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Sulfur-bridged Linkage of $[Ni(thiolato)_2(amine)_2]$-type Complexes with Linear Gold(I) Ions Assisted by Aurophilic Interaction

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The reaction of $[Ni(aet)_2]$ (aet = $^{-}SCH_2CH_2NH_2$) with Au^I in water gave a S-bridged $Ni^{II}{}_2Au^I{}_2$ tetranuclear structure in $[Au_2\{Ni(aet)\}_2]^{2+}$, while the corresponding reaction using $[Ni(L)]$ (L = $[^{-}SCH_2CH_2N{=}C(CH_3){-}]_2$) led to the formation of a $Ni^{II}{}_4Au^I{}_4$ octanuclear structure in $[Au_4\{Ni(L)\}_4]^{4+}$. Their molecular structures exhibiting aurophilic interactions were established by X-ray crystallography.

It has been recognized that thiolato groups coordinated to a Ni^{II} center possess relatively high nucleophilicity to bind with a second transition metal center.[1–3] Utilizing this property, a large number of S-bridged polynuclear structures composed of $[Ni(thiolato)_2(amine)_2]$-type square-planar units have been constructed, since the pioneering work by Busch et al. who prepared a S-bridged $Ni^{II}{}_3$ trinuclear complex, $[Ni\{Ni(aet)_2\}_2]^{2+}$, by the reaction of $[Ni(aet)_2]$ with Ni^{II}.[1] While a variety of three-coordinate and four-coordinate transition metal centers have been employed to link $[Ni(thiolato)_2(amine)_2]$-type units, reports on the linkage with use of two-coordinate metal centers are relatively rare.[3] Furthermore, no study has appeared on the reactions of $[Ni(thiolato)_2(amine)_2]$-type complexes with linear Au^I ions, although heterometallic polynuclear structures containing Au^I ions have attracted increasing attention because of the presence of Au^I–Au^I aurophilic interactions that may lead to unusual stereochemical and spectroscopic features.[4] Thus, as part of our efforts to rationally construct S-bridged polynuclear structures with novel heterometallic arrays based on simple thiolato complexes and to find key factors to control their structures and properties,[5] we started to investigate the reactions of $[Ni(thiolato)_2(amine)_2]$-type complexes with Au^I. Here we report that the reaction of $[Ni(L)]$ with Au^I created a unique S-bridged $Ni^{II}{}_4Au^I{}_4$ octanuclear complex, $[Au_4\{Ni(L)\}_4]^{4+}$ ($[\mathbf{2}]^{4+}$), in which a $Ni_4Au_4S_8$ metallamacrocycle is folded in a pillar-like structure, although the corresponding reaction using $[Ni(aet)_2]$ gave an expected $Ni^{II}{}_2Au^I{}_2$ tetranuclear complex, $[Au_2\{Ni(aet)\}_2]^{2+}$ ($[\mathbf{1}]^{2+}$).

Treatment of a green aqueous suspension of $[Ni(aet)_2]$ with a colorless aqueous solution containing equimolar of $[AuCl\{S(CH_2CH_2OH)_2\}]$, which was prepared from $Na[AuCl_4]$ and 2,2′-thiodiethanol in situ,[6] gave a clear red solution, from which red plate crystals ($[\mathbf{1}](ClO_4)_2$) were isolated by adding $NaClO_4$.[7] The yield of $[\mathbf{1}](ClO_4)_2$ was low (11%), because of the partial decomposition of $[Ni(aet)_2]$ in the course of the reaction with Au^I. X-ray fluorescence spectrometry showed that $[\mathbf{1}](ClO_4)_2$ contains Ni and Au atoms in a ca. 1:1 ratio, and its elemental analytical data were in agreement with the formula of a 1:1 adduct $[Ni(aet)_2](AuClO_4)$. The crystal structure of $[\mathbf{1}](ClO_4)_2$ was determined by X-ray analysis.[8]

As shown in Figure 1, $[\mathbf{1}]^{2+}$ is composed of two square-planar *cis*-$[Ni(aet)_2]$ units that are linked by two roughly linear Au^I atoms to from a S-bridged $Ni^{II}{}_2Au^I{}_2$ structure in $[Au_2\{Ni(aet)\}_2]^{2+}$ (av. Au–S = 2.294(2) Å, Ni–S = 2.185(2) Å, S–Au–S = 175.47(6)°).[9] The bridging S1 (S1′) and S2 (S2′) atoms in the *cis*-$[Ni(aet)_2]$ unit adopt the *R* and *S* chiral configurations, respectively, which results in the formation of a normal chair-like geometry consisting of two *cis*-$[Ni(N)_2(S)_2]$ planes. Both of the S–Ni–S (91.46(6)°) and N–Ni–N (91.2(2)°) angles in each *cis*-$[Ni(aet)_2]$ unit are slightly larger than 90° owing to the somewhat acute N–Ni–S chelating angles (av. 88.7(2)°). The Au···Au separation is 3.0044(3) Å, indicative of the presence of an aurophilic interaction that sustains the S-bridged $Ni^{II}{}_2Au^I{}_2$ structure.[4,10]

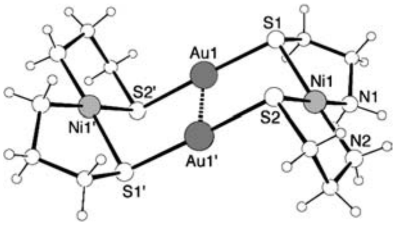

Figure 1. A perspective view of the complex cation $[\mathbf{1}]^{2+}$.

In order to restrain the decomposition of $[Ni(N)_2(S)_2]$ units during the reaction, the mononuclear $[Ni(L)]$ bearing a tetradentate-*N*,*S*,*S*,*N* ligand, which was obtained from Haet and biacetyl in the presence of $Ni(CH_3COO)_2$,[11] was used as the starting complex, instead of $[Ni(aet)_2]$. As expected, dark red crystals ($[\mathbf{2}]Cl_4$) were isolated in a high yield (77%) from the 1:1 reaction mixture of $[Ni(L)]$ and $[AuCl\{S(CH_2CH_2OH)_2\}]$ in water, after the addition of NaCl.[12] The elemental analysis and X-ray fluorescence spectrometry indicated that this product contains $[Ni(L)]$ units and Au atoms in a 1:1 ratio, as does $[\mathbf{1}]^{2+}$. However, X-ray analysis of $[\mathbf{2}](BF_4)_4$ revealed the presence of four $[Ni(L)]$ units and four Au^I atoms in $[\mathbf{2}]^{4+}$.[13]

As shown in Figure 2, $[\mathbf{2}]^{4+}$ has a S-bridged $Ni^{II}{}_4Au^I{}_4$ octanuclear structure in $[Au_4\{Ni(L)\}_4]^{4+}$, in which four $[Ni(L)]$ units are alternately connected by four Au^I atoms in a folded cyclic form (av. Ni–S = 2.161(3) Å, Au–S = 2.311(2) Å). The S–Ni–S angles (av. 96.7(1)°) in $[\mathbf{2}]^{4+}$ is considerably expanded owing to the compressed N–Ni–N chelating angles (av. 83.3(7)°).[14] It appears that such a large S–Ni–S angle is not suitable for the formation of a S-bridged $Ni^{II}{}_2Au^I{}_2$ structure sustained by a $Au^I\cdots Au^I$ interaction, thus leading to a larger, more adoptable $Ni^{II}{}_4Au^I{}_4$ macrocyclic structure. In $[\mathbf{2}]^{4+}$, the two S atoms in each $[Ni(L)]$ unit have the *R* and *S* configurations and the two S atoms in each S–Au–S linkage are regulated to have the same configuration. As a result, a $[(S{-}Au{-}S)_4]$ rhombic pillar is constructed in $[\mathbf{2}]^{4+}$, which is attached to four nearly perpendicular

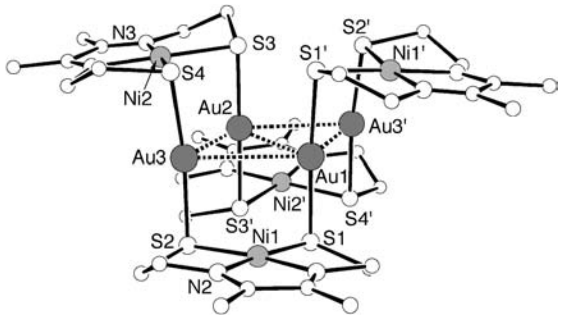

Figure 2. A perspective view of the complex cation $[\mathbf{2}]^{4+}$. Hydrogen atoms are omitted for clarity.

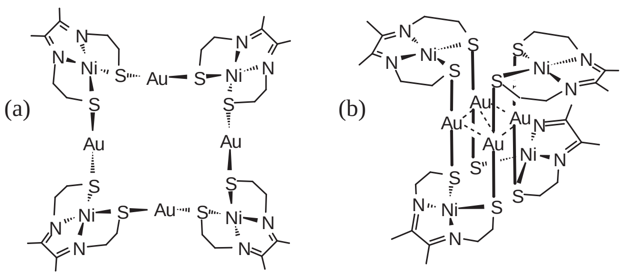

Figure 3. Two geometrical structures, (a) open-type and (b) folded-type, for $[Au_4\{Ni(L)\}_4]^{4+}$.

$[Ni(N)_2(S)_2]$ planes on its upper and lower sides. Molecular model examinations pointed out that in the folded pillar-like $Ni^{II}_4Au^{I}_4$ structure of $[\mathbf{2}]^{4+}$ there is an unfavorable non-bonding interaction between thiolato groups belonging to the neighboring [Ni(L)] units. On the other hand, no serious interaction between thiolato groups would exist in the open-type $Ni^{II}_4Au^{I}_4$ structure, which is formed when the chiral configurations of all the eight bridging S atoms are unified (Figure 3). Of note is the presence of a multiple aurophilic interaction between four Au^{I} atoms (3.162(1)–3.291(1) Å) to form a rhombic Au^{I}_4 core in $[\mathbf{2}]^{4+}$, accompanied by the bending of the S–Au–S lines toward the center of the Au^{I}_4 core (av. 174.2(2)°). Since no appreciable aurophilic interaction is expected in the open-type $Ni^{II}_4Au^{I}_4$ structure, it is reasonable to assume that a multiple aurophilic interaction between the Au^{I}_4 core, which overcomes a non-bonding interaction between thiolato groups, is responsible for the construction of the folded pillar-like structure in $[\mathbf{2}]^{4+}$. The ^{1}H NMR spectrum of $[\mathbf{2}]^{4+}$ in d^6-DMSO exhibits only one methyl signal (δ 2.25).[15] Furthermore, its ^{13}C NMR spectrum gives only one set of four signals (δ 18.80, 33.96, 58.20, and 178.09) due to four kinds of carbon atoms of the ligand L. These results imply that the S-bridged $Ni^{II}_4Au^{I}_4$ structure is retained in solution. Compatible with this, the electrospray mass (ES-MS) spectrum of $[\mathbf{2}](BF_4)_4$ in water showed a main cluster of signals at $m/z =$ 458 corresponding to $[Au_4\{Ni(L)\}_4]^{4+}$.

In summary, the $[Ni(thiolato)_2(amine)_2]$-type square-planes, $[Ni(aet)_2]$ and [Ni(L)], were successfully linked by linear Au^{I} ions for the first time. Remarkably, the linkage of [Ni(L)] created a S-bridged $Ni^{II}_4Au^{I}_4$ octanuclear structure in $[\mathbf{2}]^{4+}$, despite the fact that the linkage of $[Ni(aet)_2]$ gave an expected $Ni^{II}_2Au^{I}_2$ tetranuclear structure in $[\mathbf{1}]^{2+}$. In addition, it was found that the $Ni_4Au_4S_8$ metallamacrocycle is folded in a unique pillar-like structure, so as to form a $[Au^{I}_4]$ core showing a multiple aurophilic interaction. Finally, the present results point out that not only the molecular geometry but also the nuclearity of S-bridged structures composed of $[Ni(thiolato)_2(amine)_2]$-type units could be controlled by the subtle tuning of the S–Ni–S angles assisted by aurophilic interactions.

References and Notes

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7 Calcd for $[\mathbf{1}](ClO_4)_2$: C, 9.47; H, 2.38; N, 5.52%. Found: C, 9.65; H, 2.37; N, 5.58%. UV–vis spectrum in H_2O [σ_{max}, 10^3 cm^{-1} ($\log \varepsilon$, mol^{-1} dm^3 cm^{-1})]: 19.88 (2.28), 37.5 (4.1 sh), 42.48 (4.43). This complex is sparingly soluble in water.

8 Crystal Data for $[\mathbf{1}](ClO_4)_2$: fw = 1014.78, monoclinic, $P2_1/c$, $a =$ 12.578(2) Å, $b =$ 9.806(2) Å, $c =$ 9.623(1) Å, $\beta =$ 93.45(1)°, $V =$ 1184.7(3) Å^3, $Z = 2$, $D_c =$ 2.845 g cm^{-3}, $R(R_w) =$ 0.029 (0.101) for 2722 reflections with $>2.0\sigma(I)$.

9 A related $Ni^{II}_2Au^{I}_2$ complex, $[Au_2\{Ni(\textsc{d}\text{-penicillaminato-}N,S)\}_2]^{2-}$, has been prepared directly from the mixture of D-penicillamine, Ni^{II}, and Au^{I}. P. J. M. W. L. Birker and G. C. Verschoor, *Inorg. Chem.*, **21**, 990 (1982).

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12 Calcd for $[\mathbf{2}]Cl_4 \cdot 18H_2O$: C, 16.72; H, 4.04; N, 4.88%. Found: C, 16.59; H, 3.84; N, 4.94%. UV–vis spectrum in H_2O [σ_{max}, 10^3 cm^{-1} ($\log \varepsilon$, mol^{-1} dm^3 cm^{-1})]: 19.6 (3.5 sh), 22.8 (4.2 sh), 24.19 (4.22), 33.4 (4.3 sh), 36.44 (4.84). The BF_4^- salt of $[\mathbf{2}]^{4+}$, which was obtained by adding $NaBF_4$ to the reaction mixture, showed absorption, NMR, and ES-MS spectra identical with those of $[\mathbf{2}]Cl_4$. Calcd for $[\mathbf{2}](BF_4)_4$: C, 17.64; H, 2.59; N, 5.14%. Found: C, 17.47; H, 2.50; N, 5.19%.

13 Crystal Data for $[\mathbf{2}](BF_4)_4$: fw = 2179.21, monoclinic, $C2/c$, $a =$ 23.8755(7) Å, $b =$ 14.4047(7) Å, $c =$ 17.8405(6) Å, $\beta =$ 104.897(1)°, $V =$ 5929.5(4) Å^3, $Z = 4$, $D_c =$ 2.441 g cm^{-3}, $R(R_w) =$ 0.050 (0.130) for 6757 reflections with $>2.0\sigma(I)$.

14 The bond distances and angles about each [Ni(L)] unit in $[\mathbf{2}]^{4+}$ are very similar to those found in the mononuclear [Ni(L)]. Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, **4**, 1726 (1965).

15 In CD_3OD, as well as in d^6-DMSO, $[\mathbf{2}]^{4+}$ shows very broad CH_2 proton signals at 20 °C. The signals appear as four distinct signals (δ 2.94, 3.26, 3.58, and 3.95) at −50 °C, implying the conformational fixation of *N,S*-chelate rings. See Supporting Information.

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