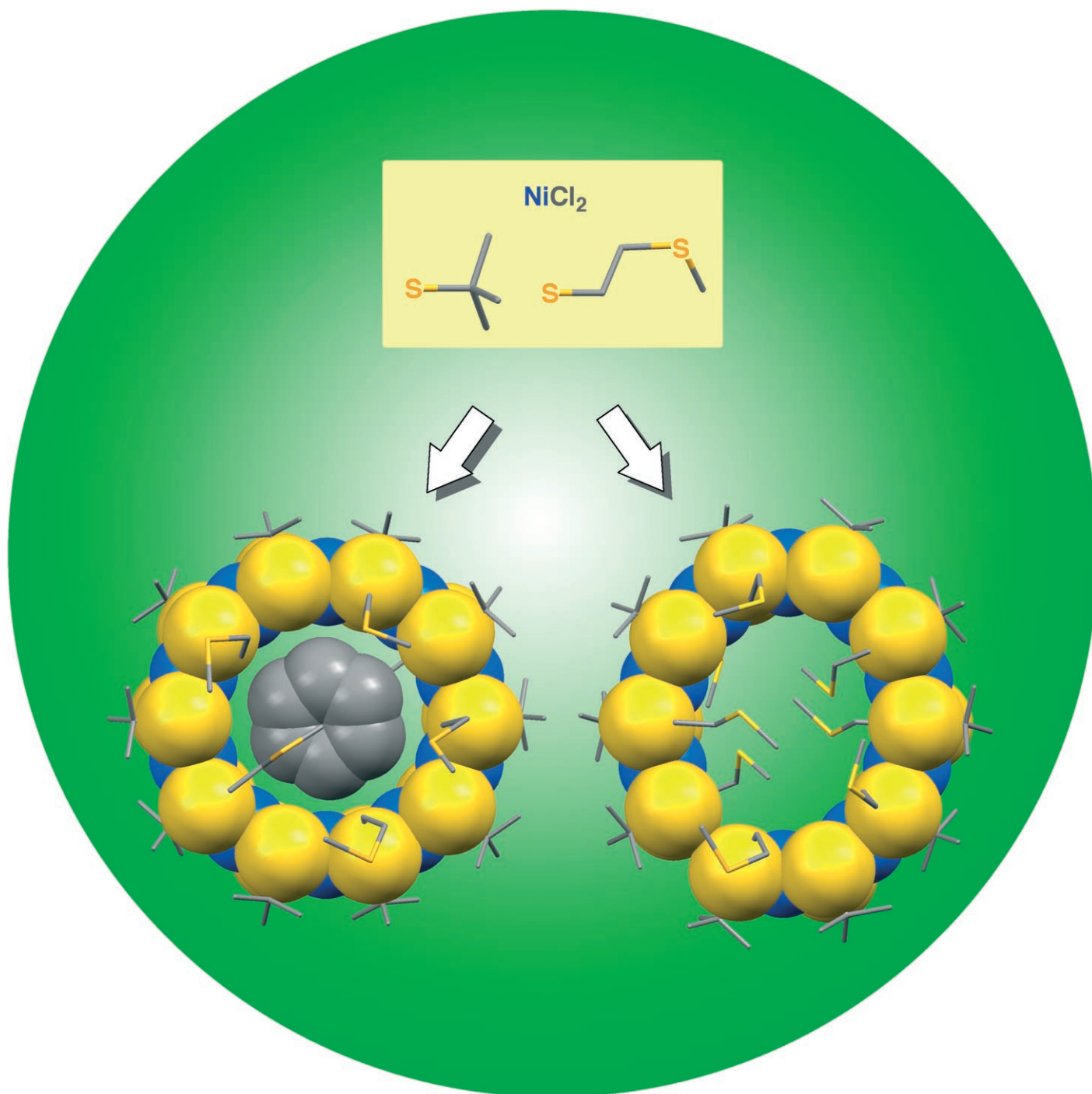


Zuschriften



Die flexible Konfiguration des neuen $\text{cyclo-Ni}_{10}\text{S}_{20}$ -Toroids wurde durch Röntgenstrukturanalyse aufgedeckt: kreisförmig oder ellipsoidal, je nach An- oder Abwesenheit eines eingeschlossenen Benzolmoleküls. Eine detaillierte Diskussion der Synthese und Strukturen ist in der Zuschrift von K. Tatsumi und Mitarbeitern auf den folgenden Seiten nachzulesen.

Nickel(II) Thiolate Complexes with a Flexible *cyclo*-[Ni₁₀S₂₀] Framework**

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Tsuyoshi Matsumoto, and Kazuyuki Tatsumi*

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 $[\{\text{Ni}(\mu\text{-SR})_2\}_n]$ occasionally generate cyclic structures by forming shared edges of the square NiS₄ coordination planes, and several hexanuclear ring clusters $[\{\text{Ni}(\mu\text{-SR})_2\}_6]$ 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 $[\{\text{Ni}(\mu\text{-SCH}_2\text{CO}_2\text{Et})_2\}_8]$ 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 $[\{\text{Ni}(\mu\text{-SPh})_2\}_n]$ ($n = 9, 11$) 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 $[\{\text{Ni}(\mu\text{-SSi}t\text{Bu}_3)(\mu\text{-Br})\}_{12}]$, 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 (*i*Pr or *t*Bu) and 2-methylthioethanethiolate (mtet), and the use of these ligands resulted in the selective formation of *cyclo*- $[\{\text{Ni}(\mu\text{-}i\text{Pr})(\mu\text{-mtet})\}_6]$ and *cyclo*- $[\{\text{Ni}(\mu\text{-}t\text{Bu})(\mu\text{-mtet})\}_{10}]$. 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 NiCl₂·6H₂O 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 $[\{\text{NiCl}(\mu\text{-mtet})\}_2]$ (**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 [NiClS₃] units are conjoined at an edge, and the Ni₂S₂ 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(*i*Pr) in MeOH for six hours, and subsequent crystallization from a mixture of benzene/hexane generated deep-red hexagonal plates of $[\{\text{Ni}(\mu\text{-}i\text{Pr})(\mu\text{-mtet})\}_6]\cdot\text{C}_6\text{H}_6$ (**2**) in 35 % yield (Scheme 1). The X-ray crystal analysis revealed a hexagonal {Ni₆S₁₂} framework (Figure 1), as was observed for the previously reported complexes $[\{\text{Ni}(\mu\text{-SR})_2\}_6]$.^[10,18] The cocrystallized benzene molecule is located outside the Ni₆ ring. The transannular Ni···Ni separations are in the range 5.757(2)–5.915(1) Å, and the dihedral angles between two adjacent NiS₂ 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 *i*Pr, are situated alternately above and below the Ni₆ plane. The *i*Pr groups are oriented away from the ring, and each thioether substituent of the mtet ligands extends above or below the Ni₆ plane.

When the reaction of **1** was carried out with K(*t*Bu) instead of K(*i*Pr), a decanuclear cluster $[\{\text{Ni}(\mu\text{-}t\text{Bu})(\mu\text{-mtet})\}_{10}]$ (**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 [Ni₁₀S₂₀] core geometry of **3** was determined by X-ray analysis, and analogously to the ligand conformation in **2**, the mtet and *t*Bu ligands bridge the Ni atoms alternately above and below the Ni₁₀ 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 [Ni₁₀S₂₀] toroid. Thus, the compound is formulated as $[\text{C}_6\text{H}_6\subset\{\text{Ni}(\mu\text{-}t\text{Bu})(\mu\text{-mtet})\}_{10}]\cdot 2\text{C}_6\text{H}_6$ (**3a**), and the toroidal {Ni₁₀S₂₀} 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 [Ni₁₀S₂₀] core displays an ellipsoidal shape, and the compound is formulated as $[\{\text{Ni}(\mu\text{-}t\text{Bu})(\mu\text{-mtet})\}_{10}]\cdot\text{CH}_3\text{C}_6\text{H}_5$ (**3b**).^[18]

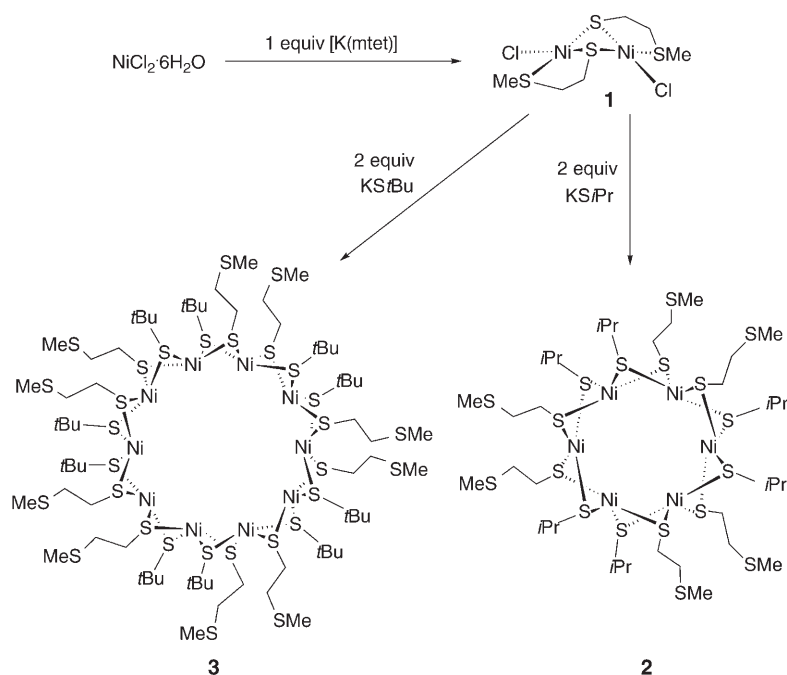
In the crystal structure of **3a** (Figure 2), the benzene molecule inside the cavity lies approximately in the Ni₁₀ plane but is tilted by 16.6°. As was the case for $[\{\text{Ni}(\mu\text{-}i\text{Pr})(\mu\text{-mtet})\}_6]\cdot\text{C}_6\text{H}_6$ (**2**), the *t*Bu groups are each oriented outward from the [Ni₁₀S₂₀] toroid. The mtet substituents are oriented above and below the Ni₁₀ plane, except for two of the mtet

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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



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

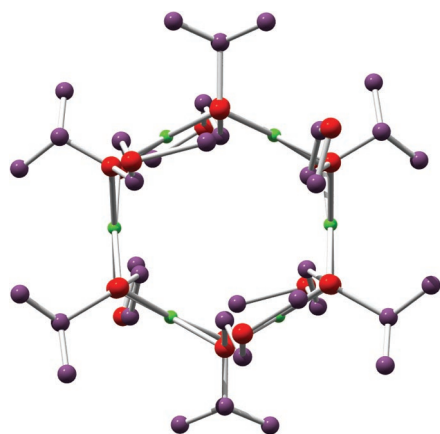


Figure 1. Molecular structure of **2** (Ni green, S red, C purple). All protons and the solvent molecule are omitted for clarity. Neighboring interatomic distances [Å]: Ni–S 2.188(2)–2.207(2) (av: 2.20), Ni–Ni 2.893(1)–2.951(1) (av: 2.92).

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 {Ni₁₀S₂₀} toroid. The dihedral angles between adjacent NiS₂ 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 {Ni₁₀S₂₀} toroid, and two of these penetrate into the central cavity where the benzene molecule is incorporated for **3a**. In addition, the {Ni₁₀S₂₀} toroid in **3b** possesses an ellipsoidal shape, and the consequences of this shape are the varied

dihedral angles between two adjoining NiS₂ 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 {Ni₁₀S₂₀} 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 *Si*Pr to *Sr*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 -*Sr*Bu ligands is 310° (**3a**) or 311° (**3b**), while the corresponding sum for the μ -*Si*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 pyramidity at the thiolate sulfur atoms to minimize steric repulsion between the *t*Bu groups and the {Ni₂(μ -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 {Ni₂S₂} 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(μ -

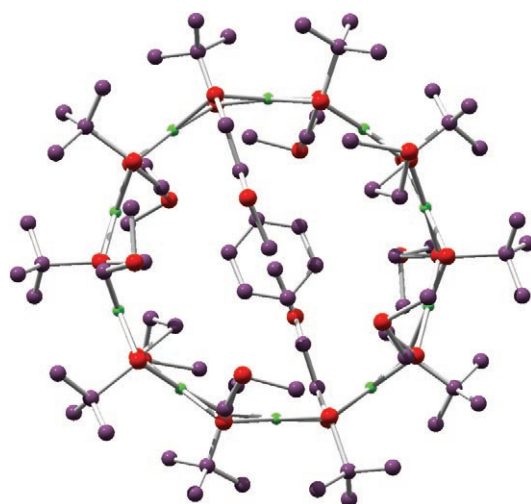


Figure 2. Molecular structure of **3a** (Ni green, S red, C purple). All protons and the solvent molecules are omitted for clarity. Neighboring interatomic distances [Å]: Ni–S 2.190(1)–2.214(1) (av: 2.20), Ni–Ni 3.1307(8)–3.172(1) (av: 3.16).

SR)₂Ni} units tend to increase as the pyramidity 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(μ -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 NiS₂ planes of **3a** and **3b**, and the larger decanuclear ring is the consequence.

In conclusion, the decanuclear nickel(II) thiolato cluster [{Ni(μ -*Sr*Bu)(μ -mtet)}₁₀] with a flexible core was synthesized by the reaction of the preformed complex [{NiCl(μ -mtet)}₂] with *KSr*Bu. This approach using stepwise introduction of two

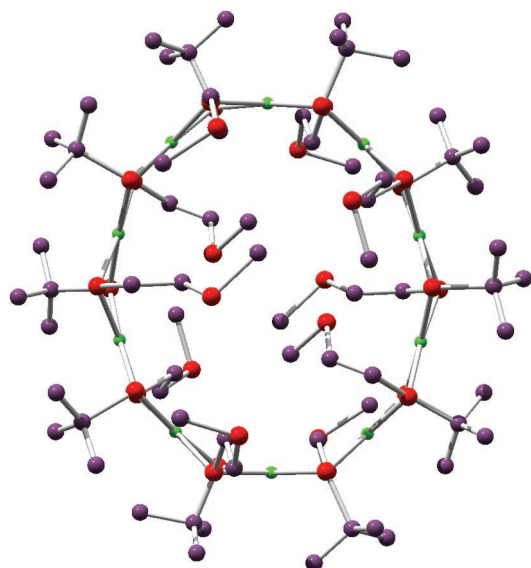


Figure 3. Molecular structure of **3b** (Ni green, S red, C purple). All protons and the solvent molecule are omitted for clarity. Neighboring interatomic distances (Å): Ni–S 2.196(1)–2.224(1) (av: 2.21), Ni–Ni 3.098(1)–3.224(1) (av: 3.17).

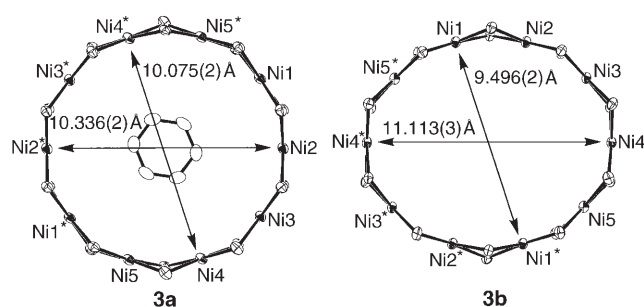


Figure 4. Top view of the $\{Ni_{10}S_{20}\}$ core configurations of **3a** and **3b**.

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 KOtBu (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: KSiPr, prepared from HSiPr (0.076 g, 1 mmol) and KOtBu (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 KStBu was added instead of KSiPr, 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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