[$Ni_6(SCH_2CH_2OH)_{12}$]: A Double Crown [12]Metallacrown-6 Nickel(II) Cluster[**]

Fang-Fang Jian, Kui Jiao, Yan Li, Pu-Su Zhao, and Lu-De Lu*

Metallacrowns represent a new class of multinuclear clusters that are analogous to crown ethers in both structure and function.[1,2] 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 metallacrown chemistry owing to potential applications in chemically modified electrodes, anion-selective separation agents, liquid-crystal precursors, and magnetic materials.[3]

Generally, the metallacrowns can be synthesized using either multidentate ligands that bridge two metal ions[4] or bridging chalcogen ligands, such as NaSR,[5] NaSeR,[6] and OR anions.[7] We wanted to synthesize the bidentate ligand [$NaS_2COCH_2CH_2SCS_2Na$] from 2-sulfanylethanol [$HSCH_2CH_2OH$] by reaction with carbon bisulfide in aqueous NaOH solution, and then treat this ligand with aqueous nickel sulfate to produce the polymer [$NiS_2COCH_2CH_2SCS_2Ni$]$_n$. However, we unexpectedly obtained [$Ni_6(SCH_2CH_2OH)_{12}$] (**1**), a novel [12]metallacrown-6 nickel cluster as shown by single-crystal X-ray diffraction. We repeated the experiment and were able to form this product in high yield. Herein we report the spontaneous self-assembly and crystal structure of compound **1** as well as investigations on its UV/Vis spectrum and thermal stability.

The crystal lattice of compound **1**[8] is made up of a centrosymmetric [$Ni_6(SCH_2CH_2OH)_{12}$] molecule (Figure 1). Each Ni atom is surrounded by four S atoms of the μ_2-SCH_2CH_2OH ligands in a distorted square-planar fashion. As a result, the edge-sharing NiS_4 planes connect to form a ring. The six nickel atoms approximately form a hexagon, with Ni–Ni separations in the range of 2.9010(15)–2.9378(17) Å, vertex angles of 119.08(5)–121.38(5)°, and an average deviation of ±0.001 Å from the best least-squares Ni_6 plane. The diameter of the ring, defined as the average distance between two opposing nickel atoms, is 5.84 Å. Two μ_2-S bridges

---

[*] Prof. Dr. F.-F. Jian, Prof. Dr. K. Jiao, Y. Li
New Materials & Function Coordination Chemistry Laboratory
Qingdao University of Science and Technology
Qingdao, 266042 (P.R. China)
Fax: (+86) 532-4023-606
E-mail: ffj2003@163169.net

Dr. P.-S. Zhao, Prof. Dr. L.-D. Lu
Materials Chemistry Laboratory
Nanjing University of Science and Technology
Nanjing, 210094 (P.R. China)

[**] This work was supported by the Natural Science Foundation of Shandong province (no. Y2002B06).

Supporting information for this article (views of the crystal structure) is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351896

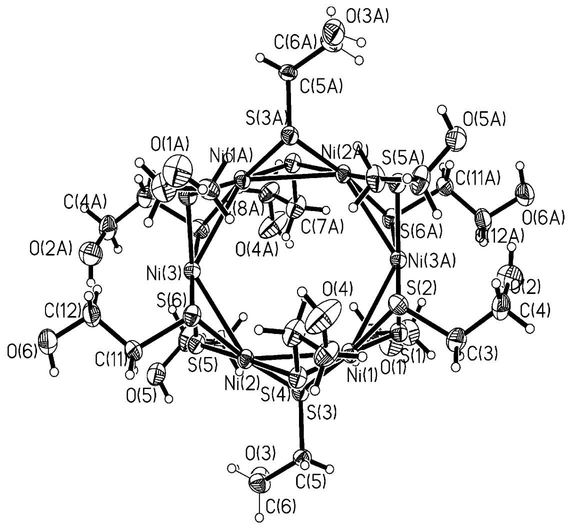

Figure 1. Molecular structure of $[Ni_6(SCH_2CH_2OH)_{12}]$ (**1**). Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ni(1)-S(3) 2.194(2), Ni(1)-S(1) 2.197(2), Ni(1)-S(4) 2.200(2), Ni(1)-S(2) 2.208(2), Ni(1)-Ni(2) 2.934(2), Ni(1)-Ni(3)#1 2.9378(17), Ni(2)-S(5) 2.183(2), Ni(2)-S(4) 2.198(2), Ni(2)-S(3) 2.204(2), Ni(2)-S(6) 2.214(2), Ni(2)-Ni(3) 2.9010(15), Ni(3)-S(1)#1 2.192(2), Ni(3)-S(5) 2.204(2), Ni(3)-S(2)#1 2.205(2), Ni(3)-S(6) 2.213(2); S(3)-Ni(1)-S(1)97.21(8), S(3)-Ni(1)-S(4)82.28(8), S(1)-Ni(1)-S(4)178.64(9), S(3)-Ni(1)-S(2)173.95(9), S(1)-Ni(1)-S(2)81.86(8), S(4)-Ni(1)-S(2)98.78(8), Ni(2)-Ni(1)-Ni(3)#1 121.38(5), S(5)-Ni(2)-S(4) 178.55(9), S(5)-Ni(2)-S(3) 97.69(8), S(4)-Ni(2)-S(3) 82.11(8), S(5)-Ni(2)-S(6) 82.25(8), S(4)-Ni(2)-S(6) 98.11(8), S(3)-Ni(2)-S(6) 173.29(8), Ni(3)-Ni(2)-Ni(1) 119.53(5), S(1)#1- Ni(3)-S(5) 179.39(8), S(1)#1-Ni(3)-S(2)#1 82.05(8), S(5)-Ni(3)-S(2)#1 98.51(8), S(1)#1-Ni(3)-S(6) 97.60(8), S(5)-Ni(3)-S(6) 81.82(8),S(2)#1-Ni(3)-S(6) 174.20(9), Ni(2)-Ni(3)- Ni(1)#1 119.08(5). Symmetry transformations used to generate equivalent atoms: #1: $-x+1,-y+2,-z+1$; #2: $-x,-y+2,-z+1$.

originating from two 2-sulfanylethanol ligands connect adjacent nickel atoms. One of the μ_2-S atoms is above and the other is below the Ni_6 plane. As a consequence, the six nickel(II) atoms nearly show virtual C_6 symmetry, and the twelve μ_2-S atoms form double crowns, one above and the other below the nickel ring (Figure 2). This type of complex with a Ni_6 ring and a double-crown structure is to our knowledge the first of its kind.

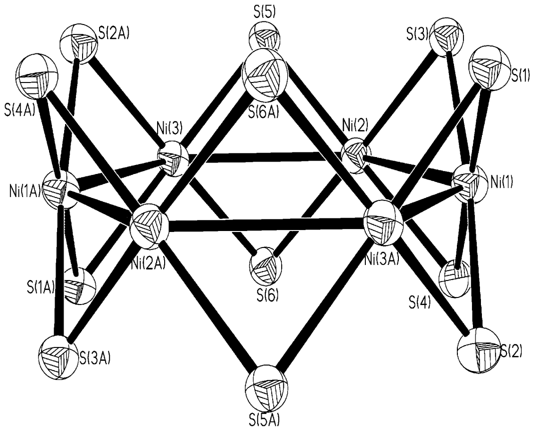

Figure 2. The double crowns in **1** made up of a Ni_6 ring and twelve μ_2-S atoms.

Owing to geometrical restrictions introduced by the bridging sulfur atoms, the NiS_4 units are not strictly planar, with S-Ni-S bond angles ranging from 81.82 to 98.78°. The Ni–S bond lengths are 2.183–2.213 Å, and thus slightly longer than that found in another nickel(II) complex with square-planar coordination (2.172(2) Å).[9] Within the Ni_6 ring, the average Ni–Ni separations of 2.9276 Å are significantly longer than the Ni–Ni separations between nearest neighbors in cubic close-packed nickel (2.492 Å) and hexagonal close-packed nickel (2.492 Å).[10] They are also longer than the mean Ni–Ni separations in nickel metal (2.49 Å),[11] but are comparable to the Ni–Ni bond lengths in other nickel clusters such as $[Ni_6Se_4Cp'_5]$ (2.502–3.194 Å) and $[Ni_{15}Se_{10}(CO)_3Cp'_8]$ (2.523–2.948 Å; Cp′ = methylcyclopentadienyl).[12] In addition, the triangle plane laminas (NiSNi) of the double crown are not perpendicular to the Ni_6 ring. The plane comprising Ni(2), S(5), and Ni(3) makes a dihedral angle of 58.65° with the plane formed by Ni(2), S(6), and Ni(3). These two planes form dihedral angles of 57.60° and 63.74° with the Ni_6 ring plane, respectively.

The salient feature in the crystal packing of compound **1** is that the hydroxy groups of 2-sulfanylethanol form strong intermolecular hydrogen bonding interactions with each other, with donor–acceptor separations of 2.6458–2.8811 Å. This situation results in the formation of a one-dimensional chain structure (Figure 3), in which hydrogen bonding plays a

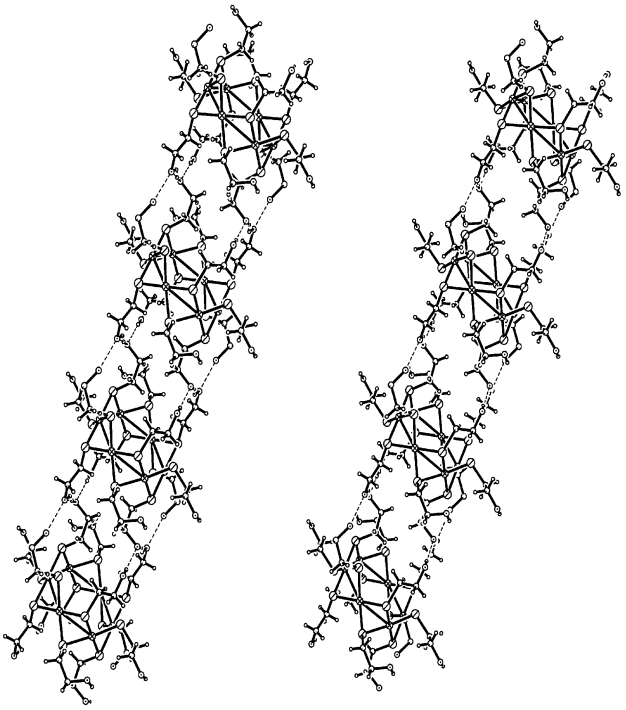

Figure 3. Crystal packing of **1** as viewed down the *a* axis, showing the one-dimensional chain formed by hydrogen-bonding interactions. Selected hydrogen-bond lengths [Å] and angles [°]: O(1)-H···O(5) $[x,1+y,z]$ 2.8811, 161.24; O(2)-H···O(3) $[-1+x,y,z]$ 2.6802, 175.41; O(3)-H···O(4) $[x,-1+y,z]$ 2.6458, 142.85; O(4)-H···O(5) $[x,1+y,z]$ 2.7033, 146.76; O(5)-H···O(4) $[x,-1+y,z]$ 2.7033, 172.64; O(6)-H···O(2) $[-x,1-y,-z]$ 2.6933, 160.59.

significant part in sustaining the assembly of the metallacrown complex.

The solid-state UV/Vis spectrum of **1** shows there is a low-energy absorption band at $\lambda = 782$ nm. This band can be attributed to an electronic transition based on principal d orbital contribution for nickel ions because of the direct metal–metal bonding system.

Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) analysis show that the thermal decomposition of compound **1** includes four transitions (Figure 4). There are three peaks corresponding to endothermic processes—that is, weak heat-absorbing processes at 146.6, 174.2, and 217.0 °C—and a broad peak for an exothermal process at about 300 °C. Decomposition occurs at 146.6 °C. On the basis of weight changes in the TG curve, the first process of weight loss corresponds to the loss of hydroxy groups from the 2-sulfanylethanol ligands (146.6–174.2 °C; found 8.04, calcd 7.98 %) with a weak endothermic event; the second process of the weight loss is attributed to the cleavage of C–S bonds (174.2–217.0 °C; found 40.81, calcd 42.26 %). Finally, Ni_6S_{12} decomposes gradually (217.0–1000 °C) with the broad peak for this exothermal is at about 300 °C, the residue may be Ni atom (found 71.69, calcd 72.43 %).

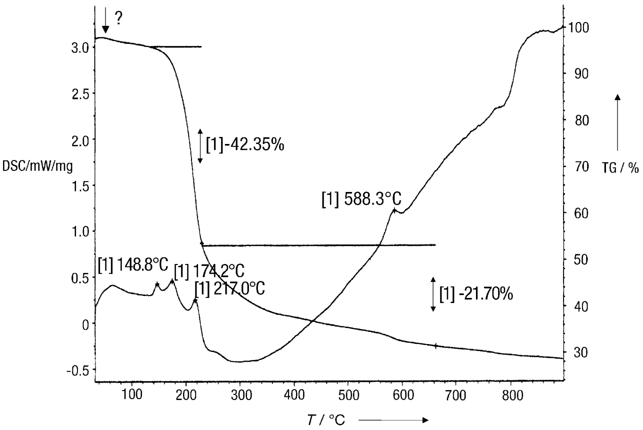

Figure 4. The TG and DSC curves obtained for compound **1**.

Noteworthy is that we could not obtain the novel nickel cluster if 2-sulfanylethanol was allowed to react with aqueous NaOH solution and nickel sulfate directly, without adding carbon bisulfide. Further studies on this reaction, including the use of other metals, are in progress.

Experimental Section

1: Warm aqueous NaOH solution (1.1 mL, 50 wt %) was added in a dropwise manner to $HOCH_2CH_2SH$ (1.00 g, 13.0 mmol) and carbon bisulfide (1.00 g 13.0 mmol) in acetonitrile (10 mL) with stirring, and the mixture was allowed to reflux for 1.5 h at 30 °C. The solution turned light yellow and then formed an orange-red viscous matter that dissolved in water easily. Then an excess of aqueous $NiSO_4$ solution (1.5 g, 8.0 ml) was added, upon which brown gelatinous precipitates formed. The brown precipitate was isolated by filtration, washed with water, and dried overnight in air. Yield 2.5 g, 92.3 % based on $HOCH_2CH_2SH$; elemental analysis: found C 21.08, H 2.38 %; the identity of this substance is not yet clear. The brown solid was ground into dust, and then recrystallized from EtOH; thus, large, dark green crystals suitable for X-ray diffraction experiments were obtained. These crystals were all collected and dried (Yield 0.4 g, 16 %. Elemental analysis calcd (%) for $C_{24}H_{60}Ni_6O_{12}S_{12}$: C 22.56, H 4.73; found: C 22.23, H 4.38.

Received: May 14, 2003
Revised: July 24, 2003 [Z51896]

Keywords: cluster compounds · crown compounds · nickel · S ligands

---

[1] V. L. Pecoraro, A. J. Stemmler, B. R. Gibeny, J. J. Bodwin, H. Wang, J. W. Kampf, A. Barwinski, *Prog. Inorg. Chem.* **1997**, *45*, 83–177.

[2] M. S. Lah, V. L. Pecoraro, *J. Am. Chem. Soc.* **1989**, *111*, 7258.

[3] a) M. S. Lah, M. L. Kirk. W. Hatfield, V. L. Pecoraro, *J. Chem. Soc. Chem. Commun.* **1989**, 1606; b) M. S. Lah, V. L. Pecoraro, *Comments Inorg. Chem.* **1990**, *11*, 59.

[4] a) S. X. Liu, S. Lin, B. Z. Lin, C. C. Lin, J. Q. Huang, *Angew. Chem.* **2001**, *113*, 1118; *Angew. Chem. Int. Ed.* **2001**, *40*, 1084; b) B. Kwak, H. Rhee, S. Park, M. S. Lah, *Inorg. Chem.* **1998**, *37*, 3599.

[5] a) T. Krüger, B. Krebs, G. Henkel, *Angew. Chem.* **1989**, *101*, 54; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 61; b) G. Henkel, M. Kriege, K. Matsumoto, *J. Chem. Soc. Chem. Commun.* **1988**, 657.

[6] D. Fenske, A. Fischer, *Angew. Chem.* **1995**, *107*, 340; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 307.

[7] A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467.

[8] Crystal data for compound **1** ($C_{24}H_{60}Ni_6O_{12}S_{12}$): $M_r = 1277.7$, $0.3 \times 0.5 \times 0.5$ mm, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, triclinic space group, $P\bar{1}$, $a = 10.500(2)$, $b = 11.110(2)$, $c = 11.390(2)$ Å, $\alpha = 108.30(3)$, $\beta = 103.30(3)$, $\gamma = 100.90(3)°$, $Z = 1$, $V = 1177.5(4)$ Å^3, $T = 293(2)$ K, $\rho_{calcd} = 1.802$ Mg m^{-3}, $F(000) = 660$, $\mu = 2.930$ mm^{-1}. Of 4392 reflections collected $[(2\theta)_{max} = 49.94°]$, 4144 were unique ($R_{int} = 0.0723$) and 2867 with $I > 2\sigma(I)$ were used for structure solution and refinement on F^2 by full-matrix least-squares techniques (SHELXL-97); $R1 = 0.0380$, $wR2 = 0.1328$, GOF (F^2) = 1.073; max./min. residual electron density = 0.978/−0.948 e Å^{-3}. CCDC-221211 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[9] M. B. Ferrari, S. Capacchi, F. Bisceglie, G. Pelosi, P. Tarasconi, *Inorg. Chim. Acta* **2001**, *312*, 81.

[10] H. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**, p. 213.

[11] A. I. Baranov, L. Kloo, A. V. Olenev, B. A. Popovkin, A. I. Romanenko, A. V. Shevelkov, *J. Am. Chem. Soc.* **2001**, *123*, 12375.

[12] D. Fenske, A. Hollnagel, *Angew. Chem.* **1989**, *101*, 1412; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1390.

Entschuldigung

Über die in der Zuschrift „$[Ni_6(SCH_2CH_2OH)_{12}]$: A Double Crown [12]Metallacrown-6 Nickel(II) Cluster“ von F.–F. Jian et al. (*Angew. Chem.* **2003**, *42*, 5900–5902) beschriebene Struktur der Titelverbindung im Kristall ist bereits an anderer Stelle berichtet worden: „Nickel and Palladium Complexes of 1-Hydroxyethane-2-thiol and Analogues. Part 1. Crystal Structure of Cyclohexakis[bis-(μ-1-hydroxyethane-2-thiolato)-nickel(II)]“: R. O. Gould, M. M. Harding, *J. Chem. Soc. A* **1970**, 875–881. Die Autoren haben außerdem einige relevante Literaturstellen nicht erwähnt, darunter: „A New Type of Cyclic Transition Metal Complex, $[Ni(SC_2H_5)_2]_6$“: P. Woodward, L. F. Dahl, E. W. Abel, B. C. Crosse, *J. Am. Chem. Soc.* **1965**, *87*, 5251–5253; „The Structure of a Toroidal, Neutral, Homoleptic Ni(II) Complex with a Chelate Dithiolate Ligand, $[Ni_6(SCH_2CH_2CH_2S)_6]$“: J. Sletten, J. A. Kovacs, *Acta Chem. Scand.* **1994**, *48*, 929–932; „Cyclo-$[Ni(\mu_2\text{-}SPh)_2]_9$ and Cyclo-$[Ni(\mu_2\text{-}SPh)_2]_{11}$: New Oligomeric Types of Toroidal Nickel(II) Thiolates Containing Geometrically Unprecedented 9- and 11-Membered Ring Systems“: S. A. Ivanov, M. A. Kozee, W. Alex Merrill, S. Agarwal, L. F. Dahl, *J. Chem. Soc. Dalton Trans.* **2002**, 4105–4115. Die Autoren bitten um Entschuldigung für ihre Versäumnisse.