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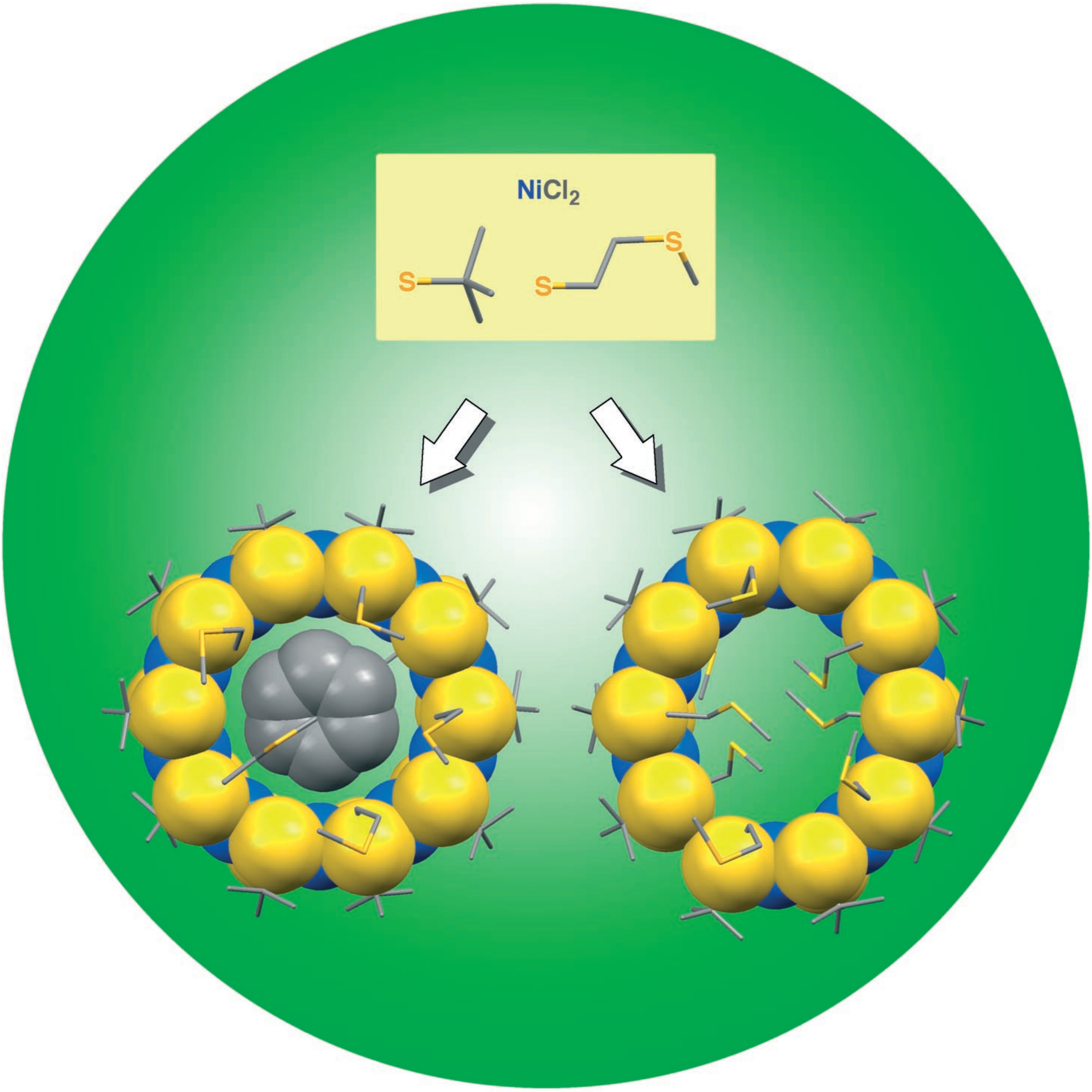

The flexible configuration of the new *cyclo*-$Ni_{10}S_{20}$ toroid was revealed by X-ray structural analysis to be circular or ellipsoidal, depending on the presence or absence of an encapsulated benzene molecule. For a more detailed discussion on the synthesis and structure, see the Communication by K. Tatsumi and co-workers on the following pages.

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Nickel(II) Thiolate Complexes with a Flexible *cyclo*-$\{Ni_{10}S_{20}\}$ Framework**

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First-row transition-metal toroidal architectures are important motifs for potential applications in molecular recognition and magnetic materials.[1,2] In contrast to the ubiquitous O- or N-bridged metal rings, which exhibit fascinating cluster configurations,[3–9] the study of the S-bridged variants remains limited. Homoleptic nickel(II) thiolates $[\{Ni(\mu\text{-}SR)_2\}_n]$ occasionally generate cyclic structures by forming shared edges of the square NiS_4 coordination planes, and several hexanuclear ring clusters $[\{Ni(\mu\text{-}SR)_2\}_6]$ have been reported.[10] Tetranuclear[11] and pentanuclear cyclic complexes have also been isolated,[11c,12] but reports of the synthesis of larger cyclic complexes are still limited. The structure of $[\{Ni(\mu\text{-}SCH_2CO_2Et)_2\}_8]$ was reported by Dance et al. in which the substituent of one thiolate bridge is tilted inward to fill the cavity of the octanuclear ring.[13] Recently, the intriguing cyclic structures of nona- and undecanuclear complexes $[\{Ni(\mu\text{-}SPh)_2\}_n]$ ($n = 9$, 11) were determined by Dahl and co-workers, although in low yield.[14] Each of the cyclic nickel thiolates described above is composed of one kind of thiolate ligand. In contrast, Wolczanski and co-workers synthesized a dodecanuclear cyclic complex $[\{Ni(\mu\text{-}SSi\mathit{t}Bu_3)(\mu\text{-}Br)\}_{12}]$, in which the nickel atoms, in a tetrahedral geometry, are linked by a sterically demanding thiolate ligand and a bromine atom; however, the complex was obtained as a mixture with by-products.[15] As an extension of our study on transition-metal thiolates,[16] we became interested in thioether–thiolate hybrid ligands. Reported herein is a new synthetic route to cyclic nickel thiolate complexes with two different thiolate bridges, namely an alkylthiolate ligand (S*i*Pr or S*t*Bu) and 2-methylthioethanethiolate (mtet), and the use of these ligands resulted in the selective formation of *cyclo*-$[\{Ni(\mu\text{-}S\mathit{i}Pr)(\mu\text{-}mtet)\}_6]$ and *cyclo*-$[\{Ni(\mu\text{-}S\mathit{t}Bu)(\mu\text{-}mtet)\}_{10}]$. We found that the ring configuration of the decanuclear nickel cluster is flexible and exhibits either a circular or ellipsoidal form which is dependent on the presence or absence of an encapsulated guest molecule.

The reaction of $NiCl_2\cdot 6\,H_2O$ with one equivalent of [K(mtet)] at room temperature led to an immediate color change from light green to deep red, and the thiolate-bridged dinuclear nickel complex $[\{NiCl(\mu\text{-}mtet)\}_2]$ (**1**) was isolated in 70% yield as brown-red block-shaped crystals.[17,18] In the structure of **1**, the two mtet ligands link the Ni atoms through the thiolate sulfur atoms, and the thioether sulfur atoms and chloride atoms occupy the terminal positions. Thus, two square $\{NiClS_3\}$ units are conjoined at an edge, and the Ni_2S_2 rhombus is puckered (dihedral angle: 117.8°). This complex was found to be a suitable precursor for the synthesis of a series of mixed-thiolato complexes of nickel. Thus, **1** was treated with two equivalents of K(S*i*Pr) in MeOH for six hours, and subsequent crystallization from a mixture of benzene/hexane generated deep-red hexagonal plates of $[\{Ni(\mu\text{-}S\mathit{i}Pr)(\mu\text{-}mtet)\}_6]\cdot C_6H_6$ (**2**) in 35% yield (Scheme 1). The X-ray crystal analysis revealed a hexagonal $\{Ni_6S_{12}\}$ framework (Figure 1), as was observed for the previously reported complexes $[\{Ni(\mu\text{-}SR)_2\}_6]$.[10,18] The cocrystallized benzene molecule is located outside the Ni_6 ring. The transannular Ni···Ni separations are in the range 5.757(2)–5.915(1) Å, and the dihedral angles between two adjacent NiS_2 planes (121.6–125.6°) are close in value to the interior angle of the ideal hexagon. The two kinds of thiolate ligands, mtet and S*i*Pr, are situated alternately above and below the Ni_6 plane. The *i*Pr groups are oriented away from the ring, and each thioether substituent of the mtet ligands extends above or below the Ni_6 plane.

When the reaction of **1** was carried out with K(S*t*Bu) instead of K(S*i*Pr), a decanuclear cluster $[\{Ni(\mu\text{-}S\mathit{t}Bu)(\mu\text{-}mtet)\}_{10}]$ (**3**) was obtained in 62–66% yield as dark-red block-shaped crystals after recrystallization from benzene/HMDSO or toluene/HMDSO (HMDSO = hexamethyldisiloxane). The toroidal $\{Ni_{10}S_{20}\}$ core geometry of **3** was determined by X-ray analysis, and analogously to the ligand conformation in **2**, the mtet and S*t*Bu ligands bridge the Ni atoms alternately above and below the Ni_{10} plane. Interestingly, **3** was found to crystallize in different forms depending on the solvent used for crystallization. In the X-ray structure of crystals obtained from a mixture of benzene/HMDSO, one of the three benzene molecules is encapsulated in the cavity formed by the $\{Ni_{10}S_{20}\}$ toroid. Thus, the compound is formulated as $[C_6H_6\subset\{Ni(\mu\text{-}S\mathit{t}Bu)(\mu\text{-}mtet)\}_{10}]\cdot 2\,C_6H_6$ (**3a**), and the toroidal $\{Ni_{10}S_{20}\}$ core assumes a circular shape.[18] However, no solvent molecule was incorporated inside the ring when compound **3** was crystallized from a mixture of toluene/HMDSO. In this case, the $\{Ni_{10}S_{20}\}$ core displays an ellipsoidal shape, and the compound is formulated as $[\{Ni(\mu\text{-}S\mathit{t}Bu)(\mu\text{-}mtet)\}_{10}]\cdot CH_3C_6H_5$ (**3b**).[18]

In the crystal structure of **3a** (Figure 2), the benzene molecule inside the cavity lies approximately in the Ni_{10} plane but is tilted by 16.6°. As was the case for $[\{Ni(\mu\text{-}S\mathit{i}Pr)(\mu\text{-}mtet)\}_6]\cdot C_6H_6$ (**2**), the *t*Bu groups are each oriented outward from the $\{Ni_{10}S_{20}\}$ toroid. The mtet substituents are oriented above and below the Ni_{10} plane, except for two of the mtet

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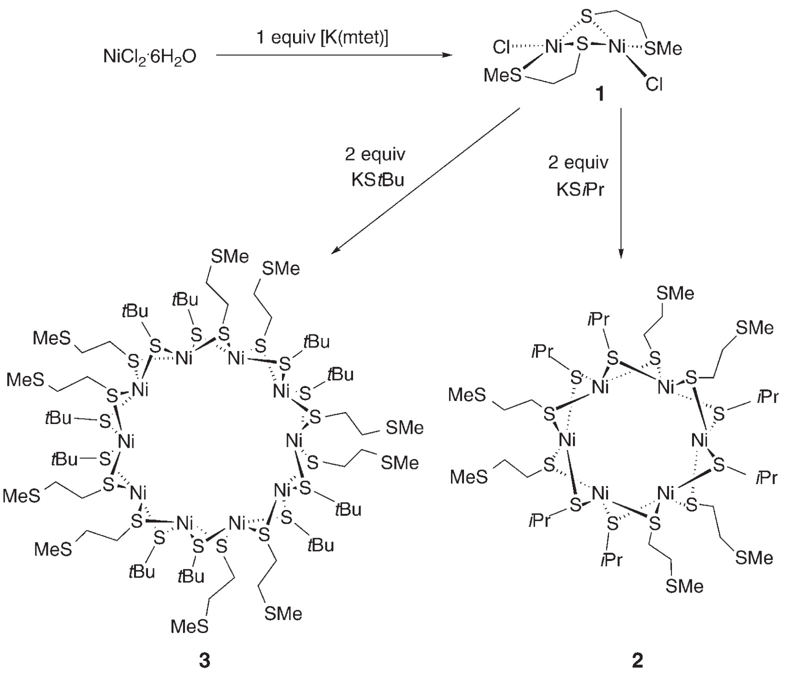


Scheme 1. The synthesis of **2** and **3**.

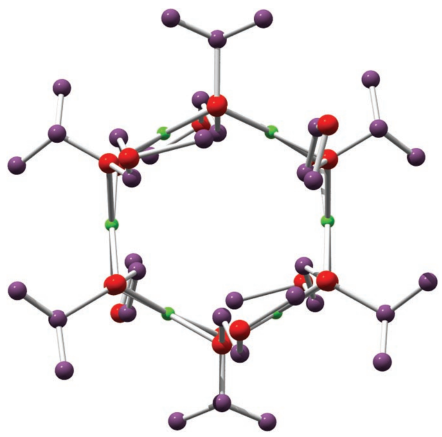


Figure 1. Molecular structure of **2** (Ni green, S red, C purple). All protons and the solvent molecule are omitted for clarity. Neighboring interatomic distances [Å]: Ni–S 2.188(2)–2.207(2) (av: 2.20), Ni–Ni 2.893(1)–2.951(1) (av: 2.92).

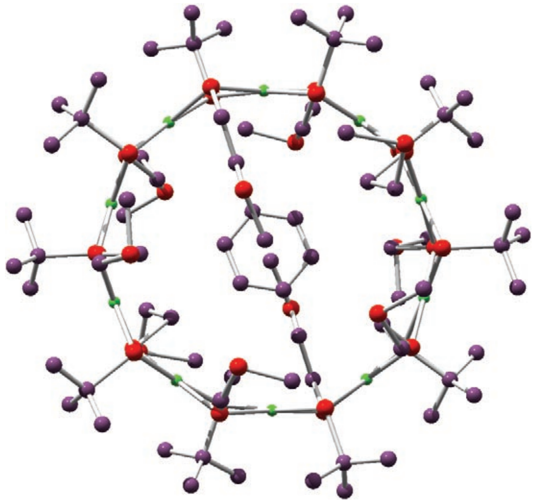


Figure 2. Molecular structure of **3a** (Ni green, S red, C purple). All protons and the solvent molecules are omitted for clarity. Neighboring interatomic distances [Å]: Ni–S 2.190(1)–2.214(1) (av: 2.20), Ni–Ni 3.1307(8)–3.172(1) (av: 3.16).

ligands which are extended toward the center of the toroid cavity such that the thioether groups clamp the encapsulated benzene molecule from above and below. The transannular Ni···Ni separations are nearly constant (10.075(2)–10.336(2) Å), thus consistent with the round shape of the $\{Ni_{10}S_{20}\}$ toroid. The dihedral angles between adjacent NiS_2 planes also do not vary significantly (144.1–147.8°) and are understandably larger than those of the hexanuclear core of **2**.

In the case of **3b** (Figure 3), the thioether substituents of four of the mtet ligands are extended toward the center of the $\{Ni_{10}S_{20}\}$ toroid, and two of these penetrate into the central cavity where the benzene molecule is incorporated for **3a**. In addition, the $\{Ni_{10}S_{20}\}$ toroid in **3b** possesses an ellipsoidal shape, and the consequences of this shape are the varied dihedral angles between two adjoining NiS_2 planes (138.4 to 152.4°) and the varied transannular Ni···Ni separations (9.496(2) to 11.113(3) Å, Figure 4). Thus, the geometry of the $\{Ni_{10}S_{20}\}$ toroid is flexible.

Expansion of the ring size from the hexanuclear cluster **2** to the decanuclear cluster **3a** or **3b** appears to be promoted by the change of bridging thiolate ligand, from S*i*Pr to S*t*Bu. A close inspection of the X-ray structures reveals that the averaged sum of the bond angles at the S atoms of the μ-S*t*Bu ligands is 310° (**3a**) or 311° (**3b**), while the corresponding sum for the μ-S*i*Pr ligands in hexanuclear **2** is distinctively smaller (294°). Although the difference is not large, we speculate that the bulkier *t*Bu group, relative to *i*Pr, would have caused the decrease in pyramidality at the thiolate sulfur atoms to minimize steric repulsion between the *t*Bu groups and the $\{Ni_2(\mu\text{-}S)_2\}$ core atoms. The steric hindrance is revealed in the short contacts between protons of the *t*Bu groups and both the S atoms of each μ-mtet ligand and Ni atoms within each $\{Ni_2S_2\}$ quadrangular unit;[19] these separations are close to the sums of the van der Waals radii of the individual atoms.[20] Dance et al.[13] pointed out that the Ni-S(R)-Ni bond angles of doubly bridged $\{Ni(\mu\text{-}SR)_2Ni\}$ units tend to increase as the pyramidality of the μ-S atoms decreases.[10–13,21] The averaged Ni-S(*t*Bu)-Ni bond angle of 92° for **3a** (and for **3b**) is evidently larger than that of **2** (83°) and those of the related complexes $[\{Ni(\mu\text{-}SR)_2\}_n]$ (n = 4, 5, 6, 8).[10–13] The larger Ni-S(*t*Bu)-Ni bond angles, in turn, bring about the larger dihedral angles between the adjacent NiS_2 planes of **3a** and **3b**, and the larger decanuclear ring is the consequence.

In conclusion, the decanuclear nickel(II) thiolato cluster $[\{Ni(\mu\text{-}S\textit{t}Bu)(\mu\text{-}mtet)\}_{10}]$ with a flexible core was synthesized by the reaction of the preformed complex $[\{NiCl(\mu\text{-}mtet)\}_2]$ with KS*t*Bu. This approach using stepwise introduction of two

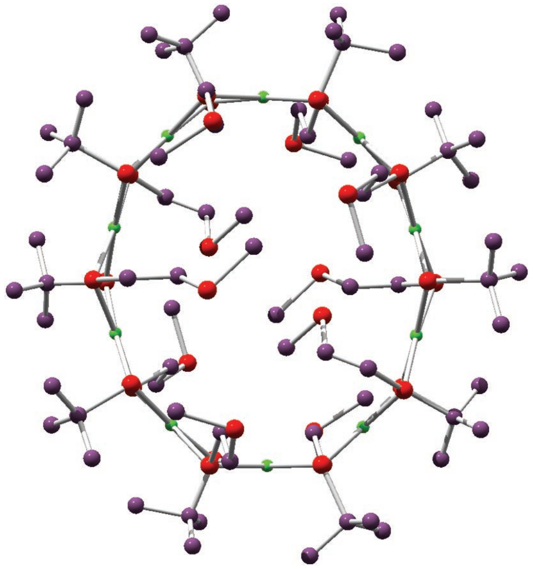
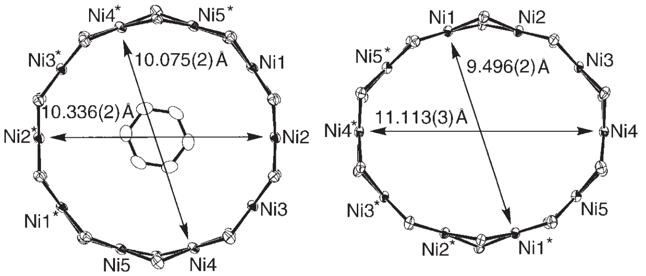


Figure 3. Molecular structure of **3b** (Ni green, S red, C purple). All protons and the solvent molecule are omitted for clarity. Neighboring interatomic distances (Å): Ni–S 2.196(1)–2.224(1) (av: 2.21), Ni–Ni 3.098(1)–3.224(1) (av: 3.17).



3a **3b**

Figure 4. Top view of the $\{Ni_{10}S_{20}\}$ core configurations of **3a** and **3b**.

kinds of thiolate ligands to a nickel(II) center expands the scope of synthetic routes to cyclic polynuclear nickel(II) thiolates with various sizes and functions.

Experimental Section

1: The reported synthetic method was modified as follows.[17] [K(mtet)], prepared from H(mtet) (0.108 g, 1 mmol) and KO*t*Bu (0.112 g, 1 mmol), was slowly added to a solution of $NiCl_2{\cdot}6H_2O$ (0.237 g, 1 mmol) in MeOH (15 mL), and the mixture was stirred at room temperature for 4 h. The volatiles were removed, and the resulting brown residue was extracted with toluene and then dried in a vacuum. The dark red powder was dissolved in toluene and layered with hexane to afford brown-red block-shaped crystals of **1** (yield: 0.141 g, 70 %).

2: KS*i*Pr, prepared from HS*i*Pr (0.076 g, 1 mmol) and KO*t*Bu (0.112 g, 1 mmol), was slowly added to a solution of $[NiCl(\mu\text{-mtet})]_2$ (**1**; 0.201 g, 0.5 mmol) in MeOH (20 mL) and stirred at room temperature for 6 h. A work up similar to that for **1** afforded a dark red powder, which was dissolved in benzene and layered with hexane to give **2** as deep-red hexagonal plates (yield: 0.089 g, 35 %).

3: A similar synthetic procedure to that for **2**, except that KS*t*Bu was added instead of KS*i*Pr, gave a dark red powder, which was dissolved in benzene and layered with HMDSO to afford **3a** as black-red block-shaped crystals (yield: 0.173 g, 62 %). Alternatively, analogous crystallization using toluene and HMDSO gave **3b** as black-red block-shaped crystals (yield: 0.174 g, 66 %).

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Keywords: cluster compounds · nickel · S ligands · structure elucidation · supramolecular chemistry

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[18] Crystal data for **1**: $C_6H_{14}Ni_2S_4Cl_2$, monoclinic, space group $C2/c$ (No. 15), $a = 13.343(5)$, $b = 6.632(2)$, $c = 15.258(4)$ Å, $\beta = 91.00(2)^\circ$, $V = 1350.0(7)$ Å^3, $Z = 4$, $T = 173$ K, $\lambda = 0.71073$ Å, $F(000) = 816$, $\mu = 37.63\ \text{cm}^{-1}$, $\rho_{calcd} = 1.981\ \text{g cm}^{-3}$, 7778 reflections ($2\theta < 55.20^\circ$), 1824 independent ($R_{int} = 0.036$), $R1 = 0.029$ ($I > 2\sigma(I)$), $Rw = 0.073$ (all data). Crystal data for **2**: $C_{42}H_{90}Ni_6S_{18}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.733(2)$, $b = 12.940(2)$, $c = 12.953(3)$ Å, $\alpha = 66.44(1)$, $\beta = 66.19(1)$, $\gamma = 60.92(1)^\circ$, $V = 1650.2(5)$ Å^3, $Z = 1$, $T = 113$ K, $\lambda = 0.71073$ Å, $F(000) = 798$, $\mu = 22.75\ \text{cm}^{-1}$, $\rho_{calcd} = 1.534\ \text{g cm}^{-3}$, 12961 reflections ($2\theta < 54.96^\circ$), 7211 independent ($R_{int} = 0.036$), $R1 = 0.080$ ($I > 2\sigma(I)$), $Rw = 0.216$ (all data). Crystal data for **3a**: $C_{88}H_{178}Ni_{10}S_{30}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.337(4)$, $b = 15.542(4)$, $c = 16.396(4)$ Å, $\alpha = 104.5377(5)$, $\beta = 112.387(3)$, $\gamma = 107.078(2)^\circ$, $V = 3149(1)$ Å^3, $Z = 1$, $T = 113$ K, $\lambda = 0.71073$ Å, $F(000) = 1466$, $\mu = 19.93\ \text{cm}^{-1}$, $\rho_{calcd} = 1.468\ \text{g cm}^{-3}$, 24747 reflections ($2\theta < 54.97^\circ$), 13759 independent ($R_{int} = 0.017$), $R1 = 0.059$ ($I > 2\sigma(I)$), $Rw = 0.162$ (all data). Crystal data for **3b**: $C_{77}H_{168}Ni_{10}S_{30}$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.130(4)$, $b = 14.925(5)$, $c = 16.708(6)$ Å, $\alpha = 109.871(3)$, $\beta = 111.328(3)$, $\gamma = 98.234(2)^\circ$, $V = 2940(1)$ Å^3, $Z = 1$, $T = 113$ K, $\lambda = 0.71073$ Å, $F(000) = 1390$, $\mu = 21.31\ \text{cm}^{-1}$, $\rho_{calcd} = 1.493\ \text{g cm}^{-3}$, 22982 reflections ($2\theta < 54.97^\circ$), 12826 independent ($R_{int} = 0.020$), $R1 = 0.065$ ($I > 2\sigma(I)$), $Rw = 0.184$ (all data). All calculations were performed with the TEXSAN program package, and structures were solved by Patterson methods (DIRDIF94 PATTY) and refined by full-matrix least squares against F^2. The protons were placed at calculated positions (d(C–H): 0.97 Å). CCDC-295875 (**1**) and CCDC-294804–294806 (**2**, **3a**, **3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] The mean separations of the closest $C_{tBu}\cdots S_{mtet}$ and $C_{tBu}\cdots Ni$ contacts at the $\{Ni_2S_2\}$ quadrangle units of **3a** are 3.34 and 3.55 Å, respectively.

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