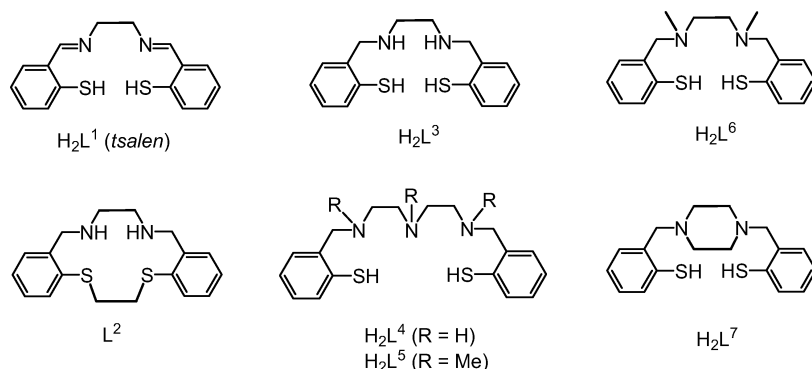
**Key words:** Nickel Complexes, Macrocyclic Ligands, N Donor, S Donor

## Introduction

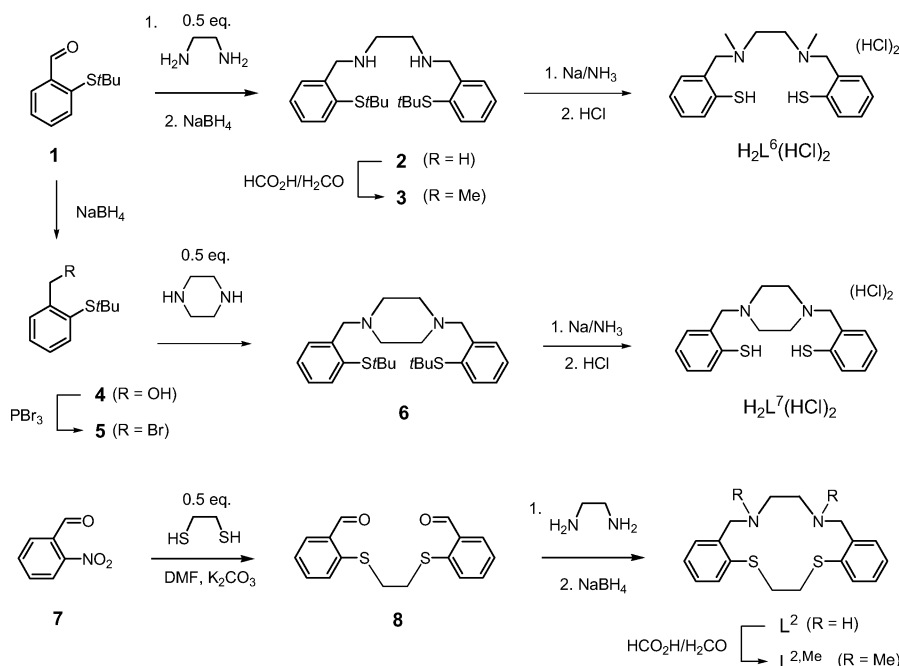
The coordination chemistry of tetradentate  $N_4$  and  $S_4$  donor ligands has been well investigated in the past several years [1, 2]. Far less is known about the metal ion-binding of tetradentate  $N_2S_2$  donor ligands. This is true in particular for the families of amine-thioether and amine-thiolate ligands derived from thiosalen ( $H_2L^1$ , see Scheme 1) [3–5]. Lindoy *et al.* reported the synthesis of the 14-membered  $N_2S_2$  macrocycle  $L^2$  [6].

Koyama and coworkers prepared  $N,N'$ -bis(2-mercaptobenzyl)-ethylenediamine ( $H_2L^3$ ) [7]. Until now only a few more ligands of this sort have been reported in the literature [8–12].

In recent work, we described the synthesis of the pentadentate amine-thiophenol ligands  $H_2L^4$  and  $H_2L^5$  [13]. We now find that the  $N_2S_2$  ligands  $H_2L^6$  and  $H_2L^7$  can be prepared in a similar manner. The synthesis of these ligands and their ligating properties towards Ni(II) are reported herein.



Scheme 1. Structure of the ligands  $H_2L^1$ – $H_2L^7$ .



Scheme 2. Synthesis of the ligands used in this study.

## Results and Discussion

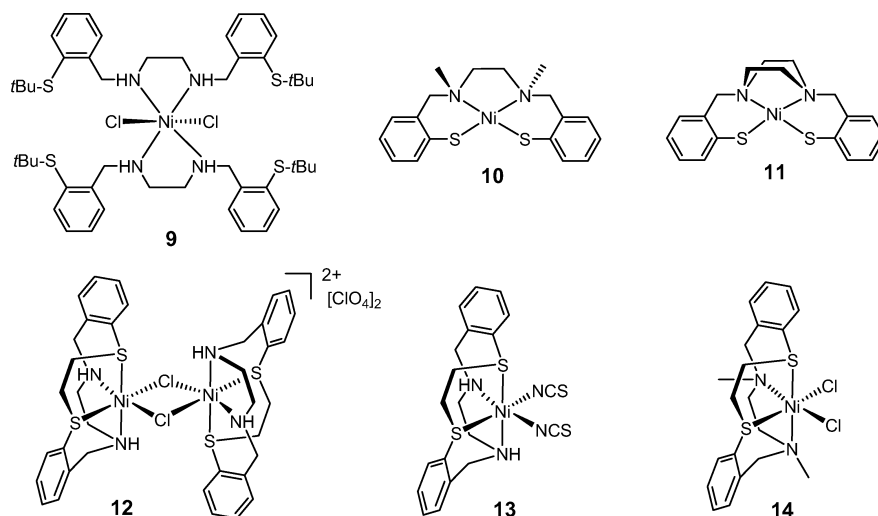
### Synthesis of ligands

The route used for the synthesis of the ligands is depicted in Scheme 2. The preparations of proligand **2** and  $\text{H}_2\text{L}^6 \cdot 2\text{HCl}$  have already been reported by other groups. Hinshaw and coworkers, for example, prepared  $\text{H}_2\text{L}^6$  in five steps starting from thiosalicylic acid and *N,N'*-dimethylethylenediamine in relatively low yield (41%) [10]. We adapted Sun's procedure [11], using 2-*tert*-butylthio-benzaldehyde (**1**) as starting material [14]. Thus, reductive amination of **1** with ethylenediamine/ $\text{NaBH}_4$ , followed by Eschweiler-Clarke methylation of **2** furnished **3**, which could be readily deprotected with  $\text{Na}/\text{NH}_3$  to give  $\text{H}_2\text{L}^6 \cdot 2\text{HCl}$ ; an overall yield of 88% was obtained. The ligand  $\text{H}_2\text{L}^7 \cdot 2\text{HCl}$  was prepared according to a protocol used for the alkylation of triazacyclononane [15]. The four-step method depicted in Scheme 2 provided  $\text{H}_2\text{L}^7 \cdot 2\text{HCl}$  in 70% yield. The synthesis of the macrocycle  $\text{L}^2$  was first described by Lindoy *et al.* [6]. We used a slight modification of the original procedure using commercially available 2-nitro-benzaldehyde as starting material. The two-step method depicted in Scheme 2 is superior to the original procedure and leads to a significantly higher yield of  $\text{L}^2$ . Finally, the permethylated derivative  $\text{L}^{2,\text{Me}}$  was obtained by Eschweiler-Clarke methylation of  $\text{L}^2$ .

The amine-thiolate ligands  $\text{H}_2\text{L}^6$  and  $\text{H}_2\text{L}^7$  were isolated as their hydrochloride salts and stored under an atmosphere of dry nitrogen. These ligands could not be obtained in analytically pure form. Nevertheless, they were of sufficient purity for metal complex syntheses.

### Synthesis and spectroscopic characterization of complexes

Scheme 3 shows the complexes prepared and their labels. Treatment of amine-thioether **2** with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in a 1 : 1 molar ratio in methanol solution produced the mononuclear 1 : 2 complex  $[\text{Ni}^{\text{II}}\text{Cl}_2(\text{2})_2]$  (**9**) as a pale-blue, air-stable, microcrystalline solid in 81% yield (based on **2**). A 1 : 1 complex could not be obtained. Complex  $[\text{Ni}^{\text{II}}(\text{L}^6)]$  (**10**) forms as the only isolable product, when  $\text{H}_2\text{L}^6 \cdot 2\text{HCl}$  is treated with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NEt}_3$  in a 1 : 1 : 2 molar ratio in methanolic solution. Similarly, the reaction of  $\text{H}_2\text{L}^7 \cdot 2\text{HCl}$  with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NEt}_3$  in methanol produced the red neutral complex  $[\text{Ni}^{\text{II}}(\text{L}^7)]$  (**11**). Addition of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to a solution of  $\text{L}^2$  in methanol, followed by treatment with solid  $\text{LiClO}_4$ , produced a pale-blue microcrystalline solid of the composition  $[\text{Ni}^{\text{II}}_2\text{Cl}_2(\text{L}^2)_2][\text{ClO}_4]_2$  (**12**) in almost quantitative yield. Treatment of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{L}^2$  in methanol, followed by the addition of  $\text{NaSCN}$ , gave a purple,



Scheme 3. The complexes prepared in this study and their labels.

crystalline powder of  $[\text{Ni}^{\text{II}}(\text{NCS})_2(\text{L}^2)]$  (**13**). Finally, reaction of  $\text{L}^{2,\text{Me}}$  with one equivalent of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  yielded  $[\text{Ni}^{\text{II}}\text{Cl}_2(\text{L}^{2,\text{Me}})]$  (**14**) as a green powder. All compounds gave satisfactory elemental analyses and were characterized by spectroscopic methods (IR, UV/vis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy) and compounds **9**–**13** also by X-ray crystallography.

The infrared spectra of the complexes **9**–**11** and **14** reveal mainly the various stretching and bending modes of the supporting ligands. The most significant feature in the IR spectrum of crystalline **9** is the band at  $3294\text{ cm}^{-1}$ , which can be readily assigned to the N–H stretching vibrations of the coordinated amine donors [16]. Similar bands are observed for **12** and **13**, but not for the complexes **10**, **11**, and **14** which contain only tertiary amine donors. The IR spectra of **12** and **13** reveal additional bands for counter ions and co-ligands. Thus, the IR spectrum of the perchlorate salt **12** reveals a strong band at  $1100\text{ cm}^{-1}$  for the  $\text{ClO}_4^-$  ions, whereas **13** shows two bands at  $2107$  and  $2089\text{ cm}^{-1}$  characteristic of thiocyanate ions  $\nu(\text{NCS})$ . The values are similar to those of other octahedral  $[\text{Ni}^{\text{II}}(\text{NCS})_2(\text{macrocycle})]$  complexes, indicative of N-bound thiocyanates [17, 18].

The diamagnetic complexes **10** and **11** were further characterized by  $^1\text{H}$  NMR spectroscopy. It is apparent from the  $^1\text{H}$  NMR data that the two halves of  $(\text{L}^6)^{2-}$  in **10** and  $(\text{L}^7)^{2-}$  in **11** are equivalent. For example, a single  $^1\text{H}$  NMR resonance is observed for the NMe protons in **10** at  $\delta = 2.49\text{ ppm}$ . The benzylic protons form an AB system, the corresponding A and B doublets being centered at  $\delta = 2.22$  and  $\delta = 4.33\text{ ppm}$ . The

geminal coupling constant was found to be 12 Hz. The benzylic protons in **11** also form an AB system ( $\delta = 2.47$  and  $3.52\text{ ppm}$ ) presumably as a consequence of a hindered inversion of the two six-membered chelate rings. These data suggest that both complexes maintain their solid state structures in the solution state (*i. e.* *trans* orientation of the two methyl groups in **10**, rigid propeller-like structure of **11**). Complexes **12**–**14** are paramagnetic and could not be investigated by NMR spectroscopy. The stereochemistry of **14** is unknown.

The electronic absorption spectra of **9**–**14** have been recorded in the 300–1600 nm range in MeCN or  $\text{CH}_2\text{Cl}_2$ . The spectra of the nickel complexes of the amine-thioether ligands **2**,  $\text{L}^2$ , and  $\text{L}^{2,\text{Me}}$  are similar but not identical. Above 500 nm, each compound displays two weak absorption bands. The absorption band in the 580 to 630 nm range can be attributed to the  $\nu_2$  transition  $[\text{A}_{2g}(\text{F}) \rightarrow \text{T}_{1g}(\text{F})]$  of an octahedral nickel(II) ( $d^8$ ) ion. The bands between 1055 and 1100 nm can be assigned to the  $\nu_1$  transition  $[\text{A}_{2g}(\text{F}) \rightarrow \text{T}_{2g}(\text{F})]$ . The slight differences in the position of the  $d-d$  transitions indicate that each complex retains its integrity in solution. The spectra of the amine-thiolate complexes **10** and **11** reveal intense absorptions in the 300 to 600 nm region, characteristic of four-coordinate  $\text{N}_2\text{S}_2\text{Ni}^{\text{II}}$  compounds. These absorptions can be attributed to  $\text{RS}^- \rightarrow \text{Ni}^{\text{II}}$  charge-transfer transitions.

#### Description of the crystal structures

The crystal structures of **9**–**13** were determined by X-ray crystallography to establish the geometries about the metal ions as well as the bonding modes of

Table 1. Selected crystallographic data for **9**–**13**.

| Compound   | [NiCl <sub>2</sub> ( <b>2</b> ) <sub>2</sub> ] ( <b>9</b> )                     | [Ni(L <sup>6</sup> )] ( <b>10</b> )                             | [Ni(L <sup>7</sup> )] ( <b>11</b> )                             | [Ni <sub>2</sub> (μ-Cl) <sub>2</sub> (L <sup>2</sup> ) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub> ( <b>12</b> ) | [Ni(NCS) <sub>2</sub> (L <sup>2</sup> )] ( <b>13</b> )          |
|--|---|---|---|---|---|
| Formula  | C <sub>48</sub> H <sub>72</sub> Cl <sub>2</sub> N <sub>4</sub> NiS <sub>4</sub> | C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> NiS <sub>2</sub> | C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> NiS <sub>2</sub> | C <sub>18</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> NiO <sub>4</sub> S <sub>2</sub>                      | C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> NiS <sub>4</sub> |
| <i>M</i> <sub>r</sub> [g mol <sup>−1</sup> ]     | 962.95  | 389.21  | 387.19  | 524.11  | 505.37  |
| Space group                                      | <i>P</i> $\bar{1}$  | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>Pca</i> 2 <sub>1</sub>                                       | <i>P</i> 2 <sub>1</sub> / <i>c</i>  | <i>P</i> 2 <sub>1</sub> / <i>n</i>                              |
| <i>a</i> [Å]                                     | 9.936(2)  | 13.623(3)   | 15.362(3)   | 10.0169(8)  | 10.271(2)   |
| <i>b</i> [Å]                                     | 10.042(2)   | 10.658(2)   | 7.895(2)  | 19.914(2)   | 13.398(3)   |
| <i>c</i> [Å]                                     | 13.592(3)   | 13.252(3)   | 14.032(3)   | 11.5659(9)  | 16.788(2)   |
| $\alpha$ [deg]                                   | 85.15(3)  | 90  | 90  | 90  | 90  |
| $\beta$ [deg]                                    | 78.00(3)  | 115.83(3)   | 90  | 112.38(3)   | 105.12(2)   |
| $\gamma$ [deg]                                   | 71.67(3)  | 90  | 90  | 90  | 90  |
| <i>V</i> [Å <sup>3</sup> ]                       | 1259.0(5)   | 1731.9(6)   | 1701.8(7)   | 2133.3(3)   | 2230.2(7)   |
| <i>Z</i>   | 1   | 4   | 4   | 4   | 4   |
| <i>d</i> <sub>calcd.</sub> [g cm <sup>−3</sup> ] | 1.270   | 1.493   | 1.511   | 1.632   | 1.505   |
| $\mu$ (MoK $\alpha$ ) [mm <sup>−1</sup> ]        | 0.693   | 1.361   | 1.385   | 1.384   | 1.259   |
| $\theta$ limits [deg]                            | 1.53–28.29  | 1.66–28.29  | 2.90–28.31  | 2.05–28.30  | 1.97–30.04  |
| Measured refl.                                   | 11386   | 10468   | 4775  | 18797   | 14784   |
| Independent refl.                                | 5843  | 4089  | 2765  | 5115  | 6117  |
| Observed refl. <sup>a</sup>                      | 4201  | 3048  | 2279  | 3615  | 2094  |
| No. parameters                                   | 268   | 208   | 208   | 262   | 262   |
| <i>R</i> <sup>b</sup> ( <i>R</i> 1 all data)     | 0.0399 (0.0649)   | 0.0260 (0.0454)   | 0.0297 (0.0399)   | 0.0338 (0.0598)   | 0.0496 (0.2025)   |
| <i>wR</i> <sup>c</sup> ( <i>wR</i> 2 all data)   | 0.0963 (0.1160)   | 0.0619 (0.0823)   | 0.0630 (0.0669)   | 0.0784 (0.0877)   | 0.0865 (0.1198)   |
| Max, min peaks [e/Å <sup>3</sup> ]               | 0.721/−0.309  | 0.372/−0.384  | 0.280/−0.428  | 0.937/−0.594  | 0.531/−0.681  |

<sup>a</sup> Observation criterion:  $I \geq 2\sigma(I)$ . <sup>b</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

the supporting ligands. Suitable crystals of **14** could not be obtained. Experimental crystallographic data are summarized in Table 1.

[Ni<sup>II</sup>Cl<sub>2</sub>(**2**)<sub>2</sub>] (**9**). This compound crystallizes in the triclinic space group *P* $\bar{1}$  with one formula unit per unit cell. The neutral complex exhibits crystallographically imposed inversion symmetry. A perspective view of the molecular structure is depicted in Fig. 1. Selected bond lengths and angles are given in the figure caption. The Ni atom is coordinated by four nitrogen atoms from the two amine-thioether ligands and two *trans*-oriented chloro ligands in a distorted octahedral fashion. The thioether functions point away from the Ni atom; the intramolecular Ni...S(1) and Ni...S(2) distances of 5.234 and 4.959 Å being out of range of bonding interactions. There are no unusual features as far as bond lengths and angles are concerned. The average Ni–N and Ni–Cl bond lengths are at 2.152(2) Å and 2.4186(8) Å, respectively. Similar distances are seen in other octahedral Ni<sup>II</sup>N<sub>4</sub>Cl<sub>2</sub> complexes [19].

[Ni<sup>II</sup>(L<sup>6</sup>)] (**10**). Crystals of **10** grown by slow diffusion of methanol into an acetonitrile solution are monoclinic, space group *P*2<sub>1</sub>/*c*. The crystal structure determination revealed the presence of discrete molecules of the neutral complex (Fig. 2). The Ni atom is coordinated by the two N and two S atoms from (L<sup>6</sup>)<sup>2−</sup> in an almost planar fashion; the maximum deviation from the least-squares plane through the atoms

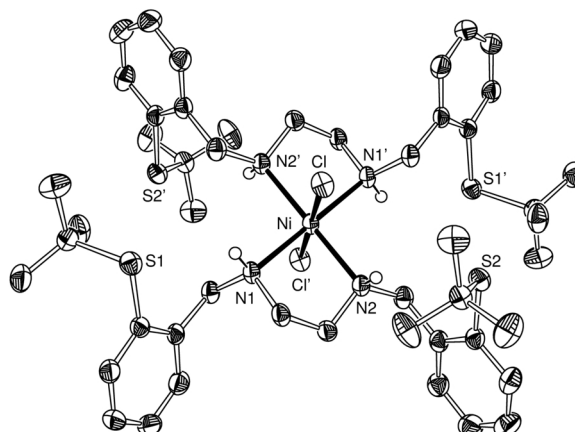


Fig. 1. Structure of the complex **9**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms, except H(1) and H(2), are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni–N(1) 2.172(2), Ni–N(2) 2.133(2), Ni–Cl 2.4186(8); L–Ni–L<sub>cis</sub> 83.6–96.4°, L–Ni–L<sub>trans</sub> 180°. Symmetry code used to generate equivalent atoms: 1 – *x*, 1 – *y*, –*z*.

Ni, N(1), N(2), S(1) and S(2) being only 0.082 Å. The average Ni–S bond length of 2.175(1) Å resembles that in [Ni<sup>II</sup>(L<sup>3</sup>)] [20] and other planar NiN<sub>2</sub>S<sub>2</sub> structures [21–25]. The average Ni–N bond length in **10** is significantly longer than in [Ni<sup>II</sup>(L<sup>3</sup>)] (by 0.108 Å), as expected for the conversion of secondary into tertiary N donors. Similar effects have been observed for Ni

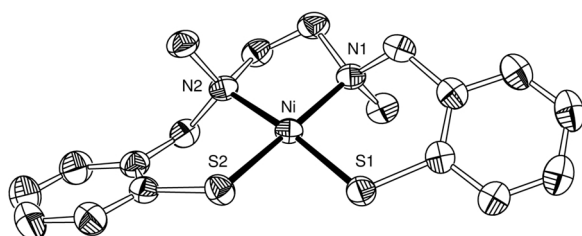


Fig. 2. Structure of the neutral complex  $[\text{Ni}^{\text{II}}(\text{L}^6)]$  (**10**). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni–N(1) 1.974(2), Ni–N(2) 1.965(2), Ni–S(1) 2.1686(7), Ni–S(2) 2.182(1); N(1)–Ni–N(2) 89.00(8), S(1)–Ni–S(2) 83.08(3), S(1)–Ni–N(1) 94.54(6), S(1)–Ni–N(2) 173.38(6), S(2)–Ni–N(1) 173.76(5), S(2)–Ni–N(2) 93.95(6).

complexes of other N donor ligands and their methylated derivatives [26], the two methyl groups are located at opposite sides of the five-membered ring.

$[\text{Ni}^{\text{II}}(\text{L}^7)]$  (**11**). This compound crystallizes in the non-centrosymmetric space group  $Pca2_1$ . The crystal structure determination revealed the presence of discrete molecules (Fig. 3). The neutral complex exhibits idealized  $C_2$  symmetry. Again, the Ni atom is four-coordinate by two *cis*-oriented S and N donors from  $(\text{L}^7)^{2-}$ . The distortion from planarity is less pronounced than in **10**, the maximum deviation from the least-squares plane through the atoms Ni, N(1), N(2), S(1) and S(2) being only 0.053 Å. The average Ni–S (2.165(1) Å) and Ni–N bond lengths (1.954(3) Å) compare well with those in **10** and other four-coordinate Ni(II) complexes with  $\text{N}_2\text{S}_2$  coordination [27, 28]. The

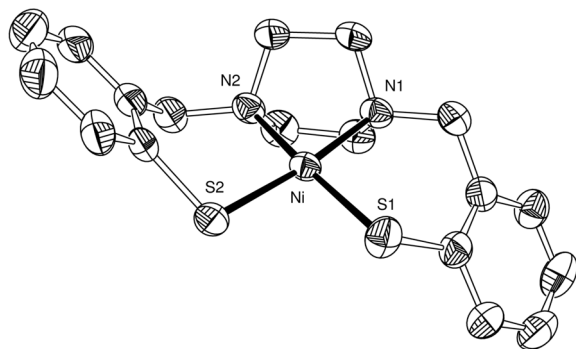


Fig. 3. Structure of the neutral complex  $[\text{Ni}^{\text{II}}(\text{L}^7)]$  (**11**). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni–N(1) 1.951(3), Ni–N(2) 1.956(3), Ni–S(1) 2.161(1), Ni–S(2) 2.170(1); N(1)–Ni–N(2) 76.40(12), S(1)–Ni–S(2) 88.62(4), S(1)–Ni–N(1) 97.52(9), S(2)–Ni–N(2) 97.67(9), S(1)–Ni–N(2) 172.43(9), S(2)–Ni–N(1) 173.34(9).

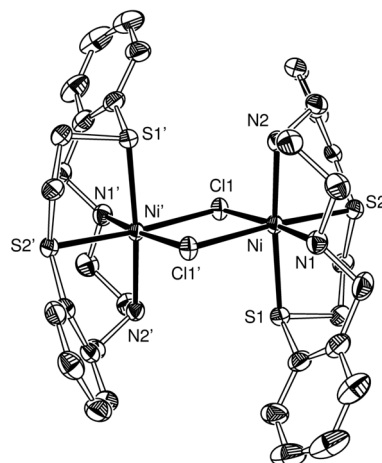


Fig. 4. ORTEP representation of the structure of complex  $[\text{Ni}^{\text{II}}_2(\mu\text{-Cl})_2(\text{L}^2)_2]^{2+}$  in crystals of **12**. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are listed in Table 2. Symmetry code used to generate equivalent atoms:  $2 - x, -y, -z$ .

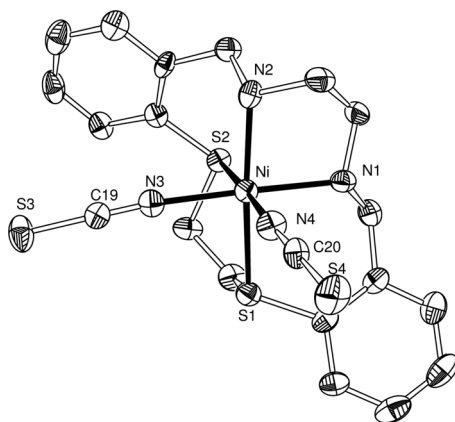
most significant structural differences between **10** and **11** concern the bond angles around the Ni atom. The deviations from the ideal values are more pronounced in **11**. For example, the N–Ni–N bond angle in **11** ( $76.4(1)^\circ$ ) is much more acute than in **10** ( $89.00(8)^\circ$ ) most likely as a consequence of the steric constraints of the piperazine backbone.

$[\text{Ni}^{\text{II}}_2(\mu\text{-Cl})_2(\text{L}^2)_2][\text{ClO}_4]_2$  (**12**). This salt crystallizes in the monoclinic space group  $P2_1/c$ . The crystal structure consists of dinuclear  $[\text{Ni}^{\text{II}}_2(\mu\text{-Cl})_2(\text{L}^2)_2]^{2+}$  dications (Fig. 4) and perchlorate counteranions. Selected bond lengths and angles are given in Table 2. Unlike in *trans*- $[\text{NiCl}_2(\text{cyclam})]$  [29], the 14-membered  $\text{N}_2\text{S}_2$  macrocycle  $\text{L}^2$  adopts a folded conformation such that the two bridging chloride atoms are arranged in *cis* positions. This can be traced back to the longer Ni–S bonds (mean value =  $2.4037(8)$  Å), which are only compatible with the folded conformation. The average Ni–N bond length at 2.084 Å closely compares with that in *trans*- $[\text{NiCl}_2(\text{cyclam})]$  and other octahedral nickel(II) complexes.

$[\text{Ni}^{\text{II}}(\text{NCS})_2(\text{L}^2)]$  (**13**). The crystal structure determination of **13** confirmed the formulation of the title compound (Fig. 5). Table 2 lists selected bond lengths and angles. The conformation of the macrocycle resembles that found in **12**, such that the N-bound thiocyanate ions are in *cis* positions. The Ni–S and Ni–N(macrocycle) bond lengths are somewhat longer than in **12**. The Ni–N(isothiocyanate)

Table 2. Selected bond lengths and angles of complexes **12** and **13**.

| <b>12</b>                    |           | <b>13</b>    |          |
|------------------------------|-----------|--------------|----------|
| Ni–S(1)                      | 2.3792(7) | Ni–S(1)      | 2.436(2) |
| Ni–S(2)                      | 2.4281(8) | Ni–S(2)      | 2.515(2) |
| Ni–N(1)                      | 2.077(2)  | Ni–N(1)      | 2.103(4) |
| Ni–N(2)                      | 2.090(2)  | Ni–N(2)      | 2.073(4) |
| Ni–Cl(1)                     | 2.4272(7) | Ni–N(3)      | 2.034(5) |
| Ni–Cl(1') <sup>a</sup>       | 2.4189(8) | Ni–N(4)      | 2.037(4) |
| M–N <sup>b</sup>             | 2.084(2)  |              | 2.088(4) |
| M–S <sup>b</sup>             | 2.4037(8) |              | 2.476(2) |
| M–L <sup>b</sup>             | 2.4231(8) |              | 2.036(4) |
| N(1)–Ni–N(2)                 | 85.40(8)  | N(1)–Ni–N(2) | 83.9(2)  |
| N(1)–Ni–S(1)                 | 91.95(6)  | N(1)–Ni–S(1) | 90.9(1)  |
| N(1)–Ni–S(2)                 | 96.33(7)  | N(1)–Ni–S(2) | 94.7(1)  |
| N(2)–Ni–S(2)                 | 89.72(6)  | N(2)–Ni–S(2) | 87.5(1)  |
| N(1)–Ni–Cl(1') <sup>a</sup>  | 86.50(6)  | N(1)–Ni–N(4) | 85.3(2)  |
| N(2)–Ni–Cl(1)                | 96.11(6)  | N(2)–Ni–N(3) | 97.2(2)  |
| N(2)–Ni–Cl(1') <sup>a</sup>  | 95.84(6)  | N(2)–Ni–N(4) | 96.3(2)  |
| S(1)–Ni–Cl(1)                | 87.00(3)  | S(1)–Ni–N(3) | 88.4(1)  |
| S(1)–Ni–Cl(1') <sup>a</sup>  | 88.21(3)  | S(1)–Ni–N(4) | 92.4(1)  |
| S(2)–Ni–Cl(1)                | 90.17(3)  | S(2)–Ni–N(3) | 87.3(1)  |
| S(1)–Ni–S(2)                 | 86.36(3)  | S(1)–Ni–S(2) | 83.78(5) |
| Cl(1)–Ni–Cl(1') <sup>a</sup> | 86.89(3)  | N(3)–Ni–N(4) | 92.7(2)  |
| N(1)–Ni–Cl(1)                | 173.34(6) | N(3)–Ni–N(1) | 177.8(2) |
| N(2)–Ni–S(1)                 | 175.01(6) | N(2)–Ni–S(1) | 169.4(1) |
| Cl(1')–Ni–S(2) <sup>a</sup>  | 173.95(2) | N(4)–Ni–S(2) | 176.2(1) |
| Ni–Cl–Ni'                    | 93.11(3)  | –            | –        |

<sup>a</sup> Symmetry code used to generate equivalent atoms: 2 – x, – y, – z.<sup>b</sup> Mean values.Fig. 5. ORTEP representation of the molecular structure of complex **13** at 50 % probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) are listed in Table 2.

bond lengths are normal for six-coordinate nickel(II) isothiocyanate complexes [17]. The nickel atom features a slightly distorted octahedral coordination environment. This is manifested in the L–Ni–L<sub>cis</sub> and L–Ni–L<sub>trans</sub> bond angles which vary from 83.78(5)° to 97.2(2)° and from 169.4° to 177.8°, respectively.

The individual complexes appear to be weakly intermolecularly hydrogen-bonded to each other. The corresponding NH···S (thiocyanate) distances lie at 2.686 Å [for N(1)H(1)···S(3')] and at 2.565 Å [for N(2)H(2)···S(3'')] [30]. These values are normal for NH···S hydrogen bonds [31–34]. In **12** and **13** the N-bound H atoms are located on the same side of the five-membered ring.

## Conclusion

In this study, a new synthetic strategy was employed for the synthesis of two known and two new N<sub>2</sub>S<sub>2</sub> ligands derived from thiosalen. This method is superior and leads to a considerably higher yield of these ligands. It has been demonstrated that the amine-thiophenolate ligands support the formation of planar NiN<sub>2</sub>S<sub>2</sub> complexes, whereas the amine-thioethers produce octahedral *cis*-[Ni(L')<sub>2</sub>(L'')]<sup>n+</sup> complexes (L' = Cl, NCS). Finally, it has also been demonstrated that the complexes exist as single isomers in the solution state.

## Experimental Section

### Materials and methods

Unless otherwise noted, all preparations were carried out under an atmosphere of argon. Reagent grade solvents were used throughout. 2-*tert*-Butylthio-benzaldehyde was prepared according to the literature procedure [35]. All other reagents were obtained from standard commercial sources and used without further purification. Melting points were determined in open glass capillaries and are uncorrected. Infrared spectra were recorded on a Bruker VECTOR 22 FT-IR-spectrometer, NMR spectra on a Bruker AVANCE DPX-200 spectrometer at 300 K. Chemical shifts refer to solvent signals converted to TMS. The electronic absorption spectra were measured on a Jasco V-570 UV / VIS / NIR spectrometer. Elemental analyses were carried out with a VARIO EL – elemental analyzer.

**CAUTION!** Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.

### Preparation of intermediate 2

To a solution of 2-*tert*-butylthio-benzaldehyde **1** (10.0 g, 51.5 mmol) in ethanol (100 mL) was added a solution of ethylenediamine (1.54 g, 25.6 mmol). After the reaction mixture was stirred for 24 h, sodium borohydride (3.00 g, 79.3 mmol) was added. The reaction mixture was stirred for further 24 h, water was added (50 mL), and the pH of the solution adjusted to 1 by addition of conc. hydrochloric acid. After

all volatiles had been distilled off, the residue was taken up in 3 M aqueous potassium hydroxide solution (100 mL) and dichloromethane (100 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 × 50 mL). The organic layers were combined and evaporated *in vacuo*. The resulting oily residue was dissolved in ethanol (20 mL) and treated with conc. aqueous hydrochloric acid to give a colorless precipitate of the dihydrochloride salt **2** · 2HCl. The crude material was recrystallized from ethanol. The hydrochloride was suspended in aqueous potassium hydroxide solution (pH = 13) and the free amine **2** extracted with dichloromethane. The combined organic fractions were dried over K<sub>2</sub>CO<sub>3</sub> and filtered. Evaporation of the solvent gave compound **2** as a colorless oil (10.1 g, 94 %). – <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD): δ = 1.15 (s, 18 H, *t*Bu), 2.58 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N), 3.89 (s, 4 H, ArCH<sub>2</sub>), 7.12–7.46 (m, 8 H, ArH). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CD<sub>3</sub>OD): δ = 32.1 (C(CH<sub>3</sub>)<sub>3</sub>), 48.5 (SC(CH<sub>3</sub>)<sub>3</sub>), 49.2 (NCH<sub>2</sub>), 53.3 (ArCH<sub>2</sub>), 128.8, 130.8, 131.4, 133.9, 140.5, 146.3. The spectroscopic data for the dihydrochloride salt are given in the literature [11].

#### Preparation of intermediate **3**

The amine-thioether **2** (7.64 g, 18.30 mmol) was dissolved in 96 % formic acid (9.57 g, 0.200 mol). To the clear solution was added a 35 % aqueous solution of formaldehyde (9.24 g, 108 mmol). The reaction mixture was heated under reflux for 20 h, after which time it was concentrated to dryness. Water (50 mL) and dichloromethane (100 mL) were added to the sticky residue, the pH of the aqueous phase was adjusted to 13 by the addition of 3 M aqueous potassium hydroxide solution, and the heterogeneous mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic fractions were dried over K<sub>2</sub>CO<sub>3</sub> and filtered. Evaporation of the solvent gave compound **3** as a colorless oil (7.91 g, 97 %). – <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>OD): δ = 1.12 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.07 (s, 6 H, NCH<sub>3</sub>), 2.50 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N), 3.74 (s, 4 H, ArCH<sub>2</sub>), 7.06–7.25 (m, 4 H, ArH), 7.40–7.45 (m, 4 H, ArH). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CD<sub>3</sub>OD): δ = 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 43.7 (NCH<sub>3</sub>), 48.3 (SC(CH<sub>3</sub>)<sub>3</sub>), 56.7 (NCH<sub>2</sub>), 61.6 (ArCH<sub>2</sub>), 128.5, 130.6 (CH), 132.0 (CH), 134.6, 140.4, 145.4. This material was used in the next step without further purification.

#### Preparation of ligand H<sub>2</sub>L<sup>6</sup> · 2HCl

To a solution of sodium (1.10 g, 47.8 mmol) in liquid ammonia (100 mL) was added a solution of compound **3** (2.74 g, 6.16 mmol) in tetrahydrofuran (30 mL) dropwise at –78 °C. The resulting blue reaction mixture was stirred at –78 °C for further 1 h to ensure complete deprotection of

the thiolate functions. Solid ammonium chloride was added in small portions at –78 °C to destroy excess reducing agent. The resulting colorless suspension was allowed to warm to r. t. After 12 h, the remaining solvent was distilled off at reduced pressure. The residue was taken up in water (20 mL) and the pH of the suspension adjusted to ≈ 1 to give a pale-yellow solution of H<sub>2</sub>L<sup>6</sup> as the dihydrochloride salt. To remove the inorganic salts the solution was concentrated in vacuum to a volume of ≈ 20 mL. Methanol (*ca.* 25 mL) was then added and the resulting solution was filtered off from NaCl and NH<sub>4</sub>Cl. The latter two steps were repeated several times in this order, until no more salts precipitated upon addition of MeOH. Concentration of the filtrate afforded the title compound as a pale-yellow, air-sensitive powder. Yield: 2.47 g (99 %). – <sup>1</sup>H NMR (200 MHz, D<sub>2</sub>O/CD<sub>3</sub>OD): δ = 2.90 (s, 6 H, NCH<sub>3</sub>), 3.72 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N), 4.48 (s, 4 H, ArCH<sub>2</sub>), 7.30–7.58 (m, 8 H, ArH). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CD<sub>3</sub>OD): δ = 41.3 (NCH<sub>3</sub>), 52.1 (NCH<sub>2</sub>), 60.3 (ArCH<sub>2</sub>), 128.9, 130.4 (CH), 132.7 (CH), 134.8, 134.9, 135.2. This material was used in the next step without further purification.

#### Preparation of intermediate **4**

To a solution of aldehyde **1** (5.00 g, 25.7 mmol) in ethanol (50 mL) was added NaBH<sub>4</sub> (500 mg, 13.2 mmol), and the resulting reaction mixture was stirred for 12 h. The excess reducing agent was destroyed by careful addition of conc. hydrochloric acid. Water (50 mL) was added and the pH of the aqueous phase was adjusted to 13 by the addition of 3 M aqueous potassium hydroxide solution. The solution was evaporated to dryness and the product extracted with dichloromethane. The combined organic fractions were dried over MgSO<sub>4</sub> and filtered. Evaporation of the solvent gave compound **4** as a colorless oil (4.18 g, 83 %). This material was used in the next step without further purification.

#### Preparation of intermediate **5**

A solution of PBr<sub>3</sub> (1.92 g, 7.10 mmol) in dichloromethane (20 mL) was slowly added to a solution of **4** (4.18 g, 21.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C. The reaction mixture was allowed to stir for 3 h. Water was then added, the organic layers were separated, and the aqueous phase extracted several times with dichloromethane. The combined organic phases were dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give **5** as a pale-yellow oil. Yield: 4.14 g (75 %). – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.23 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 4.79 (s, 2 H, ArCH<sub>2</sub>Br), 7.12–7.30 (m, 2 H, ArH), 7.45–7.50 (m, 2 H, ArH). – <sup>13</sup>C{<sup>1</sup>H} NMR (50.3 MHz, CDCl<sub>3</sub>): δ = 29.5 (C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (ArCH<sub>2</sub>Br), 45.6 (C(CH<sub>3</sub>)<sub>3</sub>), 126.6, 127.7, 129.3, 130.8, 137.1, 141.1 (ArC). This material was used in the next step without further purification.

### Preparation of intermediate **6**

To a solution of **5** (4.14 g, 16.0 mmol) and piperazine (688 mg, 8.00 mmol) in acetonitrile (100 mL) was added  $\text{K}_2\text{CO}_3$  (2.43 g, 17.6 mmol) and the resulting mixture was stirred for 2 d at ambient temperature. The mixture was evaporated to dryness, water was added to the residue, and the product extracted with dichloromethane. The combined organic phases were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to  $\approx 10$  mL. Addition of methanol resulted in the formation of colorless crystals of **6**, which were filtered and dried in air. Yield: 2.17 g (77 %). –  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.20 (s, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 2.44 (s, 8 H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.76 (s, 4 H,  $\text{ArCH}_2$ ), 7.09–7.25 (m, 4 H,  $\text{ArH}$ ), 7.43–7.54 (m, 4 H,  $\text{ArH}$ ). –  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 31.6 ( $\text{C}(\text{CH}_3)_3$ ), 47.5 ( $\text{C}(\text{CH}_3)_3$ ), 53.7 ( $\text{NCH}_2\text{CH}_2\text{N}$ ), 60.8 ( $\text{ArCH}_2$ ), 126.8, 129.2, 130.1, 132.9, 139.1, 144.1 ( $\text{ArC}$ ).

### Preparation of ligand $\text{H}_2\text{L}^7 \cdot 2\text{HCl}$

To a solution of sodium (1.00 g, 43.5 mmol) in liquid ammonia (100 mL) was added a solution of compound **6** (2.71 g, 6.12 mmol) in tetrahydrofuran (25 mL) dropwise at  $-78^\circ\text{C}$ . The resulting blue reaction mixture was stirred at  $-78^\circ\text{C}$  for 1 h to ensure complete deprotection of the thiolate functions. Solid ammonium chloride was added in small portions at  $-78^\circ\text{C}$  to destroy excess reducing agent. The resulting colorless suspension was allowed to warm to room temperature. After 12 h, the remaining solvent was distilled off at reduced pressure. The residue was taken up in water (20 mL) and the pH of the suspension adjusted to  $\approx 1$  to give a pale-yellow solution of  $\text{H}_2\text{L}^7$  as the dihydrochloride salt. To remove the inorganic salts the solution was concentrated in vacuum to a volume of  $\approx 20$  mL. Methanol (*ca.* 25 mL) was then added and the resulting solution was filtered off from NaCl and  $\text{NH}_4\text{Cl}$ . The latter two steps were repeated several times in this order, until no more salts precipitated upon addition of MeOH. Concentration of the filtrate afforded the title compound as a pale-yellow, air-sensitive powder. Yield: 2.42 g (98 %). –  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}/\text{CD}_3\text{OD}/\text{K}_2\text{CO}_3$ ):  $\delta$  = 3.02 (s, 8 H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 4.00 (s, 4 H,  $\text{ArCH}_2$ ), 7.09–7.42 (m, 8 H,  $\text{ArH}$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz,  $\text{CD}_3\text{OD}$ ,  $\text{D}_2\text{O}$ ):  $\delta$  = 51.3 ( $\text{NCH}_2\text{CH}_2\text{N}$ ), 60.6 ( $\text{ArCH}_2$ ), 129.6, 131.2, 133.1, 135.2, 135.4, 136.0. This material was used in the next step without further purification.

### Preparation of intermediate **8**

A mixture of 2-nitrobenzaldehyde (30.0 g, 0.199 mmol), potassium carbonate (32.9 g, 238 mmol), and ethanedithiol (9.35 g, 99.3 mmol) in DMF (80 mL) was stirred for 5 d at ambient temperature. After dropwise addition of water (500 mL), the resulting precipitate was filtered off, washed

with water and dried in air. The crude material was recrystallized from a mixed dichloromethane/cyclohexane solvent to give a pale-yellow microcrystalline solid. Yield: 22.8 g (76 %). M.p.  $123^\circ\text{C}$ . –  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.12 (s, 4 H,  $\text{SCH}_2\text{CH}_2\text{S}$ ), 7.25–7.32 (m, 4 H,  $\text{ArH}$ ), 7.40–7.48 (m, 2 H,  $\text{ArH}$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 32.7 ( $\text{SCH}_2$ ), 126.7, 129.3, 132.6, 134.5, 135.1, 140.1 ( $\text{C}^{\text{Ar}}$ ), 191.8 ( $\text{CHO}$ ). This material was used in the next step without further purification.

### Preparation of ligand $\text{L}^2$

Solutions of **8** (3.02 g, 10.0 mmol) in dichloromethane (100 mL) and ethylenediamine (601 mg, 10.0 mmol) in ethanol (100 mL) were added simultaneously over a period of 5 h to a mixture of dichloromethane (400 mL) and ethanol (200 mL). After complete addition, the reaction mixture was stirred for 24 h at r. t. A solution of sodium borohydride (1.50 g, 38.7 mmol) in ethanol (150 mL) was added. After stirring at r. t. for 24 h, the reaction mixture was acidified to pH = 1 with conc. hydrochloric acid and the resulting colorless suspension was evaporated to dryness. Water (150 mL) and dichloromethane (300 mL) were added to the residue, the pH of the aqueous phase was adjusted to 13 with 3 M aqueous potassium hydroxide and the heterogeneous mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with dichloromethane ( $5 \times 50$  mL). The combined organic fractions were dried over anhydrous sodium sulfate. Evaporation of the solvent gave a colorless oil which was purified by column chromatography on  $\text{SiO}_2$  using  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (10 : 1) as eluent. Addition of cyclohexane to a solution of  $\text{L}^2$  in  $\text{CH}_2\text{Cl}_2$  afforded colorless crystals. Yield: 2.28 g (69 %). M.p.  $86^\circ\text{C}$ . –  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.83 (s, 4 H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.81 (s, 4 H,  $\text{SCH}_2\text{CH}_2\text{S}$ ), 3.74 (s, 4 H,  $\text{ArCH}_2$ ), 7.05–7.34 (m, 8 H,  $\text{ArH}$ ). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (50.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 34.3 ( $\text{SCH}_2\text{CH}_2\text{S}$ ), 48.0 ( $\text{NCH}_2\text{CH}_2\text{N}$ ), 52.3 ( $\text{ArCH}_2$ ), 127.6, 128.4, 131.5, 132.1, 134.2, 141.8. This material was used in the next step without further purification.

### Preparation of ligand $\text{L}^{2,\text{Me}}$

The macrocyclic amine-thioether  $\text{L}^2$  (2.28 g, 6.90 mmol) was dissolved in 96 % formic acid (2.39 g, 50.0 mmol). To the clear solution was added a 35 % aqueous solution of formaldehyde (2.31 g, 108 mmol). The reaction mixture was heated under reflux for 20 h, after which time it was concentrated to dryness. Water (50 mL) and dichloromethane (100 mL) were added to the sticky residue, the pH of the aqueous phase was adjusted to 13 by the addition of 3 M aqueous potassium hydroxide solution and the heterogeneous mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with dichloromethane ( $3 \times 100$  mL). The combined organic frac-



tions were dried over  $K_2CO_3$  and filtered. Evaporation of the solvent gave  $L^{2,Me}$  as a colorless oil (2.40 g, 97 %). –  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  = 2.04 (s, 6 H,  $NCH_3$ ), 2.79 (s, 4 H,  $NCH_2CH_2N$ ), 3.14 (s, 4 H,  $SCH_2CH_2S$ ), 3.66 (s, 4 H,  $ArCH_2$ ), 7.01–7.19 (m, 4 H,  $ArH$ ), 7.33–7.38 (m, 4 H,  $ArH$ ). –  $^{13}C\{^1H\}$  NMR (50.3 MHz,  $CDCl_3$ ):  $\delta$  = 34.1 ( $SCH_2CH_2S$ ), 43.6 ( $NCH_3$ ), 48.4 ( $NCH_2CH_2N$ ), 61.8 ( $ArCH_2$ ), 127.4, 128.1, 131.8, 132.3, 134.2, 141.0. This material was used in the next step without further purification.

#### Preparation of $[Ni^{II}Cl_2(2)]$ (9)

To a solution of **2** (417 mg, 1.00 mmol) in methanol (10 mL) was added  $NiCl_2 \cdot 6H_2O$  (238 mg, 1.00 mmol). The resulting pale-blue solid was isolated by filtration and recrystallized from methanol. Yield: 390 mg (81 %). M.p. 213 °C (decomp.). – IR (KBr):  $\nu$  = 3294, 3251, 3055, 2967, 2864, 1436, 1363, 1007, 928, 905, 816, 765, 751, 680, 629  $cm^{-1}$ . – UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon_{max})$  = 288 (2620), 380 (36), 628 (21), 1068 nm ( $19 M^{-1}cm^{-1}$ ). –  $C_{48}H_{72}Cl_2N_4NiS_4$  (865.46): calcd. C 59.87, H 7.54, N 5.82; found C 59.80, H 7.54, N 5.79.

#### $[Ni^{II}(L^6)]$ (10)

To a solution of  $H_2L^6 \cdot 2HCl$  (2.40 g, 5.92 mmol) in methanol (40 mL) was added 5.93 mL of a 1.0 M solution of  $NiCl_2 \cdot 6H_2O$  in methanol. To the resulting pale-green solution was added dropwise a solution of triethylamine (2.39 g, 23.7 mmol) in methanol (2 mL). The resulting dark-green solid was isolated by filtration and recrystallized from acetonitrile. Yield: 1.49 g (65 %). M.p. 184 °C (decomp.). – IR (KBr):  $\nu$  = 3053, 3018, 2905, 1584, 1559, 1466, 1437, 1416, 1072, 1054, 1040, 839, 829, 796, 739, 683  $cm^{-1}$ . – UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon_{max})$  = 514 (251), 656 nm ( $313 M^{-1}cm^{-1}$ ). –  $^1H$  NMR (200 MHz,  $CD_3CN$ ):  $\delta$  = 2.22 (d,  $^2J$  = 12 Hz, 2 H,  $CH_2$ ), 2.49 (s, 6 H,  $NCH_3$ ), 3.08–3.25 (q,  $^2J$  = 12 Hz, 4 H,  $CH_2$ ), 4.33 (d,  $^2J$  = 12 Hz, 2 H,  $CH_2$ ), 6.81–6.98 (m, 6 H,  $ArH$ ), 7.28 (m, 2 H,  $ArH$ ). –  $C_{18}H_{22}N_2NiS_2$  (389.20): calcd. C 55.55, H 5.70, N 7.20; found C 55.43, H 5.72, N 7.19.

#### $[Ni^{II}(L^7)]$ (11)

To a solution of  $H_2L^7 \cdot 2HCl$  (2.10 g, 5.21 mmol) in methanol (30 mL) was added 5.21 mL of a 1.0 M solution of  $NiCl_2 \cdot 6H_2O$  in methanol. To the resulting brown-green solution was added dropwise a solution of triethylamine (2.39 g, 23.7 mmol) in methanol (10 mL). The resulting dark-red solid was isolated by filtration and recrystallized from acetonitrile. Yield: 1.45 g (72 %). M.p. 167 °C (decomp.). – IR (KBr):  $\nu$  = 2883, 2865, 1579, 1556, 1459, 1434, 1385, 1201, 1090, 1062, 803, 764, 673  $cm^{-1}$ . – UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon_{max})$  = 488 (597), 566 nm ( $233 M^{-1}cm^{-1}$ ). –  $^1H$  NMR

(200 MHz,  $[D_6]DMSO$ ):  $\delta$  = 2.47 (d,  $^2J$  = 6.1 Hz, 2 H,  $CH_2$ ), 3.16 (m, 8 H,  $CH_2$ ), 3.52 (d,  $^2J$  = 6.1 Hz, 2 H,  $CH_2$ ), 6.81–6.98 (m, 6 H,  $ArH$ ), 7.28 (m, 2 H,  $ArH$ ). –  $C_{18}H_{20}N_2NiS_2$  (387.19): calcd. C 55.84, H 5.21, N 7.24; found C 55.79, H 5.28, N 7.23.

#### $[Ni^{II}_2(\mu-Cl)_2(L^2)_2](ClO_4)_2$ (12)

To a solution of  $L^2$  (500 mg, 1.51 mmol) in methanol (20 mL) was added a solution of  $NiCl_2 \cdot 6H_2O$  (357 mg, 1.50 mmol) in methanol (5 mL). The resulting blue reaction mixture was stirred for one hour. Then solid  $LiClO_4 \cdot 3H_2O$  (481 mg, 3.00 mmol) was added. The resulting microcrystalline solid was isolated by filtration, washed with isopropanol and dried in air. The crude material was recrystallized from acetonitrile. Yield: 513 mg (65 %). M.p. 290 °C (decomp.). – IR (KBr):  $\nu$  = 3435, 3279, 2943, 2886, 2012, 1629, 1591, 1469, 1435, 1393, 1365, 1295, 1275, 1259, 1213, 1198, 1164, 1097, 1035, 1016, 992, 964, 948, 925, 903, 866, 773, 731, 688, 623, 582, 505, 463, 449  $cm^{-1}$ . – UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon_{max})$  = 580 (56), 1032 nm ( $50 M^{-1}cm^{-1}$ ). –  $C_{36}H_{44}Cl_4N_4Ni_2O_8S_4$  (1048.22): calcd. C 41.25, H 4.23, N 5.34, S 12.24; found C 41.25, H 3.79, N 5.45, S 12.49.

#### $[Ni^{II}(NCS)_2(L^2)]$ (13)

To a solution of  $L^2$  (500 mg, 1.51 mmol) in methanol (20 mL) was added a solution of  $NiCl_2 \cdot 6H_2O$  (357 mg, 1.50 mmol) in methanol (5 mL). The resulting blue-purple solution was stirred overnight and treated with a solution of  $NaSCN$  (243 mg, 3.00 mmol) in water (5 mL). The reaction mixture was stirred for one hour to give a purple crystalline powder, which was isolated by filtration, washed with isopropanol and dried in air. The crude material was purified by recrystallization from a mixed acetonitrile/methanol solvent. Large blue blocks. Yield: 515 mg (68 %). M.p. > 300 °C (decomp.). – IR (KBr):  $\nu$  = 3237, 3206  $\nu(NH)$ , 3060, 2967, 2922, 2866, 2107, 2089  $\nu(SCN)$ , 1474, 1462, 1445, 1430, 1388, 1364, 1334, 1298, 1271, 1260, 1238, 1216, 1206, 1198, 1159, 1147, 1130, 1080, 1068, 1036, 1017, 1001, 959, 942, 937, 927, 904, 870, 867, 851, 795, 790, 773, 752, 690 683, 618, 606, 581, 510, 475, 472, 467, 463, 442  $cm^{-1}$ . – UV/vis ( $CH_2Cl_2$ ):  $\lambda_{max}(\epsilon_{max})$  = 592 (78), 1055 nm ( $63 M^{-1}cm^{-1}$ ). –  $C_{20}H_{22}N_4NiS_4$  (505.37): calcd. C 47.53, H 4.39, N 11.09; found: C 47.82, H 4.22, N 10.93.

#### $[Ni^{II}Cl_2(L^{2,Me})]$ (14)

To a solution of  $L^{2,Me}$  (500 mg, 1.39 mmol) in methanol (20 mL) was added 1.39 mL of a 1.0 M solution of  $NiCl_2 \cdot 6H_2O$  in methanol to give a pale-green solution. A green solid was obtained upon concentration of the solution.

This material was filtered and recrystallized from acetonitrile. Yield: 306 mg (72 %). M. p. 202 °C (decomp.). – IR (KBr):  $\nu = 3052, 2865, 1579, 1471, 1424, 1370, 1266, 1067, 1035, 841, 610 \text{ cm}^{-1}$ . – UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}(\epsilon_{\text{max}}) = 626 (21), 1082 \text{ nm} (19 \text{ M}^{-1}\text{cm}^{-1})$ . –  $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{N}_2\text{NiS}_2$  (488.16): calcd. C 49.21, H 5.37, N 5.74; found: C 49.20, H 5.31, N 5.73.

#### X-Ray crystallography

Crystals of **9** were grown by diffusion of MeOH into a  $\text{CH}_2\text{Cl}_2$  solution. Crystals of **10** were obtained by diffusion of MeOH into a  $\text{CH}_3\text{CN}$  solution. Crystals of **11** and **12** were produced by recrystallization from acetonitrile. Crystals of **13** were grown by recrystallization from a mixed acetonitrile/methanol solvent. Crystal data and data collection details are reported in Table 1. The diffraction experiments were carried out at 210(2) K on a BRUKER CCD X-ray diffractometer using  $\text{MoK}\alpha$  radiation. The data were processed with SAINT [36] and corrected for absorption using SADABS [37]. Structures were solved by Direct Methods and refined by full-matrix least-squares on the basis of all data against  $F^2$  using SHELXL-97 [38]. H atoms were placed in

calculated positions and treated isotropically using the 1.2-fold  $U_{\text{iso}}$  value of the parent atom except methyl protons, which were assigned the 1.5-fold  $U_{\text{iso}}$  value of the parent C atoms. All non-hydrogen atoms were refined anisotropically.

In the crystal structure of **11** the Flack  $x$  parameter (absolute structure parameter) was calculated to be 0.02(1) for the present structure and 0.98(2) for the inverted structure providing strong evidence that the absolute structure has been assigned correctly.

CCDC 624429 (**9**), CCDC 624430 (**10**), CCDC 624431 (**11**), CCDC 624432 (**12**), and CCDC 624433 (**13**) contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (project KE 585/3-1,2,3). We thank Prof. Dr. H. Vahrenkamp for providing facilities for X-ray crystallographic measurements.

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