

# Unusual C–S Bond Cleavage in Hydro(solvo)thermal Reaction That Induces Two Novel Nickel Thiolates: The Crown $[\text{Ni}_{16}(\text{edt})_8\text{S}_9(\text{S}_2)]^{4-}$ with an Unprecedented 12-Membered Ring System and the Cagelike $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)_2]^{2-}$ with Two Distorted Cores

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## S Supporting Information

**ABSTRACT:** Complex **1** exhibits the crownlike structure with the unprecedented 12-membered ring system, while in **2**, a cagelike cluster has been connected with two distorted cores in nickel thiolates. The synthesis of novel clusters by way of C–S bond cleavage was first reported in the field of nickel thiolates.

Nickel thiolates, as polynuclear clusters and tiara-like compounds, play an important role in the field of metal thiolates, exhibiting dramatic controlled aggregation with the square-planar  $\text{NiS}_4$  building units.<sup>1–15</sup> Because of their specific configurations, they possess much importance in structure chemistry, redox chemistry, specific functional materials, environmental and industrial synthetic enzymes, etc.<sup>16–26</sup> Therefore, the study of nickel thiolates has been of long-standing interest in the last decades.<sup>1–26</sup> However, most of these reported nickel thiolates can be ascribed as oligonuclear clusters or small cyclic compounds,<sup>2–15</sup> which is greatly limited in abundance and structural diversity. To explore the novel nickel thiolates with a highnuclear cluster or a large ring system, a proper synthetic strategy needs to be used. Recently, the combination of hydro(solvo)thermal methods with in situ synthesis has been proven to be an attractive synthetic approach, especially in the preparation of these novel metal–organic sulfur polymers.<sup>27,28</sup> A wide range of novel clusters have been synthesized via this method, which are inaccessible in normal conditions.<sup>28–30</sup> This can be partly attributed to the processes occurring under hydro(solvo)thermal environments, such as redox, ligand oxidative coupling, substitution reactions, and desulfurization.<sup>27,28,31,32</sup> In fact, the reported nickel thiolates that are synthesized by this method are still rare up until now.

Recently, we have been interested in exploring some novel highnuclear or large tiara-like nickel thiolates. Following this strategy, a series of new crown nickel thiolates have been successfully designed and synthesized with in situ cleavage of the disulfide bond.<sup>33</sup> Reported herein are the syntheses and structures of two novel anion clusters,  $[\text{Ni}_{16}(\text{edt})_8\text{S}_9(\text{S}_2)]^{4-}$  (**1**) and  $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)_2]^{2-}$  (**2**), where edt = 1,2-ethanedithiol, which is obtained by cleavage of the C–S bonds in edt under

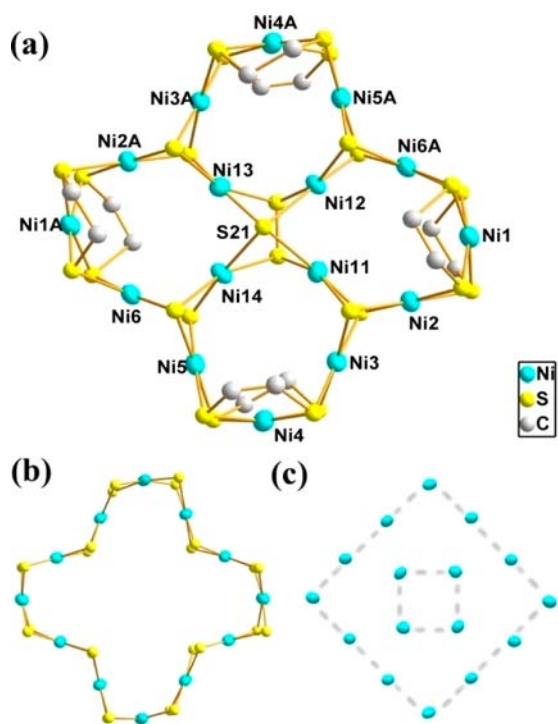
hydro(solvo)thermal conditions. **1** exhibits an unprecedented 12-membered ring system with a  $\text{Ni}_{12}$  square configuration. Up until now, to the best of our knowledge, the dodecanuclear toroidal geometry can be ascribed as the largest ring system in crown nickel thiolates, which has been reported only once before.<sup>18</sup> Meanwhile, **2** is also a rare cagelike cluster in nickel thiolates. In fact, cleavage of the C–S bonds in edt under hydro(solvo)thermal conditions would be the main cause in constructing these two unprecedented frameworks.

Black block crystals of **1** were obtained by the mixture reagents reacting at 413 K for 4 days. Simultaneously, black prism crystals of **2** can be obtained by the mixture reagents reacting at 393 K for 15 days. Moreover, there are some unknown existing byproducts that are hard to separate from the mixed products except for enough pure crystals **1** and **2** by picking them one by one. Meanwhile, after lots of attempts, the length of the reaction time may be one determinant factor, and  $\text{Et}_3\text{N}$  and  $(\text{Et}_4\text{N})\text{OH}$  in the reaction system can be replaced by similar bases, which could also act as counteranions around the same anion clusters. According to this point, it means the bases are not the determinants but just the counteranions to compensate for the whole system's charge equilibrium.

The single-crystal X-ray analysis reveals that **1** possesses a unique outside framework, the crownlike  $\text{Ni}_{12}\text{S}_{24}$  moiety. Each Ni atom is coordinated to an approximate rectangular-planar arrangement of four S atoms ( $[\text{NiS}_4]$ ), while the Ni–S distance ranges from 2.143(7) (Ni5–S11) to 2.465(15) Å (Ni14–S25). As shown in Figure 1, the  $\text{Ni}_{12}\text{S}_{24}$  framework is constructed by edge fusion with the 12 localized  $[\text{NiS}_4]$  building blocks, while the 12 Ni atoms are planar. Furthermore, the Ni–Ni distances of  $\text{Ni}_{12}\text{S}_{24}$  indicate that the nonbonding  $\text{Ni}_{12}$  plane exhibits an approximately square configuration. In addition, the  $\text{C}_2\text{H}_4$  groups derived from edt locate above and below the  $\text{Ni}_{12}$  plane. This extends the whole moiety to an approximate dodecagon, which is different from the traditional crownlike nickel thiolates with circular or elliptical geometry.<sup>1–3,10–15,18</sup>  $\text{S}_2^{2-}$  and S21 lie inside the center of the cyclic  $\text{Ni}_{12}\text{S}_{24}$  architecture, which connects the Ni11, Ni12, Ni13, and Ni14

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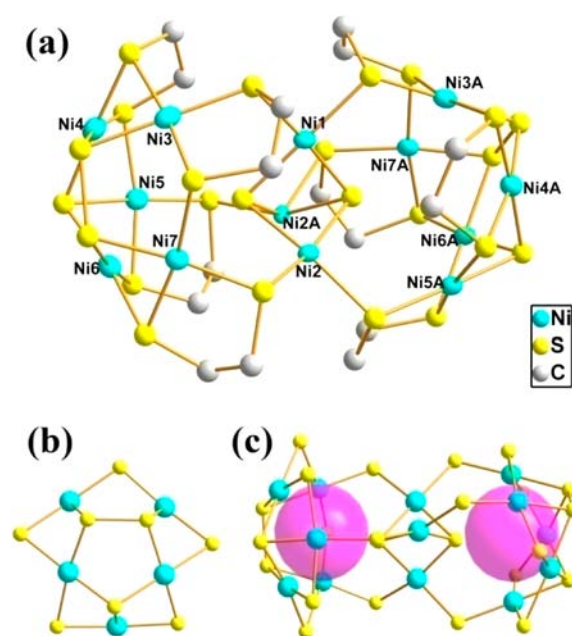


**Figure 1.** Analysis of the architecture of the  $[\text{Ni}_{16}(\text{edt})_8\text{S}_9(\text{S}_2)]^{4-}$  anion. (a) Anion framework of **1**. Symmetry code:  $-x, -y, -z$ . (b) Dodecanuclear toroidal architecture  $\text{Ni}_{12}\text{S}_{24}$ , which exhibits the approximate dodecagonal geometry from the top face view. (c) Small nonbonding  $\text{Ni}_4$  square nestled into the large nonbonding  $\text{Ni}_{12}$  square.

atoms together. The four Ni atoms are also planar and display an approximately square construction. Figure 1c shows that the small square  $\text{Ni}_4$  moiety is nestled into the big  $\text{Ni}_{12}$  frameworks and each of the four Ni atoms and  $\text{Ni}_{12}\text{S}_{24}$  are  $\mu_3$ -bridged by two S atoms. Moreover, because of the existing  $\text{S}_2^{2-}$ , the four square-planar  $\text{NiS}_4$  containing Ni11, Ni12, Ni13, and Ni14 become a little distorted.

In the crystal structure of **2**, each Ni atom is also surrounded by four S atoms in a square-planar fashion, while the Ni–S distance is arranged from 2.154(17) ( $\text{Ni}4'-\text{S}1'$ ) to 2.325(9) Å ( $\text{Ni}4'-\text{S}12$ ). Interestingly, **2** is a cage-like cluster by edge-sharing  $\text{NiS}_4$  planes, whose configuration is quite rare in nickel thiolates, which is different from the toroidal architecture of **1**. As shown in Figure 2, two caplike aggregates  $\text{Ni}_5\text{S}_8$  are located on both sides of the geometry, respectively. The atoms of Ni3, Ni4, Ni5, Ni6, and Ni7 connected with eight S atoms to form the left aggregates  $\text{Ni}_5\text{S}_8$ , which contains  $\text{S}_2^{2-}$ . Meanwhile, the right side has been built by Ni3A, Ni4A, Ni5A, Ni6A, and Ni7A and another eight S atoms. In the middle of the structure, three edge-sharing  $\text{NiS}_4$  planes, which are constructed by Ni1, Ni2, and Ni2A and eight S atoms, link the two  $\text{Ni}_5\text{S}_8$  aggregates by vertex-sharing as bridge ligands to afford two cages.

Parts of the structures of the two compounds were significantly disordered, which may be ascribed as the complex hydro(solvo)-thermal conditions. In **1**, the  $\text{Ni}_4\text{S}_3$  aggregate, including Ni11, Ni12, Ni13, Ni14, S21, and  $\text{S}_2^{2-}$ , was split into two parts, which were above or below the outside  $\text{Ni}_{12}$  plane symmetrically. In **2**, there were high *Q* values near the Ni2, Ni4, Ni8, S1, S2, S5, and C1 atoms, and we defined them as another disordered part, which were named Ni2', Ni4', Ni8', S1', S2', S5', and C1', respectively (see the Supporting Information, SI).



**Figure 2.** Analysis of the architecture of the  $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)]^{2-}$  anion. (a) Anion framework of **2**. Symmetry code:  $-x, y, -z + 1/2$ . (b) Caplike  $\text{Ni}_5\text{S}_8$  aggregate in the  $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)]^{2-}$  anion. (c) Two distorted cores in the  $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)]^{2-}$  anion.

Energy-dispersive spectrometry (EDS) analyses indicated that the two compounds were composed of only two heavy elements, the Ni and S, which is approximately in agreement with the formulas of **1** and **2** (see Figures S3 and S4 in the SI). Meanwhile, thermal behaviors of **1** and **2** were also investigated using thermogravimetric analysis–differential thermal analysis under a  $\text{N}_2$  atmosphere (see Figures S5 and S6 in the SI). There were two similar obvious steps in the whole decomposition of both compounds. The smooth decrease below 200 °C was possible because of removal of the counteranion molecules around the cluster. Also, the sharp decrease from 200 to 300 °C was perhaps due to removal of the organic parts (edt) in the anion cluster.

Desulfurization plays an important and necessary role in the field of clean fuels. As part of the fundamental desulfurizing steps, cleavage of the C–S bond always attracts intense interest. Under hydro(solvo)thermal conditions, C–S bond cleavage is still less frequent and can only be found in some special conditions,<sup>27,28,34–42</sup> instead of the familiar activation or cleavage of common chemical bonds. During our synthetic process, edt is the only sulfur source to provide S atoms. Thereby, the discrete  $\text{S}^{2-}$  and  $\text{S}_2^{2-}$  in **1** and **2** have been derived from the edt ligand, which further implies the occurrence of cleavage of the C–S bond. To our knowledge, the acyclic thiols can react with each other to generate thioether and hydrogen sulfide,<sup>34–39</sup> which could be ascribed as one possible process in the reaction system. In our synthetic process, first, Ni atoms would coordinate with the ligand edt to construct some simple segments with obvious colorimetric changes in solution.<sup>7</sup> Similar to that mentioned above, the reaction may take place among the edt molecules to generate hydrogen sulfide in the complex hydro(solvo)thermal conditions.<sup>34–39</sup> Furthermore, hydrogen sulfide can be ionized to generate  $\text{S}^{2-}$  in a strong alkali solution. Meanwhile, this also explains the reason why the whole reaction can only happen in an alkali environment. After that, the segments were slowly interacted with  $\text{S}^{2-}$  to form the final crystal structures, which would be influenced by the amount of discrete  $\text{S}^{2-}$  in the

solution. More subtly, the two structures can be ascribed as the first report to construct novel nickel thiolates by using of C–S bond cleavage derived from the acyclic thiol.

In conclusion, two unprecedented nickel thiolate frameworks,  $[\text{Ni}_{16}(\text{edt})_8\text{S}_9(\text{S}_2)]^{4-}$  and  $[\text{Ni}_{13}(\text{edt})_8\text{S}_4(\text{S}_2)_2]^{2-}$ , have been successfully directed under hydro(solvo)thermal conditions. It is clear that C–S bond cleavage from edt has occurred and induced two fascinating structures in hydro(solvo)thermal conditions. The successful syntheses of the two compounds might possess the potential to extend the synthetic methods for preparing both novel metal thiolates and organosulfur compounds. Extended work based on other acyclic mercaptans will be the subject of future investigations.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Synthetic procedures for **1** and **2**, X-ray crystallographic data of **1** and **2** in CIF format, X-ray diffraction, EDS data, and crystallographic details for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### ■ Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Zhang, C.; Takada, S.; Kölzer, M.; Matsumoto, T.; Tatsumi, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 3768–3772.
- (2) Jian, F. F.; Jiao, K.; Li, Y.; Zhao, P. S.; Lu, L. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5722–5724.
- (3) Ivanov, S. A.; Kozee, M. A.; Merrill, W. A.; Agarwal, S.; Dahl, L. F. *Dalton Trans.* **2002**, *13*, 4105–4115.
- (4) Sheng, T. L.; Wu, X. T.; Zhang, W. J.; Wang, Q. M.; Gao, X. C.; Lin, P. *Chem. Commun.* **1998**, 263–264.
- (5) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251–5253.
- (6) Dance, I. G.; Scudder, M. I.; Secomb, R. *Inorg. Chem.* **1985**, *24*, 1201–1208.
- (7) Tremel, W.; Kriege, M.; Krebs, B.; Henkel, G. *Inorg. Chem.* **1988**, *27*, 3886–3895.
- (8) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed.* **1989**, *28*, 61–62.
- (9) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed.* **1992**, *31*, 54–56.
- (10) Mahmoudkhani, A. H.; Langer, V. *Inorg. Chim. Acta* **1999**, *294*, 83–86.
- (11) Mahmoudkhani, A. H.; Langer, V. *Polyhedron* **1999**, *18*, 3407–3410.
- (12) Wark, T. A.; Stephan, D. W. *Organometallics* **1989**, *8*, 2836–2843.
- (13) Koo, B. K.; Block, E.; Kang, H. Y.; Liu, S. C.; Zubietta, J. *Polyhedron* **1988**, *7*, 1397–1399.
- (14) Capdevila, M.; Gonzalezduarte, P.; Sola, J.; Focesfoces, C.; Cano, F. H.; Martinezripoll, M. *Polyhedron* **1989**, *8*, 1253–1259.
- (15) Sletten, J.; Kovacs, J. A. *Acta Chem. Scand.* **1994**, *48*, 929–932.
- (16) Artero, V.; Fontecave, M. *Coord. Chem. Rev.* **2005**, *249*, 1518–1535.

- (17) Best, S. *Coord. Chem. Rev.* **2005**, *249*, 1536–1554.
- (18) Zhang, C.; Matsumoto, T.; Samoc, M.; Petrie, S.; Meng, S.; Corkery, T. C.; Stranger, R.; Zhang, J. F.; Humphrey, M. G.; Tatsumi, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 4209–4212.
- (19) Angamuthu, R.; Kooijman, H.; Lutz, M.; Spek, A. L.; Bouwman, E. *Dalton Trans.* **2007**, *41*, 4641–4643.
- (20) Hatlevik, Ø.; Blanksma, M. C.; Mathrubootham, V.; Arif, A. M.; Hegg, E. L. *J. Biol. Inorg. Chem.* **2004**, *9*, 238–246.
- (21) Sydora, O. L.; Henry, T. P.; Wolczanski, P. T.; Lobkovsky, E. B.; Rumberger, E.; Hendrickson, D. N. *Inorg. Chem.* **2006**, *45*, 609–626.
- (22) Sydora, O. L.; Henry, T. P.; Wolczanski, P. T.; Lobkovsky, E. B.; Rumberger, E.; Hendrickson, D. N. *Chem. Commun.* **2004**, 650–651.
- (23) Gale, E. M.; Cowart, D. M.; Scott, R. A.; Harrop, T. C. *Inorg. Chem.* **2011**, *50*, 10460–10471.
- (24) Marradi, M.; Martín-Lomas, M.; Penadés, S. *Adv. Carbohydr. Chem. Biochem.* **2010**, *64*, 211–290.
- (25) Huynh, H. V.; Schulze-Isfort, C.; Seidel, W. W.; Lügger, T.; Fröhlich, R.; Kataeva, O.; Hahn, F. E. *Chem.—Eur. J.* **2002**, *8*, 1327–1335.
- (26) Xie, M. H.; Wang, M.; Wu, C. D. *Inorg. Chem.* **2009**, *48*, 10477–10479.
- (27) Chen, X. M.; Tong, M. L. *Acc. Chem. Res.* **2007**, *40*, 162–170.
- (28) Zhu, H. B.; Gou, S. H. *Coord. Chem. Rev.* **2011**, *255*, 318–338.
- (29) Li, D.; Wu, T. *Inorg. Chem.* **2005**, *44*, 1175–1177.
- (30) Li, D.; Wu, T.; Zhou, X. P.; Zhou, R.; Huang, X. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175–4178.
- (31) Zhao, H.; Qu, Z. R.; Ye, H. Y.; Xiong, R. G. *Chem. Soc. Rev.* **2008**, *37*, 84–100.
- (32) Zhang, X. M. *Coord. Chem. Rev.* **2005**, *249*, 1201–1219.
- (33) Tang, C. H.; Jin, M. L.; Ma, X.; Zhu, Q. L.; Huang, Y. H.; Wang, Y. L.; Hu, S. M.; Sheng, T. L.; Wu, X. T. *Dalton Trans.* **2012**, *41*, 8472–8476.
- (34) Levin, E.; Anaby, A.; Diesendruck, C. E.; Berkovich-Berger, D.; Fuchs, B.; Lemcoff, N. G. *RSC Adv.* **2013**, *3*, 1735–1738.
- (35) Yadav, P. K.; Banerjee, R. *J. Biol. Chem.* **2012**, *287*, 43464–43471.
- (36) Naylor, R. F. *J. Chem. Soc.* **1947**, 1532–1539.
- (37) Routh, J. I. *J. Biol. Chem.* **1939**, *130*, 297–304.
- (38) Limido, J.; Mallah, I. A.; Jungers, J. C. *Bull. Soc. Chim. Belg.* **1949**, *58*, 350–376.
- (39) Schafer, W.; Schweig, A. *Z. Naturforsch.* **1975**, *30a*, 1785–1786.
- (40) Thompson, C. J.; Meyer, R. A.; Ball, J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3284–3287.
- (41) Thompson, C. J.; Meyer, R. A.; Ball, J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3287–3289.
- (42) Seho, A. H.; Darwent, B. D. *J. Am. Chem. Soc.* **1954**, *76*, 4806–4810.