HETEROCYCLES, Vol. 93, No. 1, 2016, pp. 406 - 410. © 2016 The Japan Institute of Heterocyclic Chemistry
Received, 25th August, 2015, Accepted, 30th September, 2015, Published online, 19th October, 2015
DOI: 10.3987/COM-15-S(T)21

SYNTHESIS OF A CAGE-SHAPED NICKEL(II) COMPLEX OF BIS(4-CYCLOHEXYLAMINO-3-PYRIDYL)DISULFIDE WITH μ_2-Cl BRIDGING

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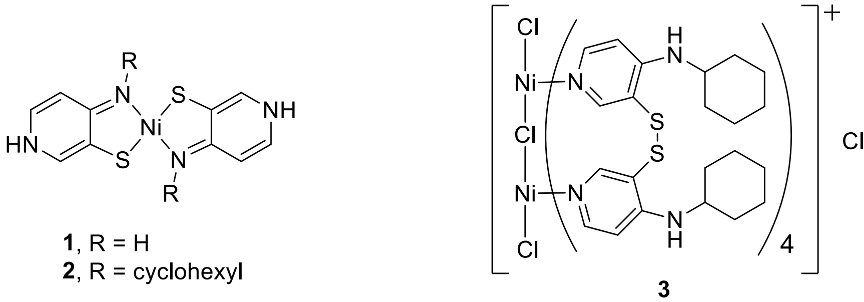
Dedicated to Professor Dr. Lutz F. Tietze on the occasion of his 75th birthday

Abstract – A cage-shaped nickel complex with μ_2-Cl bridging $[Ni_2(\mu\text{-}Cl)(\text{bis(4-cyclohexylamino-3-pyridyl)disulfide})_4Cl_2]Cl$ is isolated and characterized by X-ray crystallographic analysis.

Metal complex system $M(XYC_6H_4)_2$ (X, Y = NH, O, S) has long attracted much attention due to the potential application to electro-conductive, magnetic,[1] and third-order non-linear optical materials.[2] Recently, we have isolated a new Ni complex **1** with 4-amino-3-pyridinethiolate (apt) ligands and characterized its electrochemical and optical properties.[3] However, **1** suffered from poor solubility in most organic solvents and instability to air. In order to increase the solubility and stability of **1**, we decided to introduce a bulky substituent on the nitrogen atom that coordinates to the central Ni atom. However, contrary to our expectation for the synthesis of **2**, an unprecedented Ni complex **3**, which has a four-fold symmetric cage shape with μ_2-Cl bridging, was obtained. Herein we report the synthesis and characterization of a new cage-shaped Ni complex **3**.

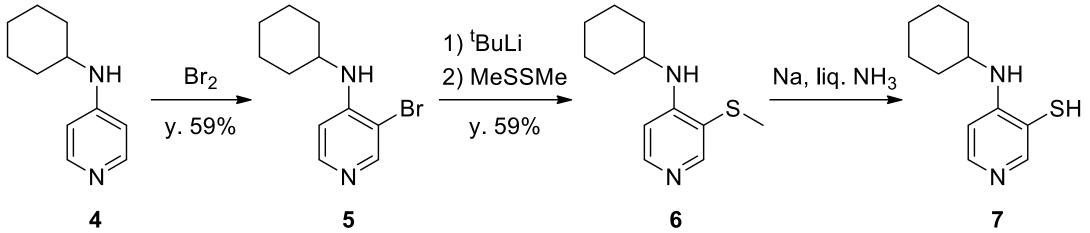


1, R = H
2, R = cyclohexyl

3

Figure 1. $Ni(apt)_2$ complexes (**1**, **2**) and a new cage-shaped Ni complex (**3**)

Synthetic route to a ligand for the metal complex **2** is shown in Scheme 1. The starting compound, **4**, was prepared according to the reported procedure.[4] The reaction of **4** with elemental bromine afforded monobromide **5** as a yellow solid, along with small amount of dibromide (< 5%). Direct replacement of the Br group with a thiol group by lithiation and subsequent reaction with S_8 was failed. Therefore, we decided to introduce a methylthio group by the reaction of lithiated **5** with dimethyl disulfide. A methylthio derivative **6** was obtained in moderate yield. Demethylation of **6** was conducted under the Birch reduction condition (Na/liq. NH_3) to afford thiol **7**. Because the purification of **7** involved difficulty due to rapid formation of a disulfide compound in air (see below), **7** was used for the next reaction without purification.



Scheme 1. Synthetic route to the ligand **7**

Initially, we tried to isolate **2** by the reaction of **7** with $NiCl_2 \cdot 6H_2O$. However, the mixing of a methanol solution of **7** with the nickel source under a N_2 or degassed condition immediately afforded brown powder and green microcrystals. ^{1}H-NMR, UV-vis, and IR spectroscopies gave no definitive information on the structure of the brown powder. Recrystallization of the brown powder from conventional solvents resulted only in the generation of colorless microcrystalline powder. On the other hand, the structure of the green compound was successfully determined by X-ray crystallographic analysis. Contrary to our expectation that the green compound is **2**, the X-ray analysis revealed that the green compound is composed of four disulfide ligands **8** bridged by a Cl–Ni(II)–Cl–Ni(II)–Cl unit. Figure 2 shows the X-ray structure of the four-fold symmetric cage compound **3**.

Each nickel atom adopts an ideal octahedral geometry and the equatorial positions are filled with four pyridine rings. The axial positions are coordinated with Cl anions and the Cl anion located on the centric position is sandwiched by two nickel atoms with a Ni–Cl bond length of 2.627(2) Å.[5] Another Cl anion as a counter anion, which locates between the disulfide ligands, are positionally disordered with a site occupancy of 0.25. Such a mono(μ-Cl) bridged Ni dinuclear structure is rarely observed, because most of the related dinuclear complexes have a bis(μ-Cl) bridge.[6] It is noted that **3** crystallizes in the chiral space group *I*422.

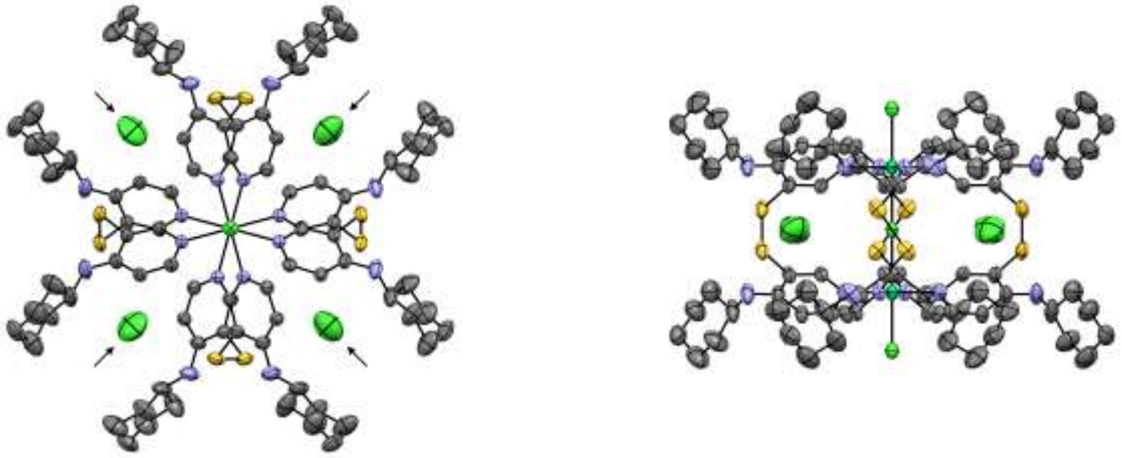
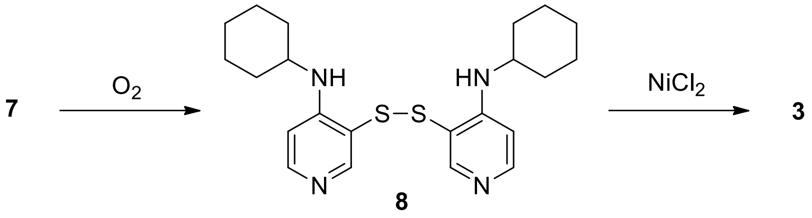


Figure 2. ORTEP drawing of **3** (30% probability). (Left) Top view and (right) side view. Hydrogen atoms are omitted for clarity. A Cl anion as a counter anion indicated by an arrow is positionally disordered with a site occupancy of 0.25.

The reactions to give **3** from thiol **7** would proceed through dimerization of **7** by oxygen that gradually penetrates into a reaction vessel, as shown in Scheme 2. Indeed, ^{1}H-NMR spectrum of **7** in air-saturated $CDCl_3$ showed a change into that of **8** with a half-life time of 3 days.[7]



Scheme 2. Proposed reactions from **7** to **3**

In summary, we isolated a new cage-shaped Ni complex with μ_2-Cl bridging, whose structure was confirmed by X-ray crystallographic analysis. Investigation on functional properties of the cage-shaped complex such as electro-conductivity and two-photon absorption are now in progress in our group.

EXPERIMENTAL

3-Bromo-4-(cyclohexylamino)pyridine (5): Bromine (4.78 mL, 93.4 mmol) was added dropwise to a mixture of 4-(cyclohexylamino)pyridine (**4**, 8.23 g, 46.7 mmol) and potassium carbonate (12.9 g, 93.4 mmol) in CCl_4 (400 mL). After stirring for 3 h at room temperature, CH_2Cl_2 and aqueous sodium sulfite were added. The organic layer was washed with water and aqueous sodium carbonate, and dried over anhydrous sodium sulfate. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on alumina (CH_2Cl_2) to give **5** as yellow solid (7.02 g, 59%). ^{1}H-NMR (400 MHz,

$CDCl_3$) δ/ppm 8.33 (s, 1H), 8.11 (d, J=5.6 Hz, 1H), 6.48 (d, J=6.0 Hz, 1H), 4.76 (brs, 1H), 3.33–3.41 (m, 1H), 2.01–2.05 (m, 2H), 1.79 (dt, J=12.8, 4.0 Hz, 3H), 1.67 (dt, J=12.4, 4.0 Hz, 1H), 1.24–1.46 (m, 5H).

4-Cyclohexylamino-3-(methylthio)pyridine (6): **5** (2.032 g, 8 mmol) was dissolved in THF (80 mL) under nitrogen atmosphere, and the solution was cooled to –78 ºC. To the solution was added *tert*-BuLi (1.6 M, 40 mL, 64 mmol) and stirred at –78 ºC for 30 min. Dimethyl disulfide (7.2 mL, 80 mmol) was added to the solution and stirred for 12 hours, and the reaction was quenched with water of 200 mL. The reaction mixture was extracted by CH_2Cl_2, and the organic layer was washed with water and dried over anhydrous sodium sulfate. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on alumina (EtOAc/hexane = 1:1, v/v) to give **6** as yellow oil (1.050 g, 59%). EIMS m/z (rel. intensity) 222 (78.68), 179 (100); HRMS (ESI) m/z calcd for $C_{12}H_{19}N_2S$ 223.1268 $[M+H]^+$; found 223.1298; ^{1}H-NMR (400 MHz, $CDCl_3$), δ/ppm 8.36 (s, 1H), 8.13 (d, J=6.0 Hz, 1H), 6.44 (d, J= 6.0 Hz, 1H), 5.44–5.45 (br, 1H), 3.33–3.41 (m, 1H), 2.26 (s, 3H), 2.00–2.05 (m, 2H), 1.76–1.82 (m, 2H), 1.64–1.70 (m, 1H), 1.24–1.47 (m, 5H).

4-(Cyclohexylamino)pyridine-3-thiol (7): A two-necked round bottom flask equipped with a cold finger was charged with **6** (940 mg, 4.23 mmol) and THF (10 mL). The cold finger was filled with a dry ice-EtOH and ammonia gas was introduced into the flask until a liquid ammonia amounted to 10 mL. Small pieces of sodium were repeatedly added to the reaction mixture at room temperature until the solution color remained unchanged for 30 minutes. Total amount of sodium was 183 mg (7.96 mmol). The reaction was quenched with solid ammonium chloride (426 mg, 7.96 mmol) and the reaction mixture was concentrated in vacuo. EtOH was added to the residue and insoluble materials were removed by filtration. The filtrate was concentrated in vacuo to give rise to **7** as yellow solid (1.136 g, 129 %, crude). HRMS (ESI) m/z calcd for $C_{11}H_{16}N_2S$ 208.1028 $[M+H]^+$; found 208.1036; ^{1}H-NMR (300 MHz, CD_3OD), δ/ppm 7.87 (s, 1H), 7.62 (d, J=6.8 Hz, 1H), 6.56 (d, J=6.8 Hz, 1H), 3.59–3.66 (m, 1H), 2.01–2.04 (m, 2H), 1.81–1.85 (m, 2H), 1.65–1.68 (m, 1H), 1.35–1.52 (m, 5H).

Cage-shaped Ni complex (3): To the solution of **7** (200 mg, 0.96 mmol) in MeOH (4 mL) was added the solution of $NiCl_2•6H_2O$ (228 mg, 0.96 mmol) in MeOH (2 mL). The reaction mixture was left to stand at room temperature for two days, giving rise to **3** as green crystals (128 mg, 28% based on **7**). The structure of **3** was confirmed by single crystal X-ray crystallographic analysis. Crystal data for **3**: $C_{88}H_{120}Cl_4N_{16}Ni_2S_8$, Mw = 1917.66, tetragonal, $I422$ (#97), a = 14.665(6), c = 22.756(9) Å, V = 4894(3) Å^3, T = 200 K, Z = 2, ρ(calcd) = 1.301 g cm^{-3}, μ(Mo$K\alpha$) = 7.15 mm^{-1}, reflections collected = 23801, unique reflections = 2775, R_{int} = 0.0887, param. refined = 141, $R1$ = 0.071 ($I > 2\sigma(I)$), $wR2$ = 0.217 (all data), GOF = 0.99. Flack parameter = 0.15(4). CCDC-1420091.

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7. Selected ^{1}H-NMR data of **8**; δ/ppm 8.05 (d, J=6.8 Hz, 1H), 7.84 (s, 1H), 6.74 (d, J=6.8 Hz, 1H).