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Proton-controlled formation and interconversion of $Au^I_2Ni^{II}$ trinuclear and $Au^I_4Ni^{II}_3$ heptanuclear complexes with mixed thiomalate and bis(diphenylphosphino)ethane

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Treatment of a newly prepared digold(I) complex, $[Au_2(dppe)(H_2msa)_2]$ ($[H_41]$; dppe = 1,2-bis(diphenylphosphino)ethane, msa = thiomalate), with Ni^{2+} gave two interconvertible multinuclear complexes, $[Ni\{Au_2(dppe)(msa)_2\}]^{2-}$ ($[2]^{2-}$) and $[Ni_3\{Au_2(dppe)(Hmsa)_2\}\{Au_2(dppe)(msa)_2\}(MeOH)_3]$ ($[3]$), dependent on solution acidities.

Thiomalic acid (mercapto succinic acid, $H_3msa = C_4H_6O_4S$) is known as one of the simplest chiral mercapto dicarboxylic acids, which possesses one thiol and two carboxyl groups.[1] Due to its high biocompatibility, H_3msa has been applied as the earliest gold-containing medicines.[2] In coordination chemistry, H_3msa is regarded as a fascinating multidentate ligand available for the construction of coordination compounds with a high anionic charge because of the trianionic nature of its fully deprotonated form. To date, the reactivities of H_3msa toward a variety of transition metal ions, such as V^V,[3] Mn^{II},[4] Fe^{II},[4] Co^{II},[4] Ni^{II},[4] Cu^{II},[5] Zn^{II},[6] Cd^{II},[6] Hg^{II},[7] Ag^I[8] and Au^I,[9] have been extensively investigated, together with the pharmacological activities of these coordination compounds. However, most of the products have not been isolated as a solid, and their characterizations have been made mainly by the absorption spectroscopy in solution.[3-9] In particular, the crystallographic characterization of this class of compounds has been limited to only five complexes, $[Mo_3S_7(Hmsa)_3]^{2-}$, $rac-[Au^I(msa-S)_2]^{5-}$, $[Au^I(R-msa-S)_2]^{5-}$, $([Au^I(\mu_2-msa-S)]^{2-})_n$, and $[Au^{III}(msa-S,O)(damp)]$ (Fig. S1).[†,10-13] The difficulty in isolation and crystallization is explained by (i) the high hydrophilicity of msa^{3-}, leading to the high solubility in polar solvents and (ii) the lack of hydrogen-bonding donor sites in msa^{3-}, unlike amino acidate species, preventing the formation of mutual hydrogen-bonding interactions. We thought that the introduction of a hydrophobic auxiliary ligand that potentially forms non-covalent interactions should improve the crystallinity of coordination compounds derived from H_3msa. Thus, we newly synthesized a digold(I) complex, $[Au_2(dppe)(H_2msa-S)_2]$ ($[H_41]$; dppe = 1,2-bis(diphenylphosphino)ethane), in which two H_2msa^- ligands are spanned by a hydrophobic $\{Au_2(dppe)\}^{2+}$ moiety, as part of our recent study on the development of multinuclear and metallosupramolecular compounds based on gold(I) metalloligands possessing both hydrophilic amino acid and hydrophobic bis(diphenylphosphino)alkane.[14,15] Herein, we report on the synthesis and characterization of $[H_41]$, together with the reactions of $[H_41]$ with Ni^{2+}. Remarkably, two multinuclear complexes with

different nuclearities, which are interconvertible to each other, were independently produced by changing solution acidities (Scheme 1). These complexes were successfully isolated and structurally characterized by X-ray crystallography. As far as we know, these are the first heterometallic coordination compounds derived from H_3msa.
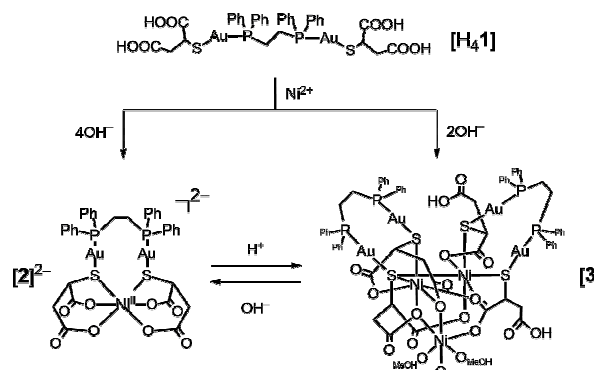
Scheme 1 Synthesis of $[2]^{2-}$ and $[3]$ from H_41 and Ni^{2+}, and their interconversion.

The digold(I) complex $[H_41]$ was prepared according to a method similar to that employed for the corresponding penicillaminato (pen) complex, $[Au_2(dppe)(pen-S)_2]^{2-}$.[15] The 1:2 reaction of $[Au_2Cl_2(dppe)]$[16] with *racemic* H_3msa in $EtOH/H_2O$ in the presence of 2 molar equiv of NaOH gave a white crystalline powder ($[H_41]$).[†] The elemental analytical data of this compound were in good agreement with a neutral formula for $[Au_2(dppe)(H_2msa)_2]$. The IR spectrum of $[H_41]$ gave a strong ν_{CO} band at $1708\ cm^{-1}$, indicative of the presence of protonated carboxyl groups (Fig. S2).[†,17] In the ^1H NMR spectrum in DMSO-d_6, $[H_41]$ showed proton signals due to dppe and msa ligands with an integration ratio of 1:2 (Fig. S3).[†] A singlet phosphorous signal due to dppe was also observed at δ 37.09 in the ^{31}P NMR spectrum of $[H_41]$ in DMSO-d_6 (Fig. S4), indicative of its high symmetric structure.[†] Based on these results, $[H_41]$ is assigned to the desirable digold(I) complex, $[Au_2(dppe)(H_2msa-S)_2]$, having two terminal H_2msa^- ligands spanned by an $\{Au_2(dppe)\}^{2+}$ moiety.

To investigate the functionality of $[1]^{4-}$ as a metalloligand, $[H_41]$ was treated with $Ni(OAc)_2\cdot4H_2O$ in a 1:1 ratio in MeOH, followed by the addition of 4 molar equiv of NaOH. This operation quickly

gave a clear green solution, from which green crystals with a block-like shape (Na₂[**2**]) were obtained after the slow evaporation of the reaction solution.[†] The IR spectrum of this compound showed a strong ν_{CO} band at 1579 cm⁻¹, indicative of the presence of deprotonated carboxyl groups (Fig. S2).[†] The presence of Ni and Au atoms in Na₂[**2**] was confirmed by the X-ray fluorescent analysis, and its elemental analytical data were in agreement with a formula for Na₂[Ni{Au₂(dppe)(msa)₂}]. The diffuse reflection spectrum of Na₂[**2**] in the solid state showed a visible band at 651 nm and a near-IR band at 1141 nm, assignable to d-d transitions for an octahedral Ni[II] center (Fig. S5).[†,18] This spectral feature is the same as the absorption spectrum of Na₂[**2**] in MeOH (Fig. S6), suggestive of the retention of the solid state structure in solution.[†]

To determine the molecular structure in [**2**]²⁻, single-crystal X-ray diffraction analysis was attempted initially for Na₂[**2**]. Unfortunately, all crystals of Na₂[**2**] isolated were too efflorescent and brittle to gain satisfactory diffraction data.[19] After screening crystallization conditions, green block crystals (Mg[**2**]) that are insoluble in any common solvents were obtained by the addition of Mg(OAc)₂ to the 1:1:4 reaction mixture of [H₄**1**], Ni(OAc)₂, and NaOH.[20] These crystals were good enough for X-ray analysis, which revealed the presence of one complex-anion ([**2**]²⁻), one octahedral *cis*-[Mg(H₂O)₄(MeOH)₂]²⁺ cation, and water molecules of crystallization in the asymmetric unit. As shown in Fig. 1a, the complex anion [**2**]²⁻ contains one [Au₂(dppe)(msa)₂]⁴⁻ moiety (av. Au–S = 2.31 Å, Au–P = 2.26 Å, S-Au-P = 177.2°) that chelates to a Ni[II] atom in a bis(tridentate-*O*,*O'*,*S*) mode, forming an S-bridged Au[I]₂Ni[II] trinuclear structure in [Au₂Ni(dppe)(msa)₂]²⁻. This is the first coordination compound with msa³⁻ that adopts a tridentate-*O*,*O'*,*S* coordination mode to a metal center; only monodentate-*S* and bidentate-*O*,*S* coordination modes have been reported for msa³⁻.[10-13] The Ni[II] center in [**2**]²⁻ is situated in an octahedral geometry with a *cis*-O₄S₂ donor set (av. Ni–S = 2.40 Å, Ni–O = 2.05 Å, trans S-Ni-O = 167.6°, trans O-Ni-O = 176.7°). The tertiary carbon atom of each msa³⁻ ligand is asymmetric, and thus three isomers, *RR*, *RS*, and *SS*, are possible for [Au₂(dppe)(msa)₂]⁴⁻. In [**2**]²⁻, however, only the *SS* and *RR* isomers exist in crystal, forming a racemic compound of [NiAu₂(dppe)(*RR*- or *SS*-msa)₂]²⁻. The intramolecular separation between two Au[I] atoms in [**2**]²⁻ is 2.9296(7) Å, suggestive of the presence of an aurophilic interaction.[19,21] In the packing structure in Mg[**2**], each complex-anion contacts with four neighboring complex-anions though intermolecular C–H⋯π interactions between
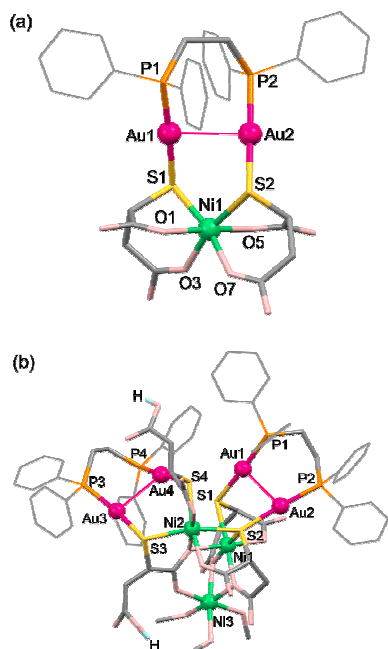

Fig. 1. Molecular structures of (a) [**2**]²⁻ and (b) [**3**].

phenyl groups, constructing a 2D sheet-like structure (Fig. S8).[†] The 2D sheets are parallel arranged to form hydrophilic layers, the surfaces of which are covered by carboxyl groups of msa³⁻. The hydrophilic layers accommodate [Mg(H₂O)₄(MeOH)₂]²⁺ cations, each of which forms multiple O-H⋯O hydrogen bonds (av. O⋯O = 2.78 Å) with msa³⁻ ligands from three different complex-anions.

Previously, we have found that the octahedral Ni[II] centers in [Au₂{Ni(D-pen-*N*,*O*,*S*)₂}₂]²⁻ (D-pen = D-penicillaminate) are converted to the square-planar ones by treatment with acid because of the removal of two carboxyl donor groups from each Ni[II] coordination sphere.[23] With the aim of checking whether such a structural conversion occurs in this system, a green solution containing [**2**]²⁻ was treated with triflic acid (TfOH). This treatment caused a gradual shift of the d-d transition band at 651 nm to the longer wavelengths side by increasing the amount of TfOH, and finally, the d-d band reached to 674 nm to give a yellow-green solution on adding 2 molar equiv of TfOH (Fig. 2). The same yellow-green solution was also obtained when [H₄**1**] was treated with Ni(ClO₄)₂·6H₂O in a 1:1 ratio, followed by the addition of 2 molar equiv of NaOH. In addition, this yellow-green solution was reverted back to a green solution by the addition of 2 molar equiv NaOH with the concomitant d-d band shift from 674 nm to 651 nm. These results clearly indicate that [**2**]²⁻ is interconvertible with a yellow-green species in response to solution acidities.
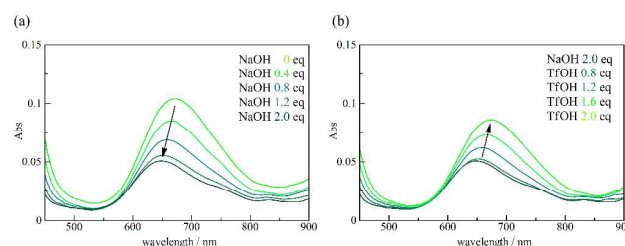

Fig. 2 (a) UV-vis absorbance spectral change of a reaction mixture containing [H₄**1**], Ni²⁺, and NaOH in a 1:1:2 ratio titrated with NaOH (from 0 to 2 equiv) in MeOH, and (b) that after titration with TfOH (from 0 to 2 equiv) in MeOH.

The yellow-green species formed under acidic conditions was successfully isolated as yellow-green crystals with a plate-like shape ([**3**]). The IR spectrum of this compound gave two ν_{CO} bands at 1583 cm⁻¹ and 1718 cm⁻¹, indicative of the presence of both deprotonated and protonated carboxyl groups (Fig. S2).[†] The structure of [**3**] was established by single-crystal X-ray analysis, which revealed the presence of a neutral complex molecule and MeOH molecules of crystallization in the asymmetric unit, with the lack of any counter ions. As shown in Fig. 1b, [**3**] consists of one fully deprotonated [Au₂(dppe)(*RR* or *SS*-msa)₂]⁴⁻ ([**1**]⁴⁻), one semi-deprotonated [Au₂(dppe)(*RS*-Hmsa)₂]²⁻ ([H₂**1**]²⁻), three Ni[II] atoms, and three MeOH molecules. The fully deprotonated [**1**]⁴⁻ chelates to Ni1 atom in a pentadentate-*O₃S₂* mode (av. Ni–S = 2.388 Å, Ni–O = 2.053 Å) so as to have a pendent deprotonated carboxyl arm. On the other hand, the semi-deprotonated [H₂**1**]²⁻ chelates to Ni2 atom in a tetradentate-*O₂S₂* mode (av. Ni–S = 2.379 Å, Ni–O = 2.104 Å) so as to have two protonated carboxyl arms. The remaining coordination site of Ni1 center is occupied by a carboxyl O atom from [H₂**1**]²⁻ (Ni–O = 2.059(6) Å), while the remaining two coordination sites of Ni2 center are filled with the pendent carboxyl arm (Ni–O = 2.024(6) Å) and the thiolato S atom of [**1**]⁴⁻ (Ni–S = 2.466(3) Å). In addition, two carboxyl groups bound to Ni1 center and one carboxyl group bound to Ni2 center coordinate to Ni3 atom (av. Ni–O = 2.049 Å), together with three MeOH molecules (av. Ni–O = 2.051 Å), completing a unique Au[I]₄Ni[II]₃ heptanuclear structure in [Ni₃{Au₂(dppe)(Hmsa)₂}{Au₂(dppe)(msa)₂}(MeOH)₃] that possesses three Ni[II] centers with *cis*-O₄S₂, *mer*-O₃S₃, and *fac*-O₃O'₃ octahedral geometries. It may be interesting to note that in [**3**], the msa³⁻ and Hmsa²⁻ ligands adopts quite versatile coordination modes.[23] In the crystal packing in [**3**], the heptanuclear complex molecules are connected with each other through intermolecular CH⋯π (av. C⋯C = 3.717 Å) and OH⋯O hydrogen-bonding (av.

O···O = 2.539 Å) interactions, constructing a 3D network structure (Fig. S9).[†]

Based on the structural determination, it was evidenced that the octahedral Ni^{II} center in $[2]^{2-}$ is not converted to a square-planar Ni^{II} center with retention of the $Au^I_2Ni^{II}$ trinuclear structure under acidic conditions, but a drastic structural transformation from its $Au^I_2Ni^{II}$ trinuclear to the $Au^I_4Ni^{II}_3$ heptanuclear structure is induced with retention of the octahedral Ni^{II} center. This is in sharp contrast to the previously reported $Au^I_2Ni^{II}_2$ coordination system with D-penicillaminate, in which the octahedral-to-square-planar conversion of Ni^{II} centers occurs under acidic conditions with retention of its tetranuclear structure.[22] It is apparent that the ligand field provided by two bidentate-*O,S* msa ligands is appreciably weaker than the ligand field provided by two bidentate-*N,S* pen ligands. Thus, the weakness of the ligand filed is most likely responsible for the present result, considering that a square-planar metal center is commonly stabilized by a strong ligand field.[24]

To evaluate the magnetic properties of $[2]^{2-}$ and $[3]$, the temperature dependence of the magnetic susceptibilities were measured for polycrystalline samples of Mg[2] and [3] in the temperature range of 2 K to 300 K (Fig. S10).[†] For Mg[2], the plot of $\chi_M T$ versus T decreases only slightly from 1.27 cm^3 K mol^{-1} at 300 K to 1.17 cm^3 K mol^{-1} at 7 K, and then decreases sharply to 0.96 cm^3 K mol^{-1} at 2 K on lowering the temperature. Since the value at 300 K is close to the spin-only value of 1.00 cm^3 K mol^{-1} for an octahedral Ni^{II} center with a d^8 electronic configuration,[25] it is assumed that no significant intermolecular magnetic interactions exist between Ni^{II} centers in Mg[2]. On the other hand, the plot of $\chi_M T$ versus T for [3] increases gradually from 3.77 cm^3 K mol^{-1} at 120 K, which is appreciably larger than the spin-only value of 3.00 cm^3 K mol^{-1} for the magnetically dilute three Ni^{II} centers. The peak value is 4.04 cm^3 K mol^{-1} at 22 K, and then the value decreases sharply to 2.64 cm^3 K mol^{-1} at 2 K on lowering the temperature.[26] This magnetic feature is suggestive of the presence of intramolecular ferromagnetic interactions between three Ni^{II} centers in [3]. Weiss temperature for [3] was estimated to be $\theta = +1.5$ K, which is also consistent with the presence of weak ferromagnetic interactions.[†]

In summary, we showed that the newly prepared $[Au_2(dppe)(H_2msa)_2]$ ($[H_4\mathbf{1}]$) acts as a versatile multidentate metalloligand using two coordinated thiolato and four free carboxyl groups, leading to the independent formation of the trinuclear $[2]^{2-}$ and the heptanuclear [3], dependent on solution acidities employed. These complexes were successfully isolated as single-crystals (Mg[2], [3]) suitable for X-ray crystallography, thanks to the presence of hydrophobic dppe that forms CH···π interactions, in combination with hydrophilic msa. Interestingly, $[2]^{2-}$ and [3] are interconvertible with each other in response to solution acidities, while the octahedral Ni^{II} centers are retained due to the weak ligand-field strength of msa. Note that, this interconversion is accompanied by the changes in color (green vs. yellow green) and magnetism (paramagnetic vs. ferromagnetic) that is potentially applicable as sensing and switching devises.

Notes and references
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† Electronic Supplementary Information (ESI) available: Details of syntheses together with spectroscopic data, and X-ray structure. CCDC reference numbers 1025668, 1025669 and 1025670. See DOI: XXXXX

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