

## Synthesis and Structure Analysis of $\alpha$ and $\beta$ Forms of [12] Metallacrown-6 Nickel(II) Complex: $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_3)_{12}]$

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Two modifications of the  $\alpha$  and  $\beta$  forms of propyl mercaptan nickel(II) cluster,  $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_3)_{12}]$ , have been synthesized and their crystal structures have been determined by single-crystal X-ray diffraction. The alkyl groups are away from  $\text{Ni}_6$  ring in  $\alpha$  form whereas they are near to the Ni atom in  $\beta$  form. The distance of Ni-H in  $\beta$  form [2.576(5) Å] is much shorter than that in  $\alpha$  form [3.101(2) Å]. In the crystal lattice of  $\beta$  form, the whole structure forms a flower shape.

**Key Words:** Polymorphism, Nickel cluster compounds, Crown compounds, Crystal structure

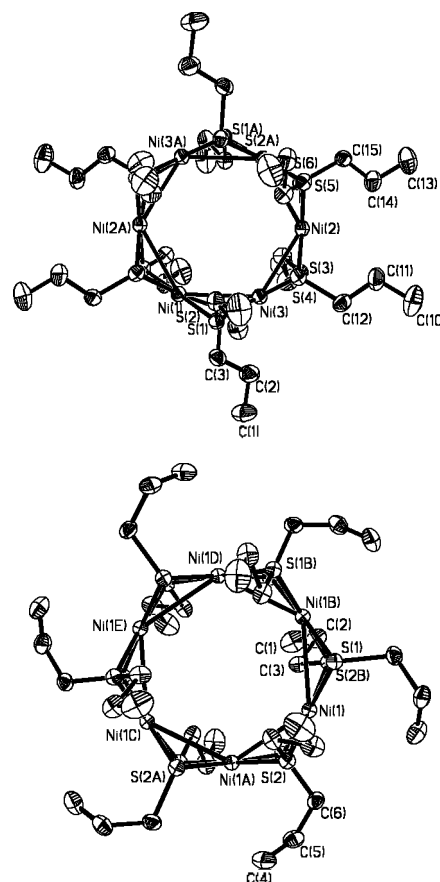
### Introduction

Metallacrowns represent a new class of multinuclear clusters that are analogous to crown ethers in both structure and function.<sup>1,2</sup> One may substitute heteroatoms, such as transition metals and nitrogen atoms, for the methylene carbon atoms of the parent ether complexes to form metallacrowns. There has been considerable interest in metallacrowns chemistry owing to potential applications in chemically modified electrodes, anion-selective separation agents, liquid-crystal precursors, and magnetic materials.<sup>3</sup> Generally, the metallacrowns could be synthesized using multidentate ligand that could bridge two metal ions,<sup>4</sup> or using bridging chalcogen ligand, such as  $\text{NaSR}$ ,<sup>5</sup>  $\text{NaSeR}$ ,<sup>6</sup> and OR anions etc.<sup>7</sup> Cyclic polynuclear nickel thiolates have been known since the pioneering work by Woodward *et al.*<sup>8</sup> on the structure of the hexanuclear  $[\text{Ni}(\mu_2\text{-SCH}_2\text{CH}_3)_2]_6$  complex. Since that time, a considerable number of other geometrically similar cyclic  $[\text{Ni}(\text{SR})_2]_6$  ring-systems<sup>9,12</sup> that likewise contain sulfur-bridged nickel hexagons and two palladium analogue<sup>13,14</sup> have been prepared and structurally characterized. So far, several *tiara*-nickel thiolates have been synthesized and characterized, including cyclic tetranuclear,<sup>15</sup> pentanuclear,<sup>14,16</sup> octanuclear complexes.<sup>17</sup> Recently, the new nickel(II) thiolates containing 9- and 11-membered ring systems, cyclo- $[\text{Ni}(\mu_2\text{-SPh})_2]_9$  and cyclo- $[\text{Ni}(\mu_2\text{-SPh})_2]_{11}$ , have been reported.<sup>18</sup> In this paper, we report the difference of the synthesis and structure between  $\alpha$  and  $\beta$  forms of propyl mercaptan nickel(II) cluster  $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_3)_{12}]$ .

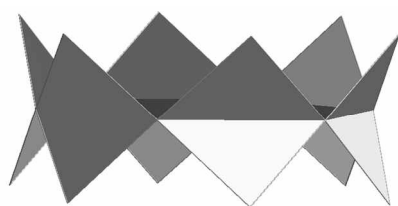
The  $\alpha$  form is an unexpected result. When use  $\text{CH}_3\text{CH}_2\text{-CH}_2\text{SH}$  reaction with  $\text{CS}_2$  and  $\text{NaOH}$ , we want to obtain  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCS}_2$ . Then added aqueous  $\text{NiSO}_4$  solution to form the complex of  $[\text{Ni}(\text{CH}_3\text{CH}_2\text{CH}_2\text{SCS}_2)_2]$ . Accidentally, we obtained the structure of  $\alpha$  form. The  $\beta$  form was obtained by hydrothermal method and has the same structure with the report before.<sup>19</sup> For comparing the difference with  $\alpha$  form, we

redetermined the  $\beta$  form.

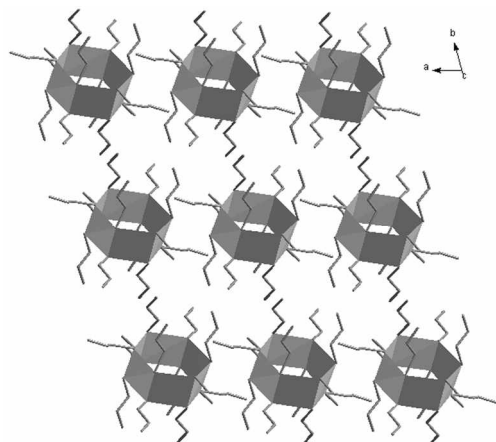
For  $\alpha$  form the six nickel atoms are located at the vertices of distorted hexagon with Ni...Ni separations in the range of



**Figure 1.** Molecular structure for  $\alpha$  (up) and  $\beta$ -form (down) along with atom labeling. The crystal of  $\alpha$  form is in triclinic crystal system with  $P\bar{1}$  space group and the crystal of  $\beta$  form is in trigonal crystal system with  $R\bar{3}$  space group.



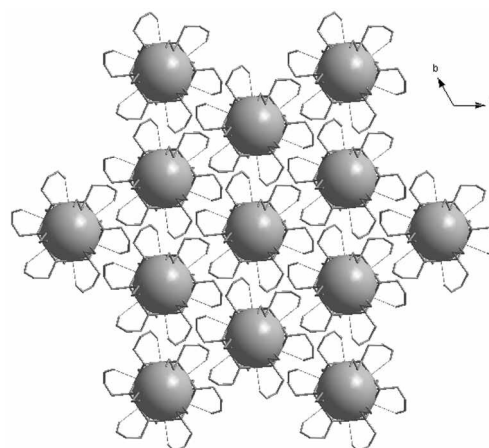
**Figure 2.** Polyhedron shows the double crowns comprising of nickel (II) ring and twelve  $\mu_2$ -sulfur atoms.



**Figure 3.** Packing diagram of  $\alpha$  form.

2.896(2)-2.999(2) Å and vertex angle of 117.97(3)-121.27(3)°. For  $\beta$  form six nickel atoms are located at the vertices of almost hexagon with Ni...Ni distance of 2.926(2) Å and vertex angle of 120°. In the crystal structure of the two complexes, each nickel atom is surrounded by four S atoms of the  $\mu_2$ -SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> ligands in a distorted square-planar fashion. As a result, edge-sharing NiS<sub>4</sub> planes connect to form a ring. The diameter of the ring, defined as the average distance between two opposing nickel atoms, are 5.873(1) Å for  $\alpha$  form and 5.852(1) Å for  $\beta$  form, respectively. Two  $\mu_2$ -sulfur bridges coming from two propyl mercaptan ligands connect adjacent nickel atoms. One of the  $\mu_2$ -sulfur atoms is above and the another  $\mu_2$ -S atom is below the plane through the six nickel(II) atoms. As a consequence, six nickel(II) atoms nearly show virtual C<sub>6</sub> symmetry, and the twelve  $\mu_2$ -S atoms form double crowns (see Fig. 2), one above and the other below the nickel ring, respectively.

Owing to geometrical restrictions introduced by the bridging sulfur atoms, the NiS<sub>4</sub> units are not strictly planar, with Ni-S-Ni bond angles ranging from 81.44(5) to 85.90(5)° for  $\alpha$  form and 82.69(3), 82.99(3)° for  $\beta$  form, respectively. The Ni-S bond lengths are 2.199(2) to 2.230(2) Å for  $\alpha$  form and 2.202(3) to 2.216(4) Å for  $\beta$  form, respectively, which are slightly longer than that found in another nickel(II) complex with square-planar coordination (2.172(2) Å)<sup>20</sup> but agreement with the similar nickel complex reported before (2.183-2.213 Å)<sup>9</sup> and (2.192-2.206 Å).<sup>19</sup> Within the Ni<sub>6</sub> ring, the average Ni-Ni separations of 2.9367 for  $\alpha$  form and 2.9258 Å for  $\beta$  form is significantly longer than the Ni-Ni separations between nearest neighbors in cubic close-packed nickel



**Figure 4.** Packing diagram of  $\beta$  form (the dashed are the bonds of Ni-H)

(2.492 Å) and hexagonal close-packed nickel (2.492 Å).<sup>21</sup> They are also longer than the mean Ni-Ni separations in nickel metal (2.49 Å),<sup>22</sup> but are comparable to the Ni-Ni bond lengths in other nickel clusters such as [Ni<sub>6</sub>Se<sub>4</sub>Cp'<sub>3</sub>] (2.502-3.194 Å), [Ni<sub>15</sub>Se<sub>10</sub>(CO)<sub>3</sub>Cp'<sub>8</sub>] (2.523-2.948 Å, Cp' = methyl-cyclopentadienyl),<sup>23</sup> [Ni<sub>6</sub>(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>12</sub>] (2.919 Å)<sup>19</sup> and [Ni<sub>6</sub>(SCH<sub>2</sub>CH<sub>2</sub>OH)<sub>12</sub>] (average 2.9276 Å).<sup>9</sup>

Fig. 3 shows the polyhedron of distorted square-planar of Ni atoms in  $\alpha$  form and Fig. 4 shows the packing of  $\beta$ -form, respectively. From Fig. 1, Fig. 3 and Fig. 4, obvious difference between the  $\alpha$  and  $\beta$  structures can be found. The alkyl groups are away from Ni<sub>6</sub> ring in  $\alpha$  form whereas they are near to the Ni atom in  $\beta$  form. The distance of Ni-H [2.576(5) Å] in  $\beta$  form is much shorter than that in  $\alpha$  form [3.101(2) Å]. Through the Ni-H, six alkyls form six pseudo rings with the Ni and S atoms in  $\beta$  form. When placed a ball with diameter of 5.0675 Å into the Ni<sub>6</sub> ring of  $\beta$  form as center, the whole structure forms a flower-shape completed with six pseudo rings as the petal.

## Experimental Section

### Preparation of [Ni<sub>6</sub>(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>12</sub>].

**$\alpha$  Form:** Warm aqueous NaOH solution (1.10 mL, 50 wt%) was added in a dropwise manner to CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH (1.27 mL, 0.013 mmol) and carbon bisulfide (1.00 g, 0.013 mmol) in acetonitrile (10 mL) with stirring, and the mixture was refluxed for 1.5 h. The solution turned light yellow and then formed an orange-red viscous matter that dissolved in water easily. Then an excess of aqueous NiSO<sub>4</sub> solution (1.50 g, 8.0 mL) was added, upon which brown precipitates formed. The brown precipitate was isolated by filtration, washed with water, and dried overnight in air. Yield 95.2% based on CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SH. The dark green block single crystal suitable for X-ray analysis was obtained by recrystallizing this brown solid from ethylacetate solution. The C and H contents were determined by elemental analysis (Anal. Calcd. for C<sub>36</sub>H<sub>34</sub>Ni<sub>6</sub>S<sub>12</sub> (%) C 34.48, H 6.75; found C 34.35, H 6.59).

**$\beta$  Form:** Firstly, NaSCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> was prepared by reacting propyl mercaptan (1.96 mL, 0.02 mol) with EtONa (1.35 g,

0.02 mol) in dry ethanol at room temperature. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. Yield ~ 90%. Then, the  $\text{NaSCH}_2\text{CH}_2\text{CH}_3$  (1.47 g, 0.015 mol) is mixed with slightly excess  $\text{NiSO}_4$  in EtOH (35 mL), and sealed in a 50 mL Teflon-lined reactor, which was heated to 120 °C for 4 hours. After cooling to room temperature, dark blue block single crystals were obtained. The C and H contents were determined by elemental analysis (Anal. Calcd. for  $\text{C}_{36}\text{H}_{84}\text{Ni}_6\text{S}_{12}$  (%) C 34.48, H 6.75; found C 34.39, H 6.61). The IR spectra for these two compounds can be found in supporting information.

### Conclusions

By using general solution method and hydrothermal synthetic method, the title compound  $[\text{Ni}_6(\text{SCH}_2\text{CH}_2\text{CH}_3)_{12}]$  having two different crystal forms of  $\alpha$  and  $\beta$  has been synthesized, respectively. In  $\alpha$  form, the compound is in triclinic crystal system with  $P-1$  space group and the alkyl groups are away from  $\text{Ni}_6$  ring. In  $\beta$  form, the compound is in trigonal crystal system with  $R-3$  space group and the alkyl groups near to the Ni atom, which results in the compound having a flower-shape like crystal packing along  $c$  axis direction.

**Supplementary Material.** CCDC-666901 and 666902 contain the supplementary crystallographic data for the  $\beta$ -form and  $\alpha$ -form, respectively. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; fax: +44(0)1222-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. The data of IR spectra for the two title compounds are available at <http://www.kcsnet.or.kr/bkcs> or upon request from the corresponding author.

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