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Note

# Square planar nickel compounds with bulky thiols

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### Abstract

Details of the syntheses and the results of X-ray structural analyses of square planar Ni compounds with aliphatic thiolato-sulfur ligands, [Ni(dpmep)<sub>2</sub>] (1) and [Ni(tptd)] (2), where Hdmep and H<sub>2</sub>tpttd are the abbreviations for 2-(2,2-diphenyl-2-mercaptoethyl)pyridine and 2,2',11,11'-tetraphenyl-1,5,8,12-tetrathiadodecane, respectively, are presented. Each of the thiolato-sulfur atoms of these compounds is sterically protected by two benzene rings at the  $\alpha$  carbon position to suppress dimerization upon synthesis. 1 · 1.5CH<sub>2</sub>Cl<sub>2</sub>·MeCN crystallizes monoclinic *P*2<sub>1</sub>/*n* with *a* = 18.362(3), *b* = 16.894(4), *c* = 13.273(4) Å,  $\beta$  = 104.59(2)°, *V* = 3984(3) Å<sup>3</sup> and *Z* = 4. 2 · 1.5MeCN crystallizes triclinic  $\vec{P1}$  with *a* = 15.091(6), *b* = 15.661(3), *c* = 14.085(7) Å,  $\alpha$  = 96.00(2),  $\beta$  = 90.89(4),  $\gamma$  = 99.70(2)°, *V* = 3261(4) Å<sup>3</sup> and *Z*=4. The Ni-S and Ni–N bond lengths of 1 were compared with those of the nickel center in the A-cluster of carbon monoxide dehydrogenase. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Electrochemistry; Carbon monoxide dehydrogenase; Nickel complexes; Thiolato complexes

#### 1. Introduction

Carbon monoxide dehydrogenase (CODH) is the nickel enzyme which catalyzes the reversible oxidation of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>) and the synthesis of acetyl coenzyme A (acetyl-CoA) from CO, coenzyme A (CoASH) and the methylated corrinoid [1]. Several Ni-S compounds of the alkane thiolate type have been reported [2] as the structural models of the nickel centers of CODH. According to the incipient work on CODH using extended X-ray absorption fine structure (EXAFS) experiments [3], we previously reported an example on CO ligation to Ni using an NiS<sub>4</sub> compound, in which the sulfur atoms of the alkane thielates were sterically protected by benzene rings at the  $\alpha$ carbon positions to suppress side reactions upon reduction as well as dimerization upon synthesis [4]. However, the EXAFS results for CODH reflected the average nickel environments. Thus, in a later EXAFS work for CODH using an isolated a-subunit, it was reported that the nickel ion, probably in the A-cluster [5], adopts an NiS<sub>2</sub>N(O)<sub>2</sub> coordination with distorted square planar geometry or a square pyramidal geometry [6]. We report here on the synthesis and the molecular structure of a square planar NiS<sub>2</sub>N<sub>2</sub> compound

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Fig. 1. [Ni(dpmep)<sub>2</sub>] (1) and [Ni(dpttd)] (2).

[Ni(dmep)<sub>2</sub>] (1) (Fig. 1) (Hdpmep = 2-(2,2-diphenyl-2mercaptoethyl)pyridine), in which the sulfur atoms are similarly protected, as well as on the details of the synthesis of [Ni(tpttd)] (2) (Fig. 1) (H<sub>2</sub>tpttd = 2,2',11,11'-tetraphenyl-1,5,8,12-tetrathiadodecane) and the results of an X-ray crystallographic analysis of the newly obtained crystal of 2 [4]. We also report the structural comparison of 1 and 2, and the nickel unit in the  $\alpha$ -subunit of CODH [6].

## 2. Experimental

#### 2.1. Materials

2-Picolylchloride hydrochloride was obtained from Aldrich Chemicals. Diphenylmethylthiotetrahydro-2*H*-pyrane was prepared according to a previously described method [7]. 1,8-Dibromo-3,6-dithiaoctane for H<sub>2</sub>tpttd synthesis was also prepared according to the previously described method [8]. [Ni(ttu)] (3) (H<sub>2</sub>ttu = 1,4,8,11-tetrathia-undecane)

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Fig. 2. Synthetic routes for [Ni(dpmep)2] (1) and [Ni(dpttd)] (2).

for comparative study was prepared as described previously [9]  $^{1}$ . H<sub>2</sub>ttu was prepared by the method of Rosen and Busch [10].

1 and 2 were synthesized according to the scheme shown in Fig. 2. The effective deprotection of the THP group [11,12] in this scheme was achieved by the method we previously developed [13].

# 2.1.1. Synthesis of 2-[2,2-diphenyl-2[(tetrahydro-2Hpyran-2-yl)thio]ethyl]pyridine hydrochloride (4)

2-Picolylchloride was freshly generated from commercially available 2-picolylchloride hydrochloride by treating the chloroform solution (1.5 g/100 ml) with 50 ml of 10% Na2SO4 aqueous solution. The chloroform layer was washed with water twice and dried with MgSO4. After the removal of the solvent, the residue was dissolved in hexane, passed through an alumina column and dried in vacuo. 2-Diphenylmethylthiotetrahydro-2H-pyrane (1.97 g, 6.93 mmol) was dissolved in 60 ml of tetrahydrofuran (THF). The solution was cooled down to -78°C, and 4.3 ml of 1.60 M n-butyllithium in hexane were added slowly. The solution immediately changed color to orange, then it gradually precipitated yellow materials. 10 ml THF solution containing 0.97 g (7.6 mmol) of 2-picolylchloride were added to this solution, and the solution was stirred overnight while the temperature was gradually lowered to  $-20^{\circ}$ C. Then, the reaction was quenched by the addition of 100 ml of water (Na<sub>2</sub>HPO<sub>4</sub>/ NaH<sub>2</sub>PO<sub>4</sub> buffer solution, pH 7). After the removal of THF, the target compound was extracted from the residue twice in 50 ml of CHCl<sub>3</sub>. This organic layer was washed with 50 ml of the buffer solution (pH 7) twice, 50 ml of water twice, and 50 ml of 1 N HCl aqueous solution twice, then dried over MgSO<sub>4</sub>. The residue was triturated in ether and dried in vacuo. The yield was 2.05 g (72.2%). Anal. Calc. for  $C_{24}H_{26}ONSCl$  ( $C_{24}H_{25}ONS \cdot HCl$ ): C, 69.97; H, 6.36; N, 3.40. Found: C, 69.68; H, 6.46; N, 3.33%.

# 2.1.2. Synthesis of 2-(2,2-diphenyl-2-mercaptoethyl)pyridine hydrochloride (5)

262.4 mg (0.637 mmol) of 4 were dissolved in 10 ml of CHCl<sub>3</sub> and treated with 10 ml of aqueous Na<sub>2</sub>CO<sub>3</sub> solution twice. The organic layer was washed with 10 ml of water twice and dried in vacuo. The oily residue was dissolved in 10 ml of CH2Cl2, into which 2.2 ml of 2-hydroxyethanethiol (31 mmol) and 140 ml of TiCl<sub>4</sub> (1.3 mmol) dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> were added. The solution was stirred for 24 h. The reaction was guenched with 1 N HCl aqueous solution. The aqueous layer was isolated and washed with 10 ml of CHCl<sub>3</sub> twice. The washings were combined with the organic layer and washed with 20 ml of 1 N HCl aqueous solution twice. The solvents were removed and dried in vacuo. The residue was recrystallized from ethyl acetate/ether. Brownblack crystals were obtained. The yield was 194.7 mg (93.2%). Anal. Calc. for C19H18NSCI . 0.5H2O: C, 67.74; H, 5.67; N, 4.16. Found: C, 67.72; H, 5.96; N, 4.27%.

# 2.1.3. Synthesis of [Ni(dpmep)<sub>2</sub>] (1)

327.8 mg of 5 (1.00 mmol) were dissolved in 15 ml of CHCl<sub>3</sub>. The solution was washed with 10 ml of 10% NaHCO<sub>3</sub> aqueous solution twice, then with 10 ml of water, and the solvent was removed. The residue was dissolved in 15 ml of CH<sub>2</sub>Cl<sub>2</sub>, into which were added 138.5 mg of Ni(acac)  $\cdot$  2H<sub>2</sub>O (0.473 mmol) and 10 ml of MeCN. The solution was stirred for 30 min, and the solvents were removed. The target compound was obtained as brown-black crystals by recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub>/MeCN. The yield was 276.4 mg (91.4%). Anal. Calc. for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>S<sub>2</sub>Ni: C, 71.37; H, 5.04; N, 4.38. Found: C, 71.48; H, 5.18; N, 4.44%.

<sup>&</sup>lt;sup>1</sup> The details of the synthesis of [Ni(ttu)] are as follows. 1.0 g (4.38 mmol) of H<sub>2</sub>ttu was dispersed in an aqueous alkaline solution (50 ml) containing 0.575 g of potassium hydroxide (8.76 mmol). Into this solution was added dropwise an aqueous solution (150 ml) of nickel chloride (1.04 g, 4.38 mmol). The solution changed color immediately to brown. Then, the reaction mixture was warmed to 50°C and filtered. The filtrate was allowed to cool down to room temperature, and stand for several days. The redbrown crystals of [Ni(ttu)] were collected and dried in vacuo. The yield was 0.57 g (45.6%). Anal. Calc. for C<sub>4</sub>H<sub>7</sub>S<sub>4</sub>Ni (3): C, 29.47; H, 4 95. Found: C, 29.17; H, 4.78%. A<sub>max</sub> (nm) in DMSO ( $\epsilon$  (×1000 dm<sup>2</sup> mol<sup>-1</sup>): 636 (51), sh, 532 (116), sh, 432 (363).

## 2.1.4. Synthesis of 1,12-dipyran-2,2',11,11'-tetraphenyl-1,5,8,12-tetrathiadodecane (6)

2-Diphenylmethylthiotetrahydro-2H-pyrane (15.6 g, 54.8 mmol) was dissolved in 260 ml of THF. The solution was cooled down to -65°C, and 34 ml of 1.68 M n-butyllithium in hexane were added slowly. After stirring for 1 h, a THF (35 ml) solution containing 8.45 g (27.4 mmol) of 1,8dibromo-3,6-dithiaoctane was added slowly. The reaction mixture was stirred for several hours at -65°C then allowed to warm to room temperature for completion of the reaction. The solvent was removed, and the residue was redissolved in 200 ml of CHCl<sub>2</sub>, and washed with 200 ml of phosphate buffer (pH 7). The organic layer was combined with the second extract from this aqueous layer, and dried over MgSO<sub>4</sub>. The solvent was removed, and the residue was recrystallized from acetone. A white powder (12.0 g, yield 61.3%, purity 98.2% by HPLC) was obtained. Further recrystallization was performed from CHCl<sub>3</sub>/MeOH. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 1.30-1.80 (12H, -CH<sub>2</sub>-), 2.05 (2H, -CH2-), 2.40-2.90 (10H, -CH2-), 3.30 (2H, -CH2-), 3.90-4.00 (2H, --CH2--), 4.05--4.15 (2H, --CH--), 7.12--7.44 (20H, Ph). Anal. Calc. for C42H50O2S4 · 0.5H2O: C, 69.67; H, 7.10. Found: C, 69.24; H, 6.87%.

## 2.1.5. Synthesis of 2,2',11,11'-tetraphenyl-1,5,8,12-tetrathiadodecane, H,tpttd (7)

4.98 g (6.96 mmol) of 6 were dissolved in 110 ml of CH<sub>2</sub>Cl<sub>2</sub>, into which were added 50 ml of 2-mercaptoethanol (713 mmol) and 10 ml of triethylamine (71.7 mmol). The solution was cooled down with an ice-water bath, and a solution of 11.2 g of TiCl<sub>4</sub> (59.0 mmol) in 110 ml of CH<sub>2</sub>Cl<sub>2</sub> was added slowly into this. The solution, which gradually changed color from yellow to orange-red, was stirred overnight, then washed with 1 M HCl aqueous solution (250 ml) and water (250 ml × 3). The solvent was removed, and the residue was dried in vacuo. A pale yellow oil (3.85 g, 91.4% purity by HPLC) was obtained. The yield was 3.52 g (92.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta 2.15-2.80$  (14H,  $-CH_2-$  and SH), 7.15-7.55 (20H,  $C_6H_5-$ ). Anal. Calc. for C<sub>33</sub>H<sub>34</sub>S<sub>4</sub>·0.5CHCl<sub>3</sub>: C, 63.25; H, 5.59; S, 20.70. Found: C, 63.31; H, 5.39; S, 19.50%.

# 2.1.6. [(2,2',11,11'-Tetraphenyl-1,5,8,12-tetrathiadodecane)nickel(II)] · 2DMF ([Ni(tpttd)] · 2DMF) (2)

Into a toluene solution (400 ml) of compound 7 (oily; 3.85 g, 6.44 mmol), 1.66 g (6.44 mmol) of Ni(acac)<sub>2</sub>·2H<sub>2</sub>O dissolved in 250 ml of toluene were added slowly. The reaction mixture, which changed color from pale brown to brown-black, then gradually to dark violet with the precipitation of a black powder, was stirred overnight. The precipitates were collected by filtration and dissolved in 400 ml of DMF. The solution was concentrated to 300 ml and stored in a refrigerator at  $-15^{\circ}$ C. The target compound, crystallized as red-violet crystals of [Ni(tpttd)]·2DMF, was collected by filtration, washed with ether, and dried in vacuo. The second crop was collected from the filtrate in the same way. The yield was 3.63 g (6.01 mmol; 75.5%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 270 MHz):  $\delta$  3.04 (4H, -CH<sub>2</sub>-), 3.37 (8H, -CH<sub>2</sub>-), 7.10-8.20 (20H, ring). *Anal.* Calc. for C<sub>38</sub>H<sub>48</sub>N<sub>2</sub>O<sub>3</sub>S<sub>4</sub>Ni (2·2DMF·H<sub>2</sub>O): C, 59.44; H, 6.30; N, 3.65. Found: C, 59.42; H, 6.12, N, 3.67%.  $\lambda_{max}$  (nm) in DMSO ( $\epsilon$  (×1000 dm<sup>2</sup> mol<sup>-1</sup>): 574 (464), 475 (695).

#### 2.2. Structure determinations

Reddish brown crystals of 1 were grown in MeCN at - 15°C. Brown-black crystals of 2 were grown by cooling a concentrated solution of 2 in  $CH_2Cl_2/MeCN$  at  $-15^{\circ}C$ . Because of the rapid loss of crystallinity at room temperature, the mounting and sealing of the crystals of 1 and 2 were performed in a glass capillary tube. The X-ray data collections were carried out on a Rigaku AFC-5 diffractometer at - 80°C for 1 and at  $-60^{\circ}$ C for 2. Graphite-monochromated Mo K $\alpha$ radiation ( $\lambda = 0.710680$  Å) was used as the X-ray source. Automatic centering and least-squares routines were carried out to determine the cell parameters with 20 reflections  $(20 < 2\theta \le 25^\circ)$  for 1 and 20 reflections  $(25 < 2\theta \le 30^\circ)$  for 2, respectively. All data were corrected for Lorentz and polarization effects. Intensities of three check reflections monitored every 100 reflections did not show any decay. The structures of 1 and 2 were solved by the direct methods (SAPI91) and expanded using Fourier techniques (DIR-DIF). All non-hydrogen atoms were refined anisotropically. The final structure of 1 was refined by full-matrix leastsquares refinements (TEXSAN) based on 3933 observed reflections  $(I > 5\sigma(I))$  with 469 variable parameters. The final structure of 2 was refined by full-matrix least-squares refinements (TEXSAN) based on 6082 observed reflections  $(I>3\sigma(I))$  with 748 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.75 and -0.95 e Å<sup>-3</sup> for 1 and to 1.21 and  $-0.69 \text{ e} \text{ Å}^{-3}$  for 2, respectively. The discrepancy indices are R = 0.057 and Rw = 0.054 for 1, and R = 0.060 and Rw = 0.063 for 2.

The crystallographic details for 1 and 2 are shown in Table 1. For further details see Section 4.

#### 3. Results and discussion

Fig. 3 shows the molecular structures of 1 and 2. As can be seen, both compounds adopt a square-planar coordination geometry. The crystal  $2 \cdot 1.5$ MeCN involved two kind of crystallographically independent [Ni(tpttd)] molecules: [Ni(tpttd)]-(1) and [Ni(tpttd)]-(2), each of which forms the mirror image of the other with respect to the NiS<sub>4</sub> plane. The structure shown exhibits [Ni(tpttd)]-(1). Selected bond angles and lengths for 1 and 2 are summarized in Tables 2 and 3, respectively.

The axial parts of the nickel ion of 1 are not sterically protected by the benzene rings, in contrast to the case of compound 2. The mean Ni-N and Ni-S bond distances of 1

Table 2

 $\label{eq:constraint} \begin{array}{l} Table \ l \\ Crystallographic details of \ [Ni(dpmep)_2] \cdot 1.5CH_2Cl_2 \cdot MeCN \ (1 \cdot 1.5CH_2 - Cl_2 \cdot MeCN) \ and \ [Ni(tptd)] \cdot 1.5MeCN \ (2 \cdot 1.5MeCN) \end{array}$ 

Complex	1 · 1.5CH2Cl2 · McCN	2 · 1.5MeCN	
Formula	C42H38N3S2NiCl3 C35H395N15S4Ni		
Formula weight	813.96	668.15	
Crystal system	monoclinic	triclinic	
Space group	$P2_1/n$	РĨ	
a (Å)	18.362(3)	15.091(6)	
ь(Å)	16.894(4)	15.661(3)	
c (Å)	13.273(4)	14.085(7)	
α (°)	90.0	96.00(2)	
β(°)	104.59(2)	90.89(4)	
γ(°)	90.0	99.70(2)	
V (Å <sup>3</sup> )	3984(3)	3261(4)	
Z	4	4	
$D_{calc}$ (g cm <sup>-3</sup> )	1.36	1.36	
Crystal size (mm)	0.4×0.2×0.1	0.5×0.5×0.45	
Radiation, $\lambda$ (Å)	graphite-monochromatized Mo Ka, 0.710680		
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	8.3	8.8	
Scan mode	ω-2θ	ω-2θ	
Scan speed (° min <sup>-1</sup> )	6.0	10.0	
Temperature (°C)	- 80	60	
20 Range (°)	3-45	3-45	
Octant measured	$\pm h$ , $+k$ , $+l$	$\pm h, \pm k, \pm l$	
Measured reflections	5419	8941	
No. observations	$3933 (I > 5\sigma(I))$	$6082 (I > 3\sigma(I))$	
No. variable parameters	469	748	
R(%)	5.69	5.97	
Rw (%)	5.43	6.30	
Goodness of fit indicators	5.14	2.58	
Max. peak (e Å <sup>-3</sup> )	1.75	1.21	
Min. peak (e Å <sup>-3</sup> )	-0.95	- 0.69	

$$\begin{split} R &= \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}, Rw = [\sum [w(|F_{o}| - |F_{c}|)^{2}] / \sum w |F_{o}|^{2}]^{1/2}, w = 1/\sigma^{2} (|F_{o}|). \end{split}$$

are 1.923(2) and 2.171(2) Å, respectively. These values are in agreement with those of previously reported NiNS<sub>3</sub> and NiN<sub>2</sub>S<sub>2</sub> compounds of alkane thiolate type: Ni-N = 1.910(3) and Ni-S = 2.177(1) Å for NiS<sub>3</sub>N [2a]; Ni-N = 1.857(3) and Ni-S = 2.179(1) Å [2b], Ni-N = 1.995(3) and Ni-S = 2.159(3) Å [2c], Ni-N = 1.991(7) and Ni-S = 2.168(2) Å [2d] for NiS<sub>2</sub>N<sub>2</sub>. On the other hand, the deviations of Ni, N1, N2, S1 and S2 from the least-squares plane of NiN<sub>2</sub>S<sub>2</sub> for 1 are 0.002(1), -0.022(2), 0.022(2), 0.133(5) and -0.173(5) Å, respectively. This indicates that

$1.5 \text{CH}_2 \text{Cl}_2 \cdot \text{MeCN} (1 \cdot 1.5 \text{CH}_2 \text{Cl}_2 \cdot \text{MeCN})$					
Bond distances (Å	)				
Ni-S1	2.180(2)	C14-C15	1.397(9)		
Ni-S2	2.162(2)	C15-C16	1.489(9)		
Ni-NI	1.926(5)	C16-C17	1.567(8)		
Ni-N2	1.919(5)	C17-C18	1.519(8)		
SI-C17	1.852(6)	C17-C24	1.543(8)		
S2-C37	1.850(6)	C34-C35	1.381(8)		
NI-C11	1.349(8)	C35-C36	1.499(8)		
N1-C15	1.350(7)	C36-C37	1.538(9)		
N2-C31	1.348(8)	C37–C38	1.536(8)		
N2-C35	1.339(7)	C37C44	1.559(8)		
Bond angles (°)					
SI-Ni-S2	81.91(7)	C15-C16-C17	110.8(5)		
SI-Ni-NI	93.6(2)	S1-C17-C16	108.4(4)		
SI-Ni-N2	172.9(2)	SI-C17-C18	105.2(4)		
\$2-Ni-N1	173.6(2)	S1-C17-C24	113.4(4)		
S2-Ni-N2	94.1(2)	C16-C17-C18	111.0(5)		
N1-Ni-N2	90.8(2)	C16-C17-C24	108.4(5)		
Ni-S1-C17	107.6(2)	C18-C17-C24	110.4(5)		
Ni-S2-C37	108.6(2)	N2-C35-C34	121.8(6)		
Ni-N1-C11	118.4(4)	N2-C35-C36	117.5(6)		
Ni-NI-C15	122.3(5)	C34-C35-C36	120.5(6)		
C11-N1-C15	119.3(6)	C35-C36-C37	110.4(5)		
Ni-N2-C31	117.3(4)	S2-C37-C36	109.4(4)		
Ni-N2-C35	124.6(4)	S2-C37-C38	104.3(4)		
C31-N2-C35	117.8(6)	S2-C37-C44	113.7(5)		
N1-C15-C14	120.2(6)	C36-C37-C38	112.8(6)		
NI-CI5-CI6	117.4(6)	C36-C37-C44	107.0(5)		
C14-C15-C16	122.3(6)	C38-C37-C44	109.8(5)		

Selected bond distances (Å) and angles (°) for  $[Ni(dpmep)_2]$ .

the coordination unit of 1 is slightly distorted from planar to tetrahedral.

The Ni-N(O) and Ni-S bond lengths obtained from the best fits of the EXAFS spectra of CODH (as isolated and reduced) are 1.89 and 2.19 Å, respectively [6]. These values agree with those of 1, as well as those of Ni-N and Ni-S referenced above [8] within the accuracy of EXAFS experiment and analysis.

The nickel ion of 2 is covered by two benzene rings from the same side of the NiS<sub>4</sub> plane in the solid state, and the observed distances between the nickel ion and the closest ring protons are 2.493 and 2.821 Å, corresponding to [Ni(tpttd)]-(1) and [Ni(tpttd)]-(2), respectively. These molecular



Fig. 3. Molecular structures of [Ni(dpmep)<sub>2</sub>] (1) and [Ni(dptd)]-(1) (2) with thermal ellipsoids drawn at 50% probabilities.

(2·1.5MeCN)					
Bond distances (Å)					
Ni1-S11	2.203(2)	C10-C11	1.56(1)		
Ni1-S12	2.165(2)	CI0-C17	1.54(1)		
Ni1-S13	2.141(2)	C10-C23	1.51(1)		
Nil-S14	2.160(2)	C23-C24	1.53(1)		
S11-C10	1.845(8)	C25-C26	1.53(1)		
\$12-C25	1.866(7)	C25-C32	1.55(1)		
S13-C39	1.811(8)	C25-C38	1.54(1)		
S13-C40	1.806(8)	C38-C39	1.51(1)		
S14-C24	1.817(8)	C40-C41	1.52(1)		
SI4-C41	1.832(9)				
Bond angles (°)					
SI1-Ni1-S12	83.61(9)	S11-C10-C23	111.5(5)		
SH1-Ni1-SI3	172.16(9)	C11C10C17	109.5(6)		
SI1-Ni1-SI4	89.68(9)	C11-C10-C23	113.3(6)		
S12-Ni1-S13	96.87(9)	C17-C10C23	107.9(7)		
SI2-Ni1-SI4	169.82(9)	C10C23C24	115.3(7)		
SI3-Ni1-S14	90.83(9)	S14-C24-C23	112.5(6)		
Nil-S11-C10	110.0(3)	S12-C25-C26	101.5(5)		
Ni1-S12-C25	113.8(3)	S12-C25-C32	113.5(6)		
Ni1-S13-C39	114.8(3)	S12-C25-C38	110.5(5)		
Ni1-S13-C40	103.5(3)	C26-C25-C32	108.4(7)		
C39-S13-C40	102.2(4)	C26-C25-C38	113.1(7)		
Ni1-S14-C24	108.9(3)	C32-C25-C38	109.7(6)		
Nil-SI4-C41	104.1(3)	C25-C38-C39	117.1(7)		
C24-S14-C41	100.5(4)	S13-C39-C38	116.1(5)		
S11-C10-C11	99.8(5)	S13-C40-C41	107.0(6)		
S11-C10-C17	114.8(5)	S14-C41-C40	106.7(6)		

 Table 3

 Selected bond distances (Å) and angles (°) for [Ni(tpttd)]-(2)·1.5MeCN

 (2·1.5MeCN)

structures of 2 differ from that obtained in our previous Xray analysis of the same compound, in which the nickel ion was covered by two benzene rings from both sides of the NiS<sub>4</sub> plane [4]. Each of the molecules found in the new crystal 2.1.5MeCN involves different forms of sixmembered rings, for example, Ni1S11C10C23C24S14 in [Ni(tpttd)]-(1) is in the chair form, whereas Ni1S12-C25C38C39S13 in [Ni(tpttd)]-(1) is in the boat form. On the other hand, both of the two six-membered rings observed in the crystal of our previous X-ray analysis are in the chair form. The isolation of the two conformers, chair-boat and chair-chair, in the solid state suggests that the solution containing 2 becomes the conformational mixture of these two. Fig. 4 shows the temperature dependent change observed in the ring proton region of the <sup>1</sup>H NMR spectrum of 2 in DMFd<sub>7</sub>. As seen in this figure, the o-, m- and p- protons of 2 behave with different coagulation temperatures. This stepwise change is not explained by the rotational motion of the benzene rings, but with conformational change including the alkane framework. In fact, we observed a similar temperature effect also in the methylene proton region (2-3.5 ppm).

The mean Ni–S bond distance in 1, 2.171(2) Å, is slightly shorter than the Ni–thiolato S distances, 2.184(2) and 2.198(2) Å of 2 and 2.201 Å of [Ni(ttu)] (3) [9], which also possesses a square planar NiS<sub>4</sub> coordination unit, but the framework differs from that of 2. This result indicates that the Ni–thiolato S bond strength is most increased in 1 com-



Fig. 4. The ring proton regions of the 'H NMR spectra of [Ni(dpttd)] (2) observed at different temperatures in DMF-d<sub>7</sub>.

pared with those in 2 and 3. The Ni-thioether S bond lengths of 2 are 2.150(2) and 2.153(2) Å<sup>2</sup>, which agree with the corresponding values (2.157 Å) in 3 [9]. Thus, 2 and 3 have almost the same Ni–S bond lengths.

The deviations of Ni, S1, S2, S3 and S4 in Ni(tpttd)]-(1) are -0.007(1), 0.145(2), -0.142(2), 0.137(2) and -0.144(2) Å, respectively. The comparison of the deviations of the atoms in coordination units, Ni, N1, N2, S1 and S2 of NiN<sub>2</sub>S<sub>2</sub> in 1 and Ni, S1, S2, S3 and S4 from NiS<sub>4</sub> in 2, from their least-squares planes indicates that the coordination unit of 2 is more distorted than that of 1. The coordination unit of 2 is twice as distorted compared with that of 1. This is simply explained by the fact that the ligand framework of 1 is disconnected, whereas that of 2 is not. However, the deviations of the ligand atoms of 2 are still smaller than the corresponding values of 3, -0.015(1), +0.265(2), -0.255(2), +0.269(2) and -0.264(2) Å. Thus the 1,5,8,12-tetrathiadodecane/Ni framework of 2 is more distorted that that of 1,4,8,11-tetrathiaundecane/Ni of 3. However, this difference in the NiS<sub>4</sub> units of 2 and 3 does not influence the S-C bond nature of these compounds 3.

### 4. Supplementary material

Full tables of bond distances and bond angles, tables of anisotropic thermal parameters, H atom coordinates, and cal-

 $<sup>^2</sup>$  The newly obtained values, 2.184(2) and 2.150(2) Å, for Ni-thiolato S and -thioether S bond distances for 2 are slightly different from those (2.177 and 2.170 Å) we observed for 2 in a previous study. This is probably due to the difference in the molecular structure caused by crystal packing. The previously analyzed crystal contained no solvent molecules in one unit cell.

<sup>&</sup>lt;sup>3</sup> The mean thiolato and thioether S-C distances for 2 are 1.852(8) and 1.816 Å, respectively, whereas these values for 3 are greater than those for 2, 1.866 and 1.828 Å, respectively.

culated and observed structural factors have been deposited with the Cambridge Crystallographic Data Center of Japan.

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