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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Penta- and hexa-nuclear nickel tiara-like clusters with two different thiolate bridges

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Six nickel tiara-like clusters, cyclo-[Ni(μ -EDT)]₅ (**1**), cyclo-[Ni(μ -SiPe)₂]₆ (**2**), cyclo-[Ni₆(μ -SiBu)₄(μ -EDT)₄] (**3**), cyclo-[Ni₆(μ -SiBu)₄(μ -PDT)₄] (**4**), cyclo-[Ni₆(μ -SPh)₄(μ -EDT)₄] (**5**) and cyclo-[Ni₆(μ -SPh)₄(μ -PDT)₄] (**6**) (SiBu=2-methyl-2-propanethiol, EDT = 1,2-ethanedithiol, PDT = isopentylthiol, SiPe = 1,3-propanedithiol) have been successfully synthesized and characterized. All the clusters derived from a designed preparation by the direct synthetic route involving reactions of Ni(ClO₄)₂ with mixed thiolate or disulfide ligands which have discrepancy in coordination ability. Intriguingly, cluster **1** is an infrequent penta-nuclear tiara. Clusters **3** and **4** are hexa-nuclear tiaras with two different types of mono- and bi-dentate aliphatic thiolates. Clusters **5** and **6** exhibit similar structure with mono-aromatic thiolate and bi-dentate aliphatic thiolate ligands. The -SPh ligands were generated from in situ reaction of the disulfide precursor through cleavage of the S-S bond. These heretofore unknown additions are of particular interest to the cyclo-[Ni(μ -SR)₂]_n tiara family which are often constructed by just one kind of thiolate ligand.

Introduction

Metallacrowns represent a new class of multinuclear clusters that are analogous to crown ethers in both structure and function.¹⁻⁷ These clusters have the ability to interact with cations, anions and neutral molecules, leading to potential applications in chemically modified electrodes, molecular recognition agents, anion-selective separation agents and so on.^{3,4,7-11} To form metallacrowns, one can substitute heteroatoms for the methylene carbon atoms of the parent ether complexes. Generally, the metallacrowns can be synthesized using either bridging chalcogen ligands, such as SR, OR anions or multidentate ligands that bridge two metal ions.¹²⁻¹⁷ Up to now, there are plenty of examples for the ubiquitous O- and/or N-bridged metallacrowns, but only a limited number of literature reports are available concerning S-bridged metallacrowns.¹⁵⁻²³

As to S-bridged metallacrowns, nickel thiolates with tiara-like structures [Ni(μ -SR₂)_n] have been a fundamental issue in the development of S-bridged metallocrowns, since the pioneering work by Woodward in the middle of the 1960s.²⁴ These complexes have been initially considered as insoluble high polymers before their definitive structural characterization was achieved through the discrete hexanuclear [Ni(μ -SCH₂CH₃)₂]₆ complex. The unique S-bridged metal rings exhibit fascinating tiara-like cluster configurations by forming the edge-shared coordination square plane MS₄. To date, only about 40 tiara-like nickel thiolates clusters [Ni(μ -SR₂)_n] (n = 4-6, 8-12) have been reported, with a range of monodentate or bidentate thiolates (R=Et,²⁴ C₆H₁₁,²⁵ *i*Pr,²⁶ (CH₂)₂N(*i*Pr)₂,²⁷ (CH₂)₂OH,²⁸ (CH₂)₂SiMe₃,²⁹ (CH₂)₃NH(CH₃)₂,³⁰ (CH₂)₂SCH₃,³¹ *t*Bu,³¹ (CH₂)₂SC₆H₄(*p*-Cl),³² CH₂C₆H₄(*p*-Cl),³³ (CH₂)₂SEt,³⁴ (CH₂)₂S(C₃H₅N),³⁴ CH₂CO₂Et,³⁵ Ph³⁶). Noticeably, almost all

these reported cyclic structures are composed of only single thiolates ligand, except for the newly reported tiaras [Ni(μ -SR1)(μ -SR2)]_n in which one ligand is the functionalized thiolate ligand, namely 2-ethylthioethanethiolate, 2-(2-mercaptoethyl)pyridine, 2-methylthioethanethiolate or 2-aminoethanethiol.^{31,34} The four tiara-like clusters were synthesized through stepwise coordination of thiolate ligands to nickel centers. By exploring a feasible new *in situ* synthetic route, our group obtained four nickel thiolate tiaras with two different aliphatic thiolate bridges, cyclo-[Ni(μ -SiPr)(μ -SMe)]₆, cyclo-[Ni(μ -SiBu)(μ -SMe)]₆, cyclo-[Ni(μ -SiPr)(μ -SEt)]₆ and cyclo-[Ni(μ -SiBu)(μ -SEt)]₁₀.³⁷ To investigate whether do different thiolate ligands influence on the structures of nickel thiolates tiaras, branched aliphatic monodentate thiolates, bidentate thiolates and aromatic disulfide were introduced in the reaction system. Inspired by the phenomenon that the in situ reductive cleavage of the disulfide bond can provide mixed -SMe or -SEt thiolates ligands for nickel tiaras,³⁷⁻⁴² we were to synthesize new tiaras by the combination of bidentate thiolates with disulfide ligands such as phenyldisulfide which may in situ generate an aromatic thiolate. Besides, reactions of Ni(ClO₄)₂ with mixed monodentate thiolates (2-methyl-2-propanethiol, isopentylthiol) and bidentate thiolates (1,2-ethanedithiol, 1,3-propanedithiol) which have discrepancy in coordination ability have also been done. Fortunately, as expected, six tiara-like nickel clusters cyclo-[Ni(μ -EDT)]₅ (**1**), cyclo-[Ni(μ -SiPe)₂]₆ (**2**), cyclo-[Ni₆(μ -SiBu)₄(μ -EDT)₄] (**3**), cyclo-[Ni₆(μ -SiBu)₄(μ -PDT)₄] (**4**), cyclo-[Ni₆(μ -SPh)₄(μ -EDT)₄] (**5**) and cyclo-[Ni₆(μ -SPh)₄(μ -PDT)₄] (**6**) have been obtained. Reported herein are the syntheses and characterizations of these nickel tiaras.

Experimental section

Synthetic methods and Materials

All reagents and solvents used were received from commercial suppliers without further purification. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS Elemental Analyzer. The infrared spectra of KBr pellet were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR Spectrometer. UV-vis-NIR absorption spectra were measured on a Perkin-Elmer Lambda 900 UV-vis spectrophotometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX-2500 diffractometer with Cu K_{α} .

cyclo-[Ni(μ -EDT)]₅ (1) and **cyclo-[Ni(μ -SiPe)₂]₆ (2)** A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (144 mg, 0.4 mmol), isopentylthiol (0.05 ml, 0.4 mmol) and sodium ethylate (56 mg, 0.8 mmol) in 12 ml ethanol was stirred at room temperature for 1 h. Then 1,2-ethanedithiol (0.018 ml, 0.2 mmol) and DMF (4 ml) were added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 16 h. After the autoclave was cooled to room temperature, black cuboid crystals of **1** and black block crystals of **2** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 31% for **1**, 16% for **2** based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd for $\text{Ni}_5\text{S}_{10}\text{C}_{10}\text{H}_{20}$ (**1**): C 15.92, H 2.67; found: C 16.29, H 2.74%. Anal. Calcd for $\text{Ni}_6\text{S}_{12}\text{C}_{60}\text{H}_{130}$ (**2**): C 45.31, H 8.36; found: C 45.40, H 8.19%. Cluster **1** and **2** can also be prepared using only 1,2-ethanedithiol or isopentylthiol respectively. The simpler synthetic procedures are provided in the supporting information.

cyclo-[Ni(μ -SrBu)₄(μ -EDT)₄] (3) A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (144 mg, 0.4 mmol), 2-methyl-2-propanethiol (0.086 ml, 0.8 mmol) and sodium ethylate (112 mg, 1.6 mmol) in 12 ml ethanol was stirred at room temperature for 1 h. Then 1,2-ethanedithiol (0.036 ml, 0.4 mmol) and acetone (2 ml) were added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 8 h. After the autoclave was cooled to room temperature, black prismatic crystals of **3** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 48% based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd for $\text{Ni}_6\text{S}_{12}\text{C}_{24}\text{H}_{52}$ (**3**): C 26.75, H 4.86; found: C 26.93, H 4.77%.

cyclo-[Ni(μ -SrBu)₄(μ -PDT)₄] (4) A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (144 mg, 0.4 mmol), 2-methyl-2-propanethiol (0.086 ml, 0.8 mmol) and sodium ethylate (112 mg, 1.6 mmol) in 12 ml ethanol was stirred at room temperature for 1 h. Then 1,3-propanedithiol (0.04 ml, 0.4 mmol) and acetone (2 ml) were added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 393 K for 8 h. After the autoclave was cooled to room temperature, black needle crystals of **4** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 8% based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd for $\text{Ni}_6\text{S}_{12}\text{C}_{28}\text{H}_{60}$ (**4**): C 29.66, H 5.33; found: C 29.51, H 5.38%.

cyclo-[Ni(μ -SPh)₄(μ -EDT)₄] (5) A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (72 mg, 0.2 mmol), phenyldisulfide (0.044 g, 0.2 mmol), 1,2-ethanedithiol (0.036 ml, 0.4 mmol) and sodium ethylate (56 mg, 0.8 mmol) in 8 ml ethanol and 4 ml DMF was

stirred at room temperature for 1 h. Then acetone 2 ml was added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 24 h. After the autoclave was cooled to room temperature, black cuboid crystals of **5** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 40% based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd for $\text{Ni}_6\text{S}_{12}\text{C}_{32}\text{H}_{36}$ (**5**): C 33.20, H 3.13; found: C 33.28, H 3.16%.

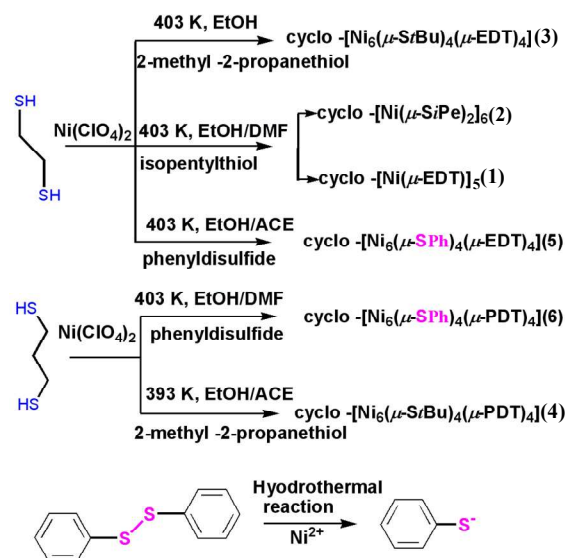
cyclo-[Ni(μ -SPh)₄(μ -PDT)₄] (6) A mixture of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (72 mg, 0.2 mmol), phenyldisulfide (0.044 g, 0.2 mmol), 1,3-propanedithiol (0.02 ml, 0.2 mmol) and sodium ethylate (28 mg, 0.4 mmol) in 8 ml ethanol and 6 ml DMF was stirred at room temperature for 1 h. Then 2 ml acetone was added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 24 h. After the autoclave was cooled to room temperature, black block crystals of **6** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 25% based on $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd for $\text{Ni}_6\text{S}_{12}\text{C}_{36}\text{H}_{44}$ (**6**): C 35.63, H 3.65; found: C 35.80, H 3.70%.

X-ray crystallography

Single crystals for **1-6** were mounted on glass fibers. Cell constants and data collections were performed on a Rigaku Mecury CCD diffractometer equipped with graphite-monochromated Mo- K_{α} radiation source ($\lambda = 0.71073 \text{ \AA}$) by ω scan mode. The structures were solved by the direct method using the SHELXTL Version 5 package of crystallographic software, and refined with a full-matrix least-squares refinement on F^2 .⁴³ Metal atoms were located from the E-maps and refined anisotropically. The other non-hydrogen atoms were located by the difference Fourier maps based on these atomic positions and refined anisotropically. Hydrogen atoms were added according to the theoretical models. Pertinent crystal data and structure refinement results are summarized in the supporting information.

Results and discussion

Syntheses of clusters 1, 2, 3, 4, 5 and 6



Scheme 1 Schematic representation of the in situ synthesized nickel thiolates tiaras (ACE=acetone).

As shown in Scheme 1, the solvothermal reaction of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 2-methyl-2-propanethiol and 1,2-ethanedithiol in ethanol at 403 K for 8 h, afforded the black crystals of complex $\text{cyclo}[\text{Ni}_6(\mu\text{-StBu})_4(\mu\text{-EDT})_4](\mathbf{3})$. The similar reactions with 2-methyl-2-propanethiol and 1,3-propanedithiol at 393 K for 8 h gave a similar complex $\text{cyclo}[\text{Ni}_6(\mu\text{-StBu})_4(\mu\text{-PDT})_4](\mathbf{4})$. This is the first time that the mono- and bi-dentate aliphatic thiolates harmoniously self-assemble together to get nickel tiaras.

Dance *et al.* stated that larger toroids (than the octagonal member) are likely to form when there is a central occupant, either a guest molecule or reentrant ligand, providing some mechanical assistance.⁴⁴ Accordingly, all the published large nickel thiolates tiaras $[(\text{Ni}(\mu\text{-SR})_2)_n]$ ($n=8-12$) are of a central occupant.^{31,34,37,44} Thus, R group, such as long carbon chain and aromatic ring, extending toward the center of the toroid cavity, will make larger nickel tiaras possible. Therefore we tried to assemble a large tiara by using isopentylthiol with a long carbon chain and phenyldisulfide with an aromatic ring. Unfortunately, the reaction of $\text{Ni}(\text{ClO}_4)_2$ with isopentylthiol and 1,2-ethanedithiol only gave $\text{cyclo}[\text{Ni}(\mu\text{-EDT})_5](\mathbf{1})$ and $\text{cyclo}\{[\text{Ni}(\mu\text{-SiPe})_2]_6\}(\mathbf{2})$, both are composed of just single thiolates ligand. Cluster **1** is a penta-nuclear tiara. Cluster **2** is a classic hexa-nuclear tiara because of the isopentylthiol ligands just extend above or below the Ni_6 plane alternatively, not as a central occupant. In addition, the combination of phenyldisulfide with 1,2-ethanedithiol or 1,3-propanedithiol just led to the formation of $\text{cyclo}[\text{Ni}_6(\mu\text{-SPh})_4(\mu\text{-EDT})_4](\mathbf{5})$ and $\text{cyclo}[\text{Ni}_6(\mu\text{-SPh})_4(\mu\text{-PDT})_4](\mathbf{6})$, respectively. In both the tiaras **5** and **6**, the aromatic thiolate ligands which was generated from the in situ cleavage of the S-S bond of phenyldisulfide (Scheme S1) bend outward the center of the toroid cavity.

Structure descriptions and analyses of clusters **1**, **2**, **3**, **4**, **5** and **6**

The crystal data and structure refinements are listed in Table S1-S5, and selected bond lengths and angles for all the clusters are given in Tables S6-S10. The detailed crystal structure data of cluster **3** is not provided here for the internal structure defects deteriorating the data quality and no perfect data collection was obtained. Single-crystal X-ray analysis revealed that all the structures are sulfur-bridged metal rings exhibit fascinating tiara-like cluster configurations by forming the edge-shared coordination square plane MS_4 . Each $\text{Ni}(\text{II})$ atom is coordinated to an approximate rectangular-planar arrangement of four sulfur atoms with Ni-S distances of 2.157(1)-2.217(1) Å for **1**, 2.193(3)-2.215(3) Å for **2**, 2.195(4)-2.231(3) Å for **4**, 2.155(2)-2.233(2) Å for **5** and 2.156(2)-2.215(2) Å for **6**, respectively. The four clusters **2**, **4**, **5** and **6** are hexa-nuclear tiaras exhibiting a hexagonal $[\text{Ni}_6\text{S}_{12}]$ framework. The side view of the core structure shows a nearly planar nonbonding Ni_6 ring sandwiched between two approximately coplanar nonbonding S_{12} rings. For cluster **2**, $\text{cyclo}\{[\text{Ni}(\mu\text{-SiPe})_2]_6\}$, the 12 thiolate ligands are in different orientations and the SiPe group sterically disposed in alternating axial and equatorial positions about the n -polygonal nickel ring. While for clusters **4**, **5** and **6**, there are two different types of mono- and bi-dentate thiolates ligand on the tiaras. The two kinds of thiolate ligands are situated alternately on the Ni_6 plane. The StBu (or SPh) groups are oriented away from the ring,

and the EDT (or PDT) groups extend above or below the Ni_6 plane. All the EDT and PDT groups are in a *-cis* mode with both sulfur atoms of each ligand being on the same side of the nickel plane (Fig. 1).^{45,46}

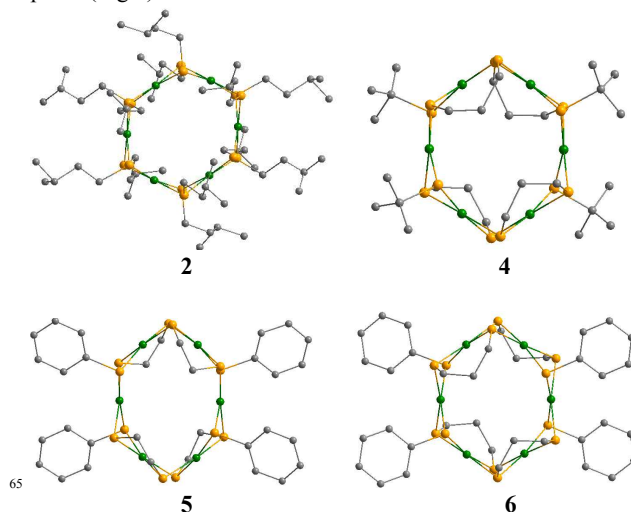


Fig.1 Molecular view of **2**, **4**, **5** and **6**. The hydrogen atoms are omitted for clarity (Ni green, S yellow).

Based on the different steric hindrance of the bridging thiolate ligands, the Ni_6 tiara conformation of clusters **2**, **4**, **5** and **6** are slightly different (Fig. 2). The Ni-Ni-Ni vertex angles in cycloidal Ni_6 ring are in the range 114.83(7)-125.24(7)° for **2**, 117.68(6)-125.94(4)° for **4**, 107.42-135.47(2)° for **5**, 114.71(4)-127.68(3)° for **6**, respectively. The adjacent and opposite nickel ions have a distance range of 2.858(3)-3.011(3) Å and 5.871(4)-6.128(4) Å for **2**, 2.855(3)-3.034(2) Å and 5.082(4)-5.620(5) Å for **4**, 2.690(1)-3.002(9) Å and 4.933(2)-6.142(2) Å for **5**, 2.794(2)-2.956(2) Å and 5.341(4)-6.004(3) Å for **6**, respectively. All these angle and length data show apparent deviations in value from those of the ideal hexagon, though they are comparable to the corresponding values in other hexa-nuclear analogues.^{29-31,45-52} It is also noticeable that the steric hindrance of the more bulky aromatic thiolate SPh aggravates the Ni_6 tiara conformation distortion.

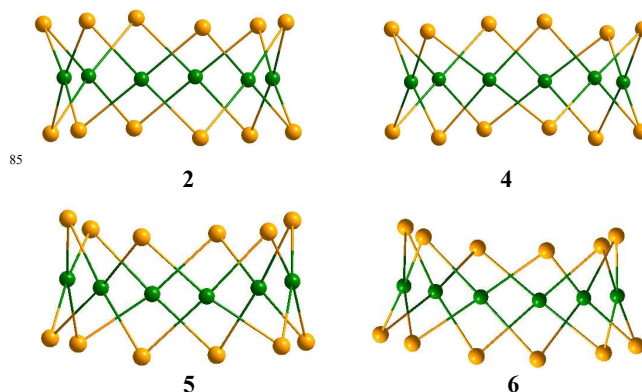


Fig.2 The slightly different tiara configuration in clusters **2**, **4**, **5** and **6** (Ni green, S yellow).

Different from clusters **2**, **4**, **5** and **6**, cluster **1** $\text{cyclo}[\text{Ni}(\mu\text{-EDT})_5]$ possesses a tiara-like $[\text{Ni}_5\text{S}_{10}]$ core configuration with chelating dithiolate ligands edt^{2-} . The cyclic molecule can also be described as a five square plane linked by opposite edges to form

a pentagonal prism. According to literatures, it seems that hexanuclear nickel structure is dominant among the tiara compounds reported by far. In contrast, pentanuclear nickel structures are rare and only three examples of pentagon-like structures have been reported, namely $[\text{Ni}(\mu\text{-SCH}_2\text{CH}_3)_2]_5$, $[\text{Ni}(\mu\text{-SCH}_2\text{SiMe}_3)_2]_5$ and $[\text{Ni}(\mu\text{-SCH}_2\text{CH}_2\text{N}(\text{i-Pr})_2)_2]_5$.⁵³⁻⁵⁵ For structures with n being even, the R substituents of the monodentate thiolate ligands were found to be sterically disposed in alternating axial and equatorial positions about the n -polygonal nickel toroids in order to minimize steric interactions of the ligands; however, complete alternation is not possible for odd-membered polygonal nickel atoms (*i.e.*, $n=5$).³⁶ In the case of **1**, n is odd and a compromise geometry must be adopted, as illustrated in Fig. 3a. The five EDT groups all act as chelating ligands, but bridge the nickel atoms in two different modes, which can be described as the hypothetical units $[\text{Ni}(\text{edt})_2]^{2-}$ (Fig. 3b, in *-cis* mode) and $[\text{Ni}(\text{edt})\text{Ni}]^{2+}$ (Fig. 3c, in *-trans* mode). This gives an arrangement where four of the S-C bonds in the $[\text{Ni}(\text{edt})_2]^{2-}$ unit are disposed in equatorial positions about the nickel toroids, while six of the bonds in the $[\text{Ni}(\text{edt})\text{Ni}]^{2+}$ units are approximately disposed in axial positions. The Ni_5 tiara conformation shows distortion with the Ni-Ni-Ni vertex angles in cycloidal Ni_5 ring are in a slightly wide range of 101.36(4)–112.64(6)°. This deviation is probably related to the occurrence of two different bridging modes of the dithiolate. While the adjacent nickel ions have a nearly constant distance range of 2.741(1)–2.790(8) Å.

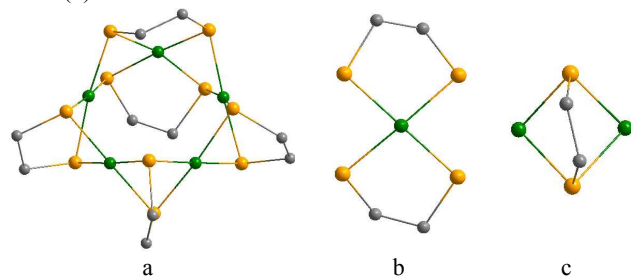


Fig.3 Molecular view of **1**(a); the hypothetical units $[\text{Ni}(\text{edt})_2]^{2-}$ (b) and $[\text{Ni}(\text{edt})\text{Ni}]^{2+}$ (c).The hydrogen atoms are omitted (Ni green, S yellow).

It's easy to notice that the structural parameters in n -polygonal nickel toroids are of their own rules. In order to make a comparative analysis of the crystal structures, we have made a brief list of the structural parameters of complexes **1**, **2**, **4-6** and some other tiara-like $[\text{Ni}(\mu\text{-SR})_2]_n$ cyclic structures (Table 1).^{24, 25, 27-30, 35, 37, 47-50, 53, 54, 56, 57} It is obvious that the average values for Ni-S bond lengths are statistically equivalent, while the mean Ni...Ni distances vary with the size of the $[\text{Ni}(\mu\text{-SR})_2]_n$ tiaras. The mean Ni...Ni distances (from 2.67 to 3.21 Å) increase systematically with increasing nuclear number n (from tetra- to dode-nuclear). Accordingly, the mean Ni-S distances in complexes **1**, **2**, **4-6** are 2.19, 2.20, 2.22, 2.20, 2.19 Å, respectively, and approximately identical to the Ni-S bond lengths in all other nickel clusters ($n=4, 5, 6, 8, 10, 12$). In particular, the average Ni...Ni separations in hexa-nuclear clusters **2**, **4**, **5** and **6** are 2.93, 2.97, 2.89, 2.90 Å, respectively, are comparable to the corresponding values in other hexa-nuclear analogues, but are shorter than those for all of the bigger size tiaras. Additionally, the average Ni...Ni separation of penta-nuclear cluster **1** is 2.76 Å, understandably slightly longer than those of the three tetra-nuclear clusters.

Table 1 Mean molecular parameters for **1**, **2**, **4**, **5**, **6** and other analogues.

$[\text{Ni}(\mu\text{-SR})_2]_n$	Ni-S/Å	Ni...Ni/Å
$n=4$		
R = C ₅ H ₉ NMe	2.21	2.67
R = C ₆ H ₁₁	2.21	2.69
R = <i>i</i> -Pr	2.21	2.68
$n=5$		
$[\text{Ni}(\mu\text{-EDT})_2]_5$ (1)	2.19	2.76
R = Et	2.20	2.82
R = (CH ₂) ₂ N(<i>i</i> -Pr) ₂	2.18	2.79
R = CH ₂ SiMe ₃	2.21	2.83
$n=6$		
R = Me	2.21	2.91
R = Et	2.20	2.92
R = <i>n</i> -Pr	2.20	2.92
R = (CH ₂) ₂ OH	2.21	2.92
R = (CH ₂) ₂ SiMe ₃	2.20	2.92
R = CH ₂ C ₆ H ₄ (<i>p</i> -Cl)	2.20	2.92
R = (CH ₂) ₃ NMe ₂	2.19	2.92
R = (CH ₂) ₃ NMe ₂ H ⁺	2.20	2.93
$[\text{Ni}(\mu\text{-SiPr})(\mu\text{-mtet})]_6$	2.20	2.92
$[\text{Ni}(\mu\text{-SiPe})_2]_6$ (2)	2.20	2.93
$[\text{Ni}_6(\mu\text{-S}t\text{Bu})_4(\mu\text{-PDT})_4]$ (4)	2.22	2.97
$[\text{Ni}_6(\mu\text{-SPh})_4(\mu\text{-EDT})_4]$ (5)	2.20	2.89
$[\text{Ni}_6(\mu\text{-SPh})_4(\mu\text{-PDT})_4]$ (6)	2.19	2.90
$n=8$		
R=CH ₂ CO ₂ Et	2.19	3.05
$n=10$		
$[\text{Ni}(\mu\text{-S}t\text{Bu})(\mu\text{-mtet})]_{10}$	2.20	3.16
$[\text{Ni}(\mu\text{-S}t\text{Bu})(\mu\text{-pyet})]_{10}$	2.21	3.16
$[\text{Ni}(\mu\text{-S}t\text{Bu})(\mu\text{-SEt})]_{10}$	2.20	3.15
$n=12$		
$[\text{Ni}(\mu\text{-S}t\text{Bu})(\mu\text{-etet})]_{12}$	2.22	3.21

Conclusions

In summary, we have synthesized and characterized six tiara-like nickel thiolate tiaras based on in situ synthesis involving reactions of $\text{Ni}(\text{ClO}_4)_2$ with mixed thiolate or disulfide ligands which have discrepancy in coordination ability. Intriguingly, cluster **1** is a rarely reported penta-nuclear tiara. Clusters **3** and **4** are hexa-nuclear tiaras with two different types of mono- and bi-dentate aliphatic thiolates, while clusters **5** and **6** are composed mono-aromatic thiolate and bi-dentate aliphatic thiolate ligands. These heretofore unknown additions would be significant for the structure diversity of metal thiolate complexes and especially for intensive study of the cyclo- $[\text{Ni}(\mu\text{-SR})_2]_n$ tiara family which are often constructed by only one kind of thiolate ligand. Further studies on other nickel thiolate complexes are in progress.

Acknowledgements

This work was supported by grants from the 973 Program (2014CB845603 and 2012CB821702) and the National Science Foundation of China (20871114, 21173223 and 21233009)

Notes and references

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† Electronic Supplementary Information (ESI) available: supplementary figures, tables and XRD. For ESI and crystallographic data in CIF or other electronic format, See DOI: 10.1039/b000000x/

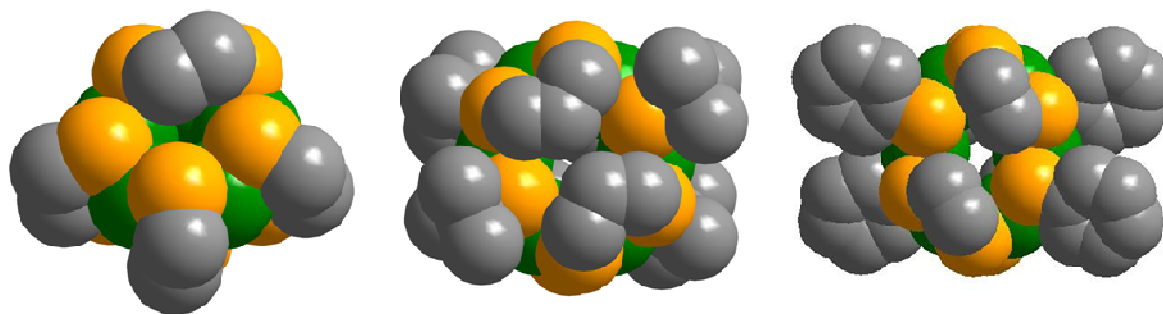
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Penta- and hexa-nuclear nickel tiara-like clusters with two different thiolate bridges

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By the direct synthetic route involving reactions of $\text{Ni}(\text{ClO}_4)_2$ with mixed thiolate or disulfide ligands, infrequent penta-nuclear tiara and hexa-nuclear tiaras with two different types of mono- and bi-dentate thiolates were obtained. These heretofore unknown additions are of particular interest to the cyclo- $[\text{Ni}(\mu\text{-SR})_2]_n$ tiara family which are often constructed by just one kind of thiolate ligand.