Electronic Supplementary Information (ESI)

Proton-controlled formation and interconversion of $Au^{I}_{2}Ni^{II}$ trinuclear and $Au^{I}_{4}Ni^{II}_{3}$ heptanuclear complexes with mixed thiomalate and bis(diphenylphosphino)ethane

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Preparation of complexes.

(a) Preparation of $[Au_2(dppe)(H_2msa)_2]$ ($[H_4\mathbf{1}]$).

To a white suspension containing 2.00 g (2.3 mmol) of $[Au_2Cl_2(dppe)]$ in EtOH (150 mL) were added a colorless solution containing 0.77 g (5.1 mmol) of racemic H_3msa in EtOH (50 mL) and a 0.1 M aqueous solution of NaOH (51 mL). The mixture was stirred at room temperature for 1 d in the dark, and the resulting white powder was collected by filteration and washed with EtOH and then $CHCl_3$. Yield: 2.14 g (83%). Anal. Found: C, 37.38; H, 3.14%. Calcd for $[Au_2(dppe)(H_2msa)_2] = C_{34}H_{34}O_8S_2P_2Au_2$: C, 37.44; H, 3.14%. IR spectrum (cm^{-1}, KBr disk): 1708, 1688 ($\nu_{C=O,COOH}$), 1436 ($\nu_{P–CH2–}$), 1105 ($\nu_{P–Ph}$). ^1H NMR spectrum (ppm from TMS, DMSO-d_6): 7.84-7.79 (m, 8H), 7.59-7.50 (m, 12H), 3.98 (dd, 2H, $J_1 = 10.1$ Hz, $J_2 = 4.6$ Hz), 2.92-2.85 (m, 6H), 2.66 (dd, 2H, $J_1 = 16.7$ Hz, $J_2 = 4.8$ Hz). ^{31}P NMR spectrum (ppm from 80 % H_3PO_4, DMSO-d_6): 37.085.

(b) Preparation of $Na_2[Ni\{Au_2(dppe)(msa)_2\}]\cdot 3MeOH$ ($Na_2[\mathbf{2}]$).

To a white suspension containing 0.50 g (0.46 mmol) of $[H_4\mathbf{1}]$ in MeOH (50 mL) was added a 0.1 M methanolic solution of NaOH (18 mL). The mixture was stirred at room temperature for 1 h. To the resulting colorless solution was added 0.11 g (0.46 mmol) of $Ni(OAc)_2\cdot 4H_2O$. The mixture was stirred at room temperature for 1.5 h, and the resulting green solution was evaporated to dryness. The green residue was recrystallized from MeOH at room temperature. The resulting green block crystals were collected by filtration. Yield: 0.37 g (60%). Anal. Found: C, 30.87; H, 3.30%. Calcd for $Na_2[Ni\{Au_2(dppe)(msa)_2\}]\cdot 7H_2O = C_{34}H_{44}O_{15}S_2P_2Au_2NiNa_2$: C, 31.00; H, 3.37%. IR spectrum (cm^{-1}, KBr disk): 1579 ($\nu_{C=O,COO-}$), 1435, (ν_{P-CH2-}), 1105 (ν_{P-Ph}).

(c) Preparation of $[Mg(H_2O)_4(MeOH)_2][Ni\{Au_2(dppe)(msa)_2\}]\cdot 6H_2O$ ($Mg[\mathbf{2}]$).

To a white suspension containing 100 mg (0.092 mmol) of $[H_4\mathbf{1}]$ in MeOH (10 mL) was added a 0.1 M methanolic solution of NaOH (3.7 mL). The mixture was stirred at room temperature for 1 h. To the resulting colorless solution was added 23 mg (0.096 mmol) of $Ni(OAc)_2\cdot 4H_2O$ in H_2O (0.5 mL). The mixture was stirred at room temperature for 1 h, and the resulting green solution was divided into 2 parts. To this green solution was added a solution containing 21 mg (0.097 mmol) of $Mg(OAc)_2\cdot 4H_2O$ in H_2O (1 mL).) The mixture was stirred at room temperature for 1 h to give a green solution. To the green solution was added a solution containing 21 mg (0.097 mmol) of $Mg(OAc)_2{\cdot}4H_2O$ in H_2O (1 mL).The mixture was stirred at room temperature for a few minutes, followed by standing at room temperature for 5 days. The resulting green plate crystals suitable for X-ray analysis were collected by filtration. Yield: 34 mg (54%). Anal. Found: C, 30.15; H, 3.66%. Calcd for $Mg[Ni\{Au_2(dppe)(msa)_2\}]{\cdot}9.5H_2O$ = $C_{34}H_{50}O_{18}S_2P_2Au_2NiMg$: C, 30.46; H, 3.68%. IR spectrum (cm^{-1}, KBr disk): 1572 ($\nu_{C=O,COO-}$), 1436, ($\nu_{P\text{-}CH2\text{-}}$), 1103 ($\nu_{P\text{-}Ph}$).

(d) Preparation of $[Ni_3\{Au_2(dppe)(Hmsa)_2\}\{Au_2(dppe)(msa)_2\}(MeOH)_3]$ ([3]).

To a white suspension containing 0.10 g (0.092 mmol) of [H_4**1**] in MeOH (10 mL) was added a 0.1 M methanolic solution of NaOH (1.8 mL, 0.18 mmol). The mixture was stirred at room temperature overnight. To the resulting colorless solution was added 0.034 g (0.093 mmol) of $Ni(ClO_4)_2{\cdot}6H_2O$. The mixture was stirred at room temperature for a few minutes, followed by standing at room temperature for 5 days. The resulting yellow-green crystalline powder was collected by filtration. Yield: 17 mg (21%). Anal. Found: C, 31.39; H, 3.32%. Calcd for $[Ni_3\{Au_2(Hmsa)_2(dppe)\}\{Au_2(msa)_2(dppe)\}]{\cdot}12.5H_2O$ = $C_{68}H_{87}O_{28.5}S_4P_4Au_4Ni_3$: C, 31.70; H, 3.40%. IR spectrum (cm^{-1}, KBr disk): 1718 ($\nu_{C=O,COOH}$), 1583 ($\nu_{C=O,COO-}$), 1437 (ν_{P-CH2-}), 1103 (ν_{P-Ph}).

Single-crystals of [**3**] suitable for X-ray analysis were obtained as follows: To a white suspension containing 0.10 g (0.092 mmol) of [H_4**1**] in MeOH (10 mL) was added a 0.1 M methanolic solution of NaOH (2.8 mL). The mixture was stirred at room temperature for 2 h. To the resulting colorless solution was added 0.034 g (0.092 mmol) of $Ni(ClO_4)_2{\cdot}6H_2O$. The mixture was stirred at room temperature for 2 h, and the resulting yellow-green solution was evaporated to dryness. The yellow-green residue was recrystallized from MeOH (10 mL) at room temperature, which gave yellow-green plate crystals.

Compound [**3**] was also obtained as a crystalline powder starting from [Na_2**2**] as follows: To a green solution containing 50 mg (0.038 mmol) of [Na_2**2**] in MeOH (3 mL) was added 7 mg (0.019 mmol) of $Ni(ClO_4)_2{\cdot}6H_2O$ and a 1 M methanolic solution of TfOH (76 μL). The mixture was stirred at room temperature for a few minutes, followed by standing at room temperature overnight. The resulting yellow-green crystalline powder was collected by filtration. Yield: 27 mg (54%).

(e) Interconversion between [2]$^{2-}$ and [3].

To a white suspension containing 50 g (0.046 mmol) of [H_4**1**] in MeOH (5 mL) was added a 0.1 M methanolic solution of NaOH (0.9 mL). The mixture was stirred at room temperature for 1 h. To the resulting colorless solution was added 17 mg (0.045 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$, followed by stirring at room temperature for 1.5 h to give a yellow-green solution that shows a d-d band at 672 nm in the absorption spectrum. To the resulting yellow-green solution was added a 0.1 M methanolic solution of NaOH (from 0.4 equiv to 2.0 equiv). As increasing the amount of the NaOH solution added, the solution color gradually changed from yellow-green to green, and finally, the absorption spectrum of the solution became to be superimposed with that of Na_2[**2**] on the addition of 2 equiv of NaOH. Subsequently, to the resulting green solution was added a 0.1 M methanolic solution of TfOH (from 0.4 equiv to 2.0 equiv). As increasing the amount of the TfOH solution added, the solution color gradually reverted back from green to yellow-green, and finally, the absorption spectrum of the solution became to be superimposed with the original spectrum with a d-d band at 672 nm on the addition of 2 equiv of TfOH.

Physical Measurements

The IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks at room temperature. The electronic absorption spectra in solution were recorded on a JASCO V-660 spectrophotometer at room temperature. The reflection spectra in the solid staye were recorded with a JASCO V-570 UV/VIS/NIR spectrometer at room temperature. The elemental analysis (C, H) was performed at Osaka University. The ^{1}H and ^{31}P NMR spectra in solution were measured on a JEOL EX-500 spectrometer at the probe temperature, using tetramethylsilane (TMS) as the internal standard for ^{1}H NMR measurements and 80% H_3PO_4 as the external standard for ^{31}P NMR measurements. The X-ray fluorescence analyses were made on a HORIBA MESA-500 spectrometer. Variable temperature magnetic susceptibility measurements were made using a SQUID magnetometer MPMS XL (Quantum Design) at 0.5 T. Diamagnetic correction was determined from Pascal’s constants. Thermal gravity (TG) and differential thermal analysis (DTA) measurements were measured on a SHIMADZU DTG-60 analyzer.

X-ray crystal structure determination.

The single crystal X-ray diffraction measurements were performed on a Rigaku RAXIS VII imaging plate and Vari-Max with graphite monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) at 200 K. The intensity data were collected by the ω-scan technique and empirically corrected for absorption. The structures of the complexes were solved by direct methods using SHELXS2013.[S1] The structure refinements were carried out using full matrix least-squares (SHELXL2013).[S1]

For Na_2[**2**]·3MeOH, two $[NiAu_2(dppe)(msa)_2]^{2-}$ anions, four Na^+ cations, and six MeOH molecules were crystallographically independent. All non-hydrogen atoms except the C atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of OH groups of methanol molecules. Several bond distances of two phenyl groups and some msa ligands were restrained.

For Mg[**2**], one $[NiAu_2(dppe)(msa)_2]^{2-}$ anion, one $[Mg(MeOH)_2(H_2O)_4]^{2+}$ cation, and water molecules were crystallographically independent. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of water molecules and OH groups of methanol molecules. The program PLATON [S2] indicated a solvent accessible void space of 2938 Å^3, corresponding to 782 electrons in a unit cell in the case of Mg[**2**]. Since the solvent molecules were grossly disordered and could not be modeled, their contribution was excluded using the subroutine SQUEEZE. [S2]

For [**3**]·4MeOH, one $[Ni_3Au_4(dppe)(Hmsa)_2(msa)_2(MeOH)_3]$ molecule and four solvated MeOH molecules were crystallographically independent. All non-hydrogen atoms, except for solvated MeOH molecules, were refined anisotropically. Hydrogen atoms were included in calculated positions, except those of OH groups of MeOH molecules.

[S1] G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122.

[S2] A. L. Spek, *Acta Cryst*. **2009**, *D65*, 148-155.

Table S1. Crystallographic data of Na_2[**2**]·3MeOH, Mg[**2**] and [**3**]·4MeOH.

	Na_2[**2**]·3MeOH	Mg[**2**]	[**3**]·4MeOH
Formula	$C_{75}H_{61}Au_4Na_4Ni_2O_{24}P_4S_4$	$C_{36}H_{46}Au_2MgNiO_{14}P_2S_2$	$C_{76}H_{93}Au_4Ni_3O_{24}P_4S_4$
Color, form	Green, block	Green, plate	Yellowish green, plate
Mw	2595.60	1391.66	2606.61
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/ Å	17.848(3)	10.6713(7)	11.8932(5)
b/ Å	21.586(3)	36.214(2)	16.9404(7)
c/ Å	33.891(3)	18.2046(13)	23.2709(9)
α(°)	90	90	84.250(6)
β (°)	106.314(10)	103.435(7)	78.433(5)
γ (°)	90	90	71.558(5)
V/ Å^3	12532(3)	6842.7(8)	4354.0(3)
Z	4	4	2
T/ K	200(2)	200(2)	200(2)
F(000)	4972	2536	2530
ρ calcd / g· cm^{-3}	1.376	1.267	2.022
μ(Mo Kα)/ mm^{-1}	5.141	4.707	7.716
Crystal size /mm^3	0.12×0.10×0.05	0.20×0.05×0.05	0.10×0.01×0.01
Limiting indices	$-22 \le h \le 23$,	$-13 \le h \le 13$,	$-15 \le h \le 13$,
	$-26 \le k \le 27$,	$-44 \le k \le 47$,	$-21 \le k \le 21$,
	$-44 \le l \le 43$	$-23 \le l \le 23$	$-30 \le l \le 28$
R1 (I>2σ(I))$^{a)}$	0.1766	0.0695	0.0683
wR2 (all data) $^{b)}$	0.5264	0.2039	0.1266
GOF	1.830	1.045	1.050

a) $R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$.

b) $wR2 = [\Sigma(w(F_o^2-F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Bond lengths [Å] and angles [°] for $Na_2[Ni\{Au_2(dppe)(msa)_2\}]\cdot 3MeOH$ ($Na_2[\mathbf{2}]\cdot 3MeOH$).

Bond lengths

Au(1)-P(1)	2.276(7)	Ni(2)-S(4)	2.412(7)
Au(1)-S(1)	2.304(7)	Ni(2)-O(9)	2.019(18)
Au(2)-P(2)	2.290(6)	Ni(2)-O(11)	2.09(2)
Au(2)-S(2)	2.303(6)	Ni(2)-O(13)	2.068(19)
Au(1)-Au(2)	2.9687(13)	Ni(2)-O(15)	2.073(17)
Au(3)-P(3)	2.275(6)	Na(1)-O(3)	2.37(2)
Au(3)-S(3)	2.321(7)	Na(1)-O(4)	2.62(3)
Au(4)-P(4)	2.248(7)	Na(2)-O(6)	2.359(19)
Au(4)-S(4)	2.321(7)	Na(2)-O(8)#1	2.41(2)
Au(3)-Au(4)	2.9568(14)	Na(2)-O(10)	2.40(2)
Ni(1)-S(1)	2.428(7)	Na(3)-O(1)#1	2.364(17)
Ni(1)-S(2)	2.410(7)	Na(3)-O(6)	2.29(2)
Ni(1)-O(1)	2.070(16)	Na(3)-O(10)	2.34(2)
Ni(1)-O(3)	2.041(16)	Na(4)-O(11)	2.41(2)
Ni(1)-O(5)	2.049(17)	Na(4)-O(12)#2	2.41(2)
Ni(1)-O(7)	2.074(16)	Na(4)-O(13)	2.45(2)
Ni(2)-S(3)	2.427(7)		

Angles

P(1)-Au(1)-S(1)	175.9(2)	O(3)-Ni(1)-O(7)	174.8(7)
P(2)-Au(2)-S(2)	174.0(2)	O(5)-Ni(1)-O(7)	88.3(7)
P(3)-Au(3)-S(3)	174.2(2)	S(3)-Ni(2)-S(4)	102.7(3)
P(4)-Au(4)-S(4)	175.8(2)	S(3)-Ni(2)-O(9)	85.0(5)
S(1)-Ni(1)-S(2)	103.5(2)	S(3)-Ni(2)-O(11)	83.8(6)
S(1)-Ni(1)-O(1)	85.3(5)	S(3)-Ni(2)-O(13)	170.3(6)
S(1)-Ni(1)-O(3)	83.3(5)	S(3)-Ni(2)-O(15)	99.1(5)
S(1)-Ni(1)-O(5)	167.9(5)	S(4)-Ni(2)-O(9)	171.1(6)
S(1)-Ni(1)-O(7)	87.1(6)	S(4)-Ni(2)-O(11)	98.8(6)
S(2)-Ni(1)-O(1)	168.3(5)	S(4)-Ni(2)-O(13)	84.4(6)
S(2)-Ni(1)-O(3)	96.0(5)	S(4)-Ni(2)-O(15)	84.5(6)
S(2)-Ni(1)-O(5)	85.5(5)	O(9)-Ni(2)-O(11)	86.5(8)
S(2)-Ni(1)-O(7)	87.1(6)	O(9)-Ni(2)-O(13)	88.6(8)
O(1)-Ni(1)-O(3)	92.7(6)	O(9)-Ni(2)-O(15)	89.8(7)
O(1)-Ni(1)-O(5)	87.1(7)	O(11)-Ni(2)-O(13)	88.5(8)
O(1)-Ni(1)-O(7)	83.7(7)	O(11)-Ni(2)-O(15)	175.0(8)
O(3)-Ni(1)-O(5)	87.7(7)	O(13)-Ni(2)-O(15)	88.1(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 -x+1,-y+2,-z+2

Table S3. Bond lengths [Å] and angles [°] for [Mg(H_2O)$_4$(MeOH)$_2$][Ni{Au$_2$(dppe)(msa)$_2$}] (Mg[**2**]).

	Bond lengths		
Au(1)-P(1)	2.259(3)	Ni(1)-O(5)	2.048(10)
Au(1)-S(1)	2.314(3)	Ni(1)-O(7)	2.032(11)
Au(2)-P(2)	2.269(4)	Mg(1)-O(9)	2.071(12)
Au(2)-S(2)	2.303(4)	Mg(1)-O(10)	2.052(13)
Au(1)-Au(2)	2.9296(7)	Mg(1)-O(11)	2.062(16)
Ni(1)-S(1)	2.388(4)	Mg(1)-O(12)	2.096(13)
Ni(1)-S(2)	2.403(4)	Mg(1)-O(13)	2.038(15)
Ni(1)-O(1)	2.078(10)	Mg(1)-O(14)	2.080(13)
Ni(1)-O(3)	2.034(10)		
	Angles		
P(1)-Au(1)-S(1)	177.61(12)	O(5)-Ni(1)-O(7)	92.8(4)
P(2)-Au(2)-S(2)	176.65(13)	O(9)-Mg(1)-O(10)	91.5(6)
S(1)-Ni(1)-S(2)	105.05(14)	O(9)-Mg(1)-O(11)	85.7(6)
S(1)-Ni(1)-O(1)	85.6(3)	O(9)-Mg(1)-O(12)	90.4(5)
S(1)-Ni(1)-O(3)	84.9(3)	O(9)-Mg(1)-O(13)	91.8(6)
S(1)-Ni(1)-O(5)	168.1(4)	O(9)-Mg(1)-O(14)	176.4(5)
S(1)-Ni(1)-O(7)	94.6(3)	O(10)-Mg(1)-O(11)	90.7(6)
S(2)-Ni(1)-O(1)	166.5(3)	O(10)-Mg(1)-O(12)	177.7(6)
S(2)-Ni(1)-O(3)	99.1(3)	O(10)-Mg(1)-O(13)	90.3(5)
S(2)-Ni(1)-O(5)	85.0(3)	O(10)-Mg(1)-O(14)	91.3(5)
S(2)-Ni(1)-O(7)	84.1(3)	O(11)-Mg(1)-O(12)	90.8(6)
O(1)-Ni(1)-O(3)	89.9(4)	O(11)-Mg(1)-O(13)	177.3(6)
O(1)-Ni(1)-O(5)	85.5(4)	O(11)-Mg(1)-O(14)	92.0(6)
O(1)-Ni(1)-O(7)	86.8(4)	O(12)-Mg(1)-O(13)	88.3(6)
O(3)-Ni(1)-O(5)	87.1(4)	O(12)-Mg(1)-O(14)	86.9(5)
O(3)-Ni(1)-O(7)	176.7(4)	O(13)-Mg(1)-O(14)	90.5(6)

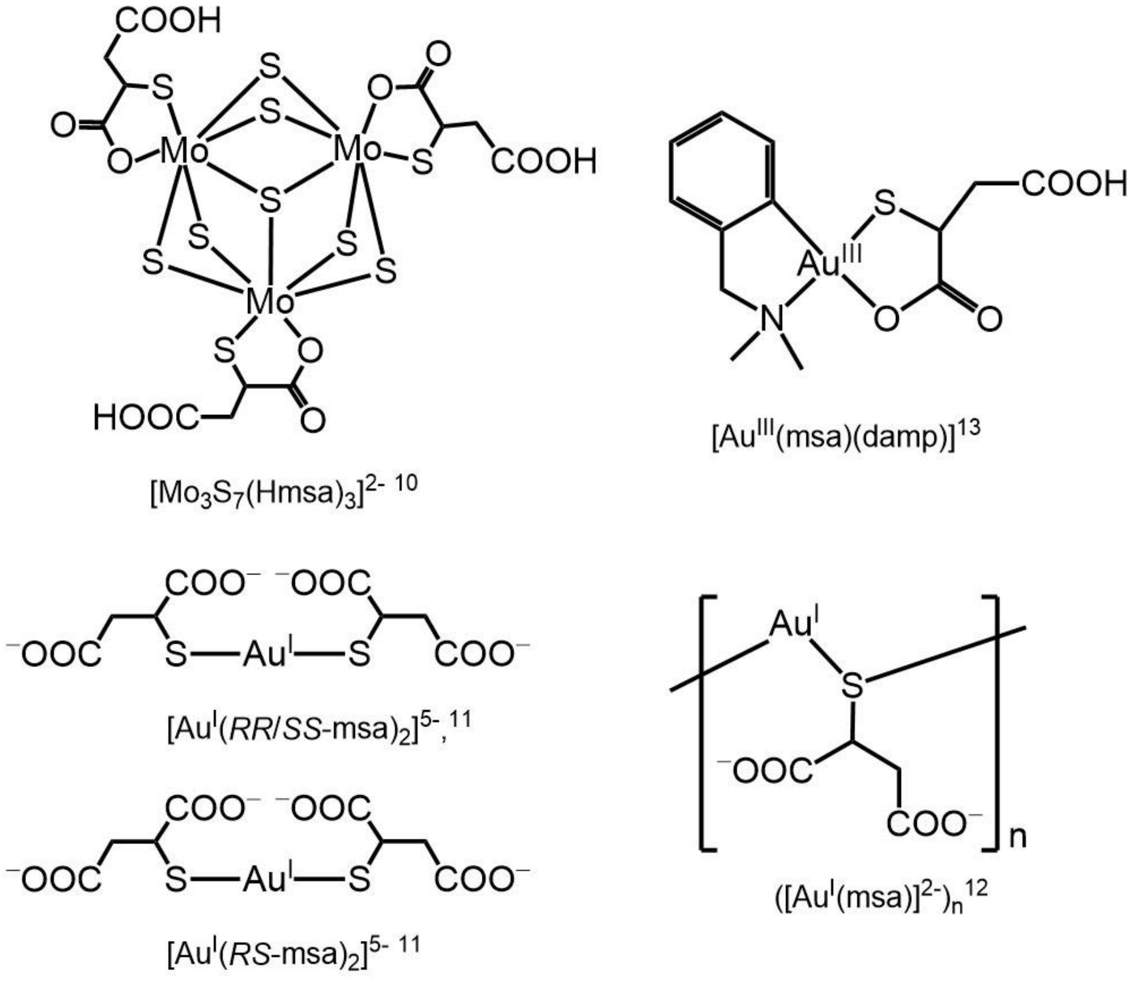
Table S4. Bond lengths [Å] and angles [°] for [Ni_3\{Au_2(dppe)(Hmsa)$_2$\}\{Au_2(dppe)(msa)$_2$\}(MeOH)$_3$]·4MeOH ([**3**]·4MeOH).

Bond lengths

Au(1)-P(1)	2.272(3)	Ni(1)-O(7)	2.059(7)
Au(1)-S(1)	2.332(3)	Ni(1)-O(11)	2.073(7)
Au(2)-P(2)	2.288(3)	Ni(2)-S(1)	2.478(3)
Au(2)-S(2)	2.335(3)	Ni(2)-S(3)	2.413(3)
Au(1)-Au(2)	3.0530(7)	Ni(2)-S(4)	2.373(3)
Au(3)-P(3)	2.282(3)	Ni(2)-O(3)	2.031(7)
Au(3)-S(3)	2.336(3)	Ni(2)-O(11)	2.151(8)
Au(4)-P(4)	2.255(3)	Ni(2)-O(15)	2.059(9)
Au(4)-S(4)	2.302(3)	Ni(3)-O(1)	2.055(8)
Au(3)-Au(4)	3.0135(6)	Ni(3)-O(5)	2.068(7)
Ni(1)-S(1)	2.405(3)	Ni(3)-O(12)	2.051(8)
Ni(1)-S(2)	2.396(3)	Ni(3)-O(17)	2.058(8)
Ni(1)-O(1)	2.072(7)	Ni(3)-O(18)	2.091(8)
Ni(1)-O(5)	2.073(8)	Ni(3)-O(19)	2.053(9)

Angles

P(1)-Au(1)-S(1)	175.41(11)	S(3)-Ni(2)-O(3)	92.5(2)
P(2)-Au(2)-S(2)	176.90(10)	S(3)-Ni(2)-O(11)	80.1(2)
P(3)-Au(3)-S(3)	169.68(11)	S(3)-Ni(2)-O(15)	97.5(3)
P(4)-Au(4)-S(4)	170.08(11)	S(4)-Ni(2)-O(3)	165.3(3)
S(1)-Ni(1)-S(2)	97.33(11)	S(4)-Ni(2)-O(11)	105.2(2)
S(1)-Ni(1)-O(1)	92.8(2)	S(4)-Ni(2)-O(15)	80.9(2)
S(1)-Ni(1)-O(5)	170.2(2)	O(3)-Ni(2)-O(11)	86.0(3)
S(1)-Ni(1)-O(7)	98.9(2)	O(3)-Ni(2)-O(15)	88.4(3)
S(1)-Ni(1)-O(11)	83.0(2)	O(11)-Ni(2)-O(15)	173.7(3)
S(2)-Ni(1)-O(1)	169.8(2)	O(1)-Ni(3)-O(5)	80.2(3)
S(2)-Ni(1)-O(5)	90.2(2)	O(1)-Ni(3)-O(12)	89.6(3)
S(2)-Ni(1)-O(7)	85.3(2)	O(1)-Ni(3)-O(17)	89.1(3)
S(2)-Ni(1)-O(11)	93.2(2)	O(1)-Ni(3)-O(18)	92.8(3)
O(1)-Ni(1)-O(5)	79.6(3)	O(1)-Ni(3)-O(19)	172.0(3)
O(1)-Ni(1)-O(7)	93.6(3)	O(5)-Ni(3)-O(12)	88.7(3)
O(1)-Ni(1)-O(11)	87.6(3)	O(5)-Ni(3)-O(17)	89.4(3)
O(5)-Ni(1)-O(7)	87.9(3)	O(5)-Ni(3)-O(18)	172.2(4)
O(5)-Ni(1)-O(11)	90.4(3)	O(5)-Ni(3)-O(19)	92.6(3)
O(7)-Ni(1)-O(11)	177.7(3)	O(12)-Ni(3)-O(17)	177.9(3)
S(1)-Ni(2)-S(3)	158.99(13)	O(12)-Ni(3)-O(18)	94.6(3)
S(1)-Ni(2)-S(4)	92.06(10)	O(12)-Ni(3)-O(19)	93.7(3)
S(1)-Ni(2)-O(3)	80.4(2)	O(17)-Ni(3)-O(18)	87.2(3)
S(1)-Ni(2)-O(11)	79.7(2)	O(17)-Ni(3)-O(19)	87.4(4)
S(1)-Ni(2)-O(15)	102.0(3)	O(18)-Ni(3)-O(19)	94.2(4)
S(3)-Ni(2)-S(4)	98.76(11)		



$[\mathrm{Mo_3S_7(Hmsa)_3}]^{2-}$ [10]

$[\mathrm{Au^{III}(msa)(damp)}]$ [13]

$[\mathrm{Au^{I}}(RR/SS\text{-msa})_2]^{5-}$, [11]

$([\mathrm{Au^{I}(msa)}]^{2-})_n$ [12]

$[\mathrm{Au^{I}}(RS\text{-msa})_2]^{5-}$ [11]

Figure S1. Metal complexes derived from H_3msa, which have been structurally characterized to date.

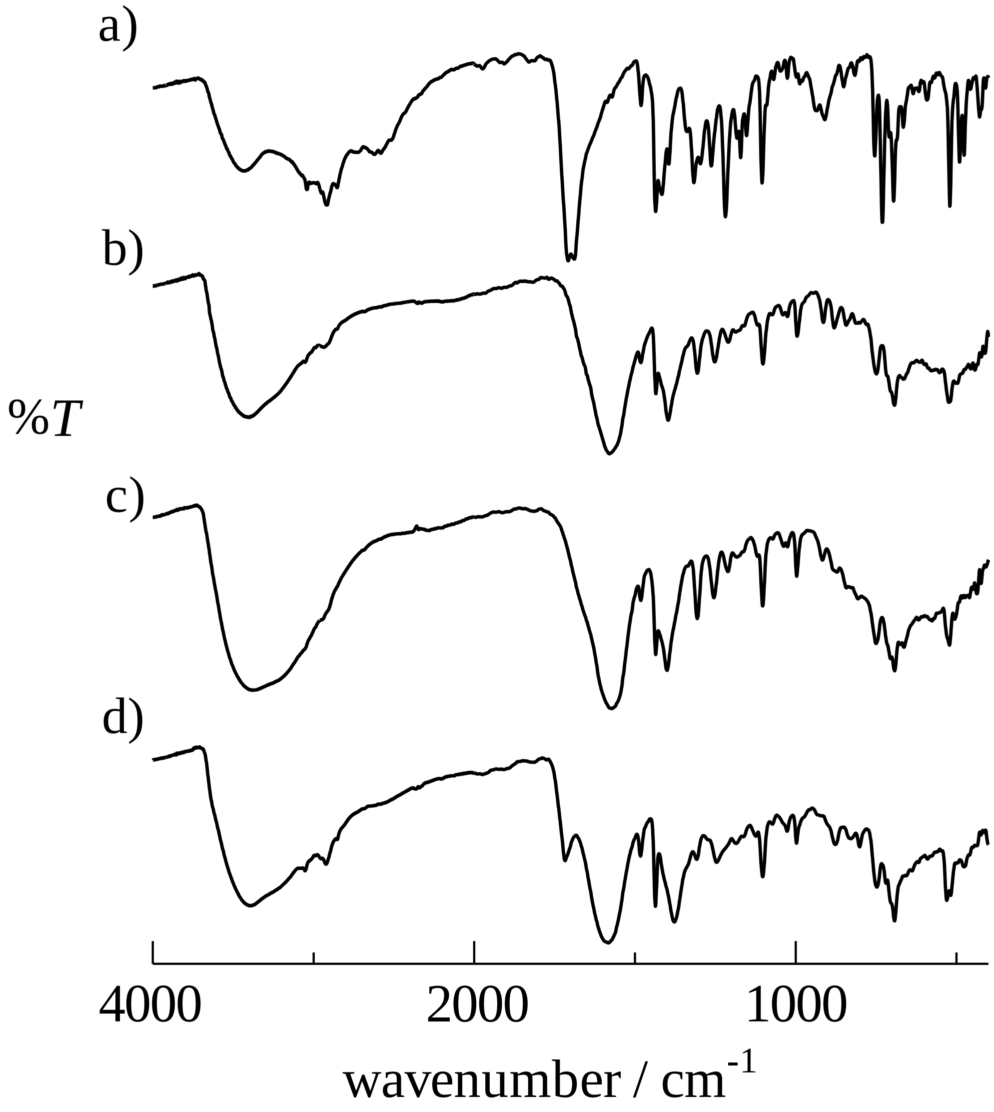


Figure S2. IR spectra of (a) $[Au_2(dppe)(H_2msa)_2]$ ($[H_4\mathbf{1}]$), (b) $Na_2[Ni\{Au_2(dppe)(msa)_2\}]$ ($Na_2[\mathbf{2}]$), (c) $Mg[Ni\{Au_2(dppe)(msa)_2\}]$ ($Mg[\mathbf{2}]$), and (d) $[Ni_3\{Au_2(dppe)(msa)_2\}\{Au_2(dppe)(Hmsa)_2\}(MeOH)_3]$ ($[\mathbf{3}]$).

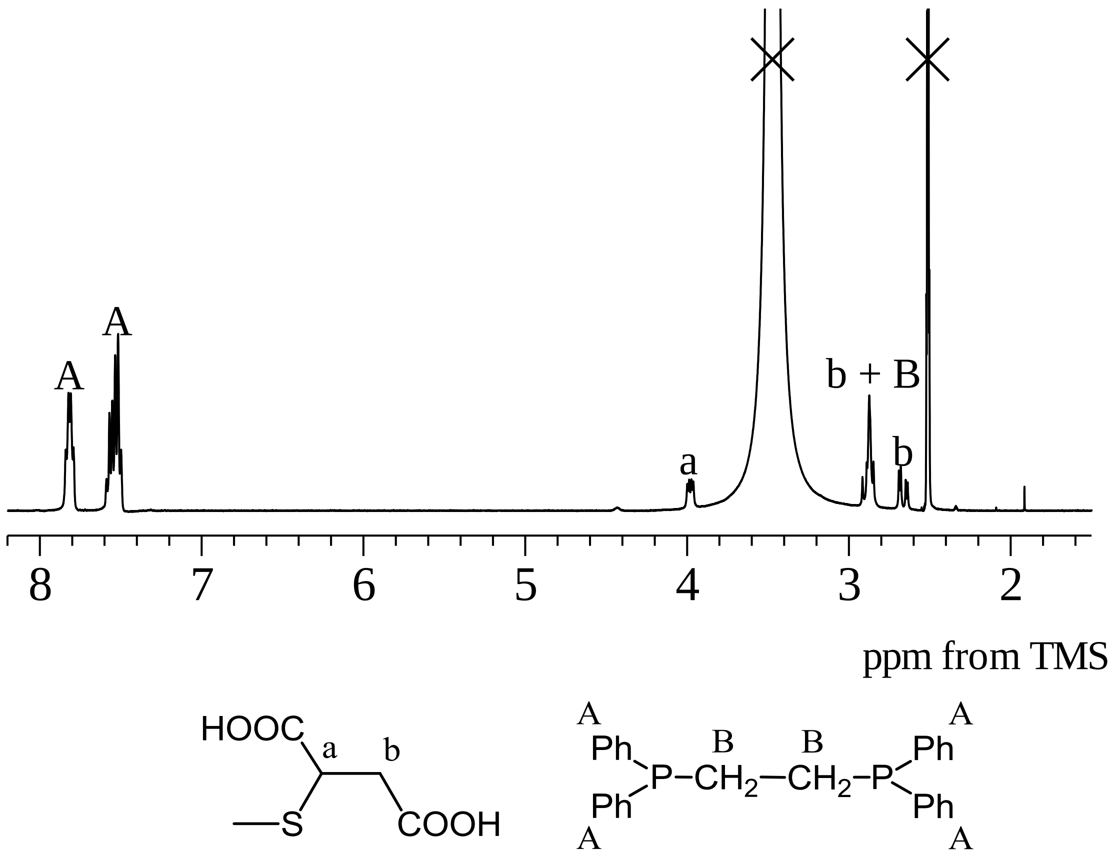


Figure S3. ^{1}H NMR spectrum of [Au_2(dppe)(H_2msa)$_2$] ([H_4**1**]) in DMSO-d_6.

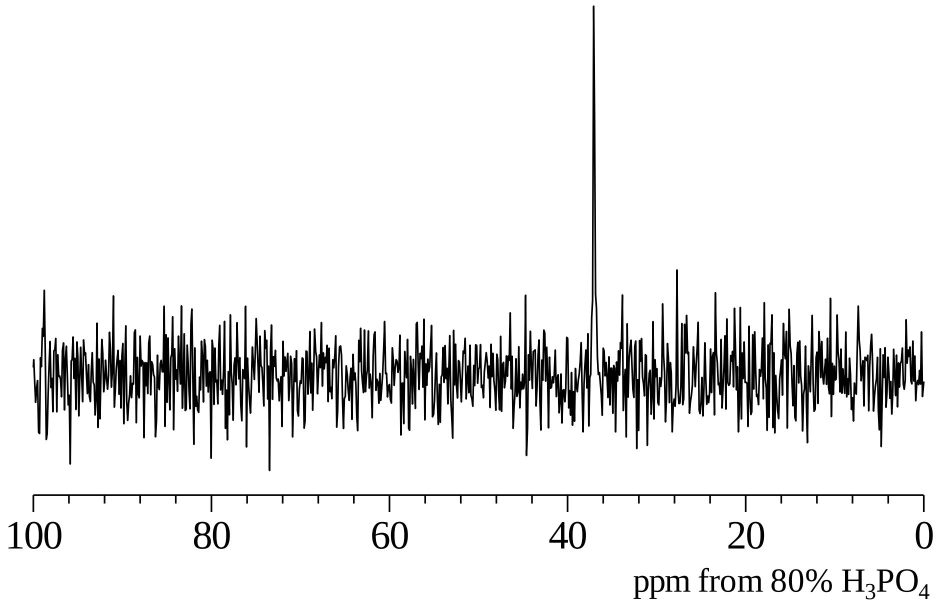


Figure S4. ^{31}P NMR spectrum of [Au_2(dppe)(H_2msa)$_2$] ([H_4**1**]) in DMSO-d_6.

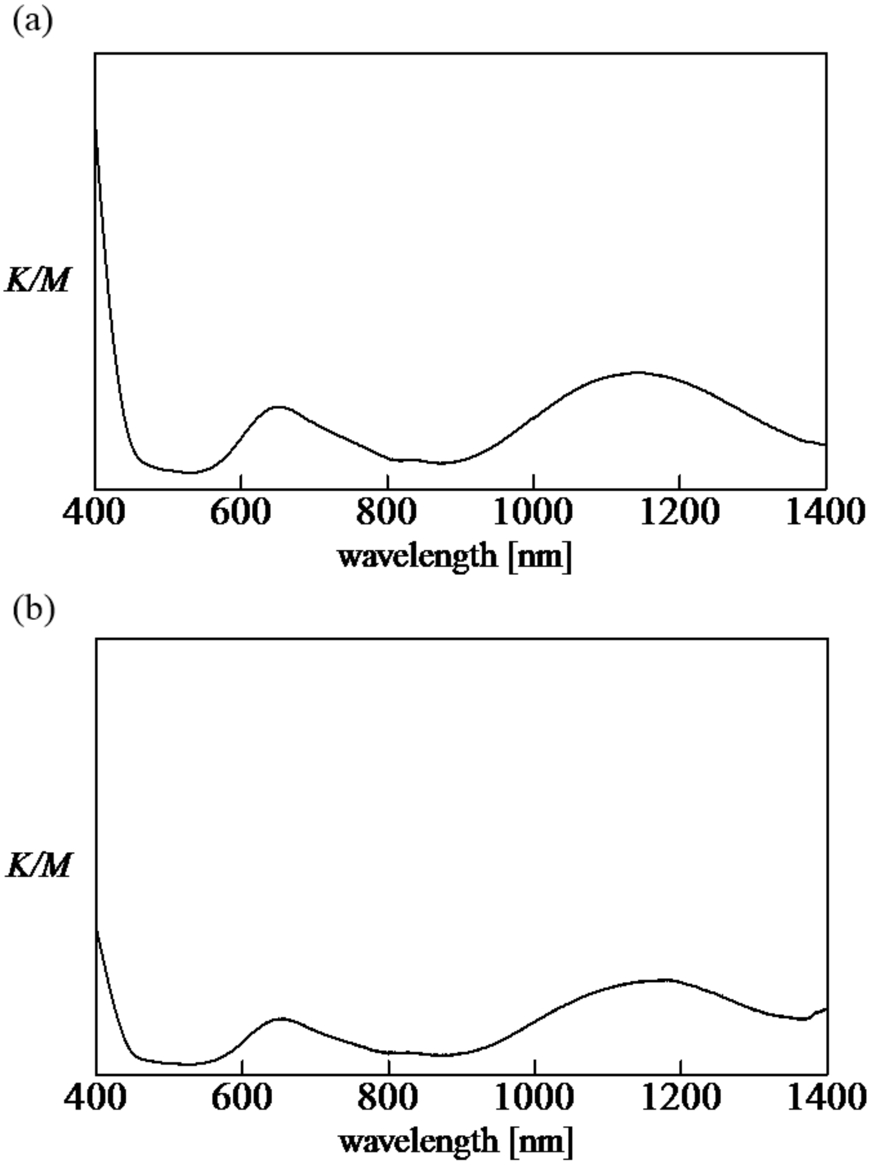


Figure S5. Diffuse reflection spectra of (a) $Na_2[Ni\{Au_2(dppe)(msa)_2\}]$ (Na_2[**2**]) and (b) $Mg[Ni\{Au_2(dppe)(msa)_2\}]$ (Mg[**2**]).

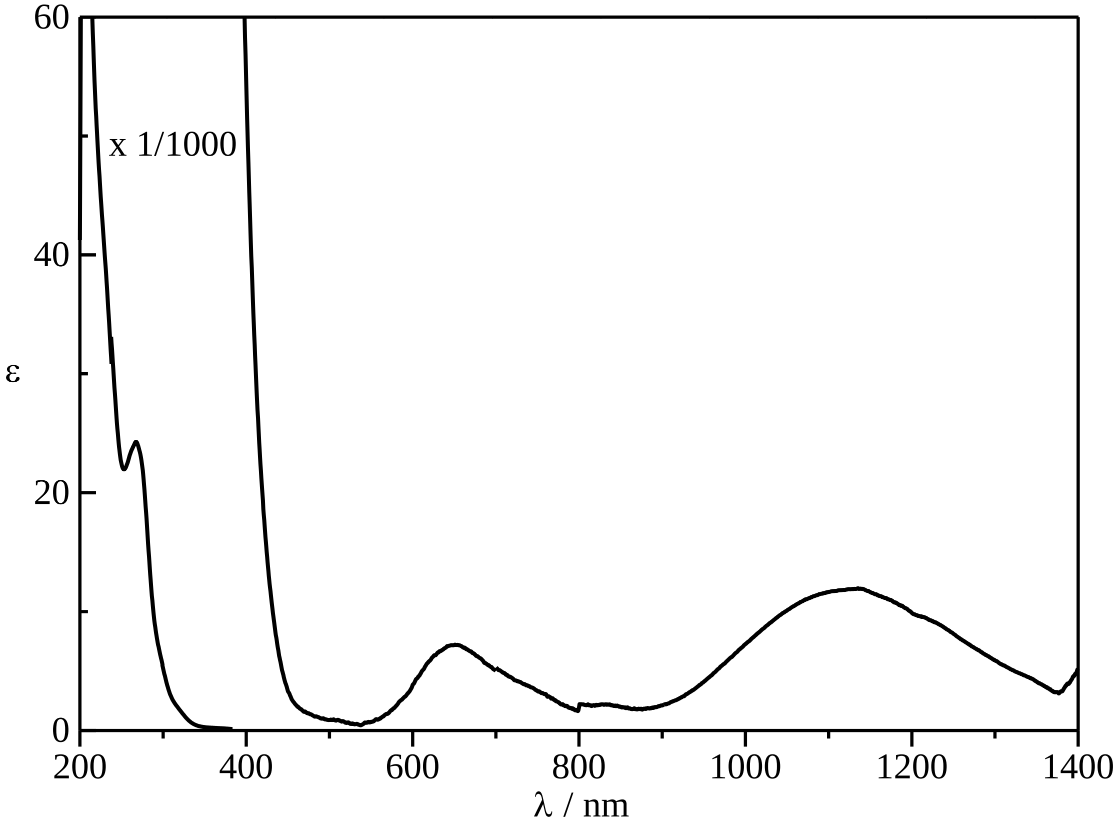


Figure S6. Absorption spectrum of $Na_2[Ni\{Au_2(dppe)(msa)_2\}]$ ($Na_2[\mathbf{2}]$) in MeOH. [λ_{max} / nm, ε / $mol^{-1}dm^3cm^{-1}$] = [1135, 12.0], [651, 7.2], [267.5, 24000].

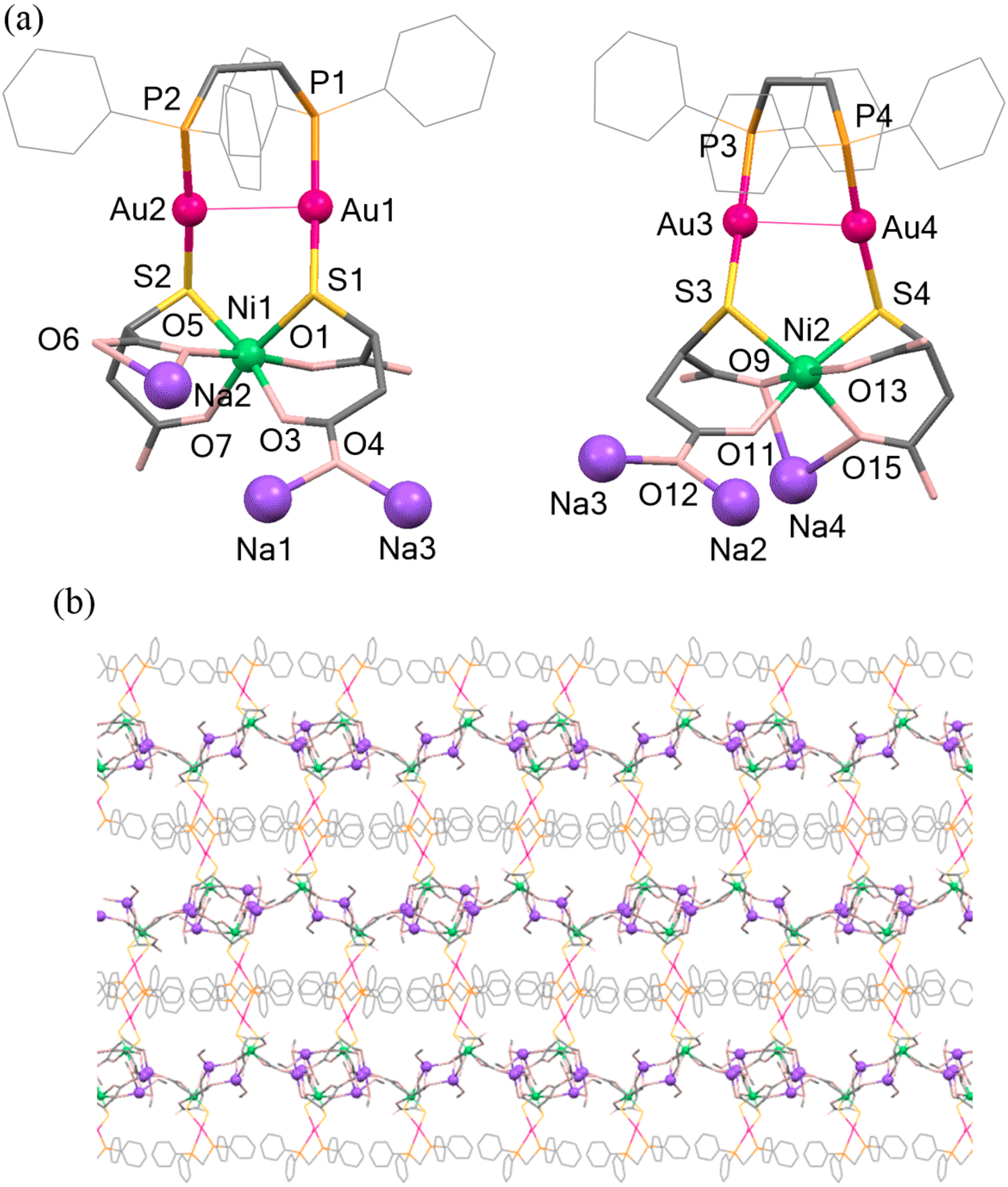


Figure S7. (a) Perspective views of two crystallographically independent complex anions and (b) a packing structure in $Na_2[Ni\{Au_2(dppe)(msa)_2\}]\cdot 3MeOH$ (Na_2[**2**]·3MeOH). Au: red purple, Ni: green, Na: purple, C: gray, O: pink, S: yellow, P: orange.

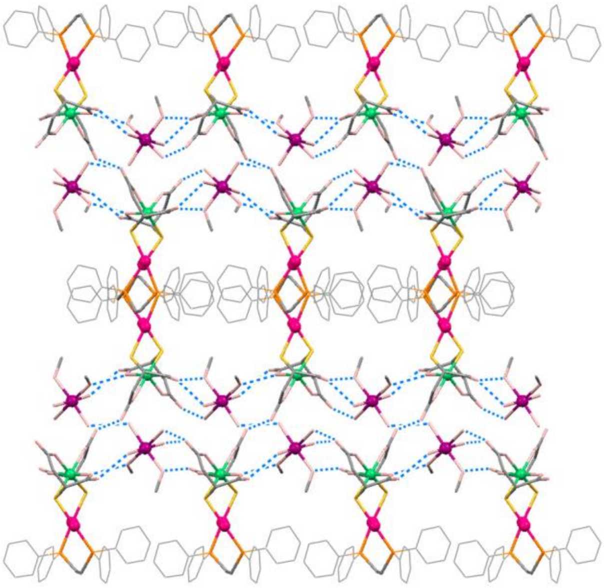


Figure S8. A packing structure viewed from *c* axis in $[Mg(H_2O)_4(MeOH)_2][Ni\{Au_2(dppe)(msa)_2\}]$ (Mg[**2**]). Dashed lines indicate OH···O hydrogen bonds. Au: red purple, Ni: green, Mg: purple, C: gray, O: pink, S: yellow, P: orange.

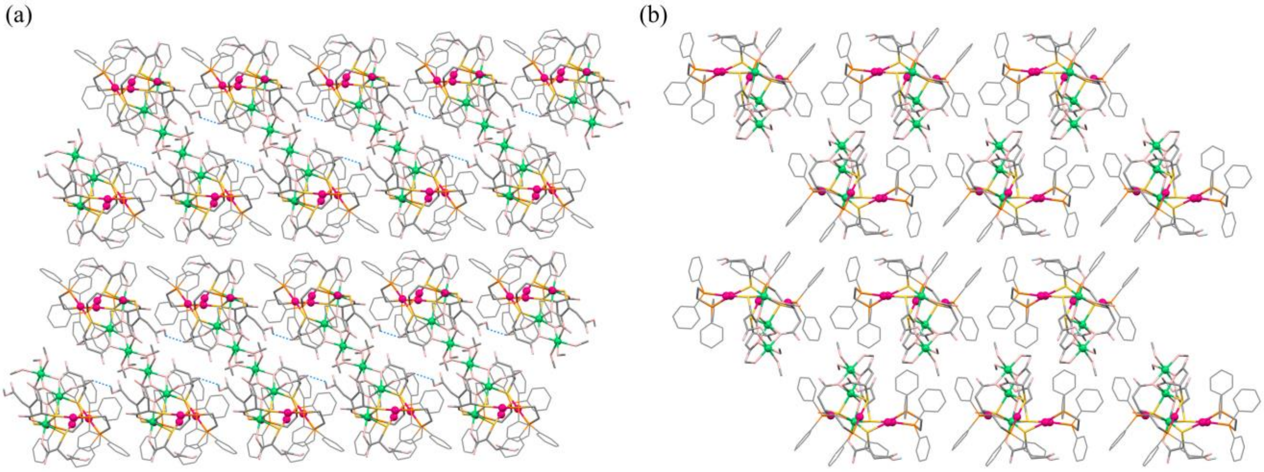


Figure S9. Packing structures viewed from (a) *b* axis and (b) *a* axis in $[Ni_3\{Au_2(dppe)(msa)_2\}\{Au_2(dppe)(Hmsa)_2\}(MeOH)_3]\cdot 4MeOH$ ([**3**]·4MeOH). Au: red purple, Ni: green, C: gray, O: pink, S: yellow, P: orange.

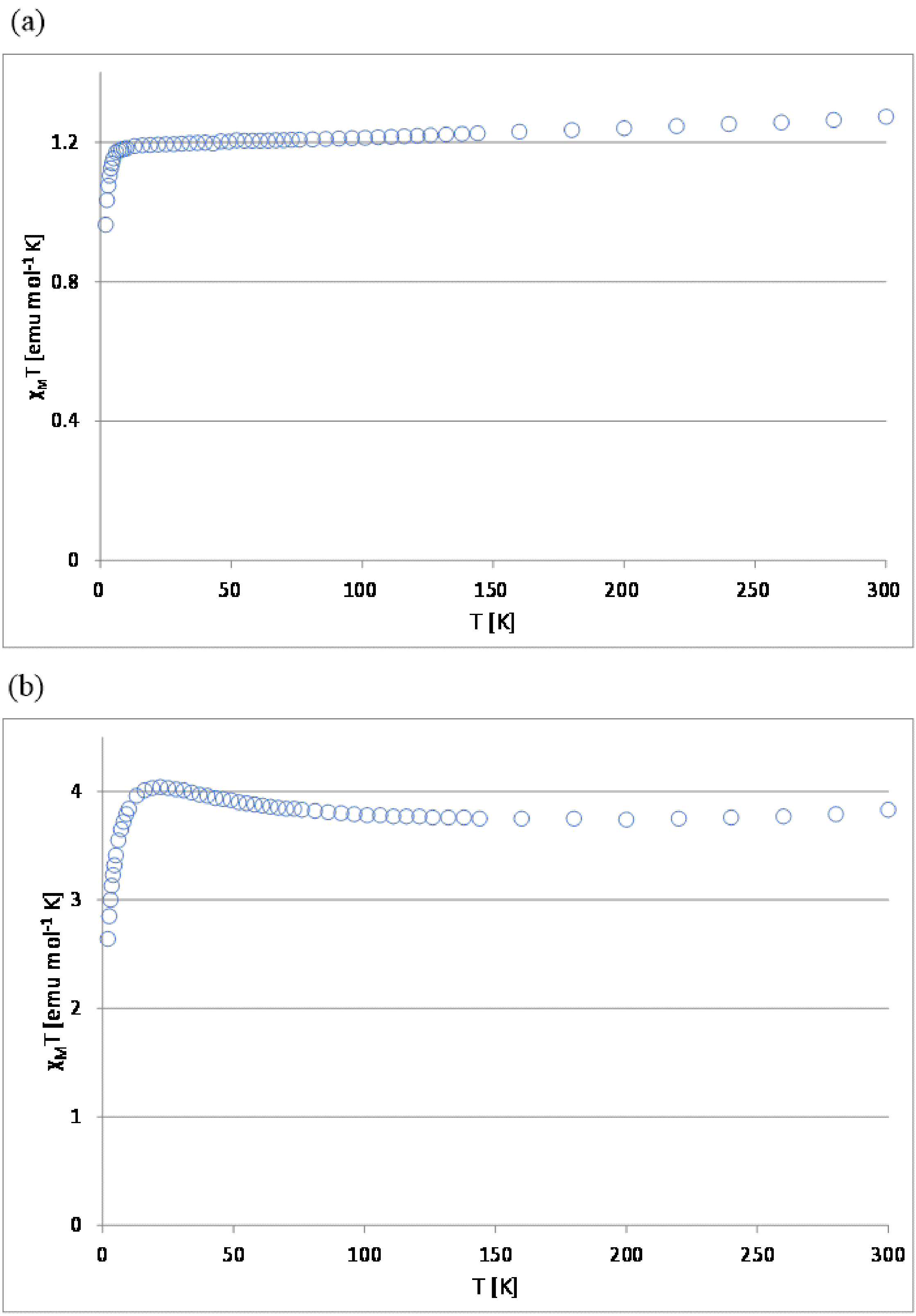


Figure S10. The $\chi_M T$ vs T plots of (a) Mg[**2**] and (b) [**3**].

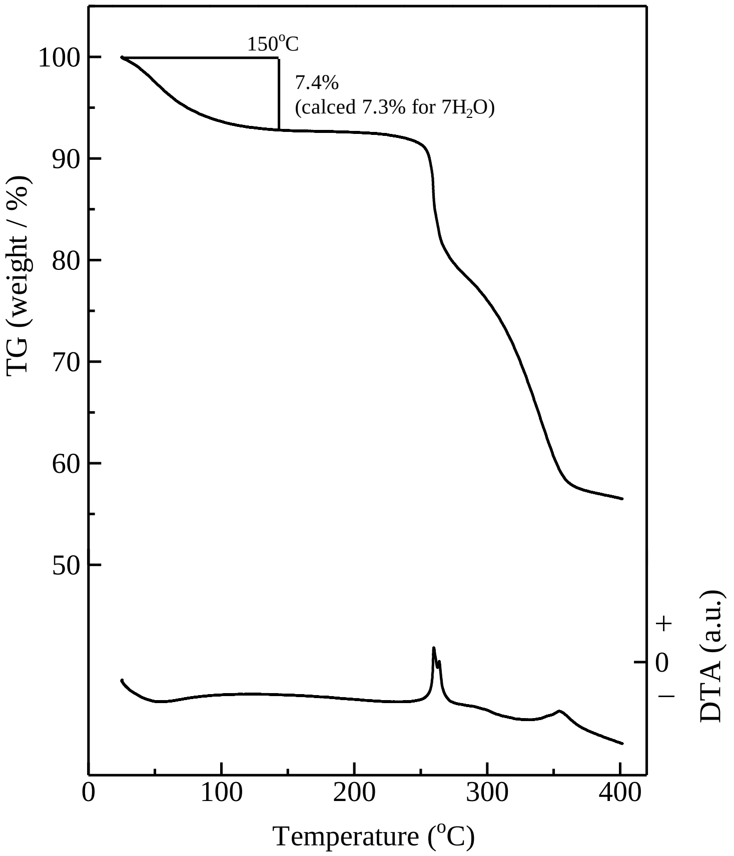


Figure S11. The thermal gravity (TG) and the differential thermal analysis (DTA) curves of Na_2[**2**].

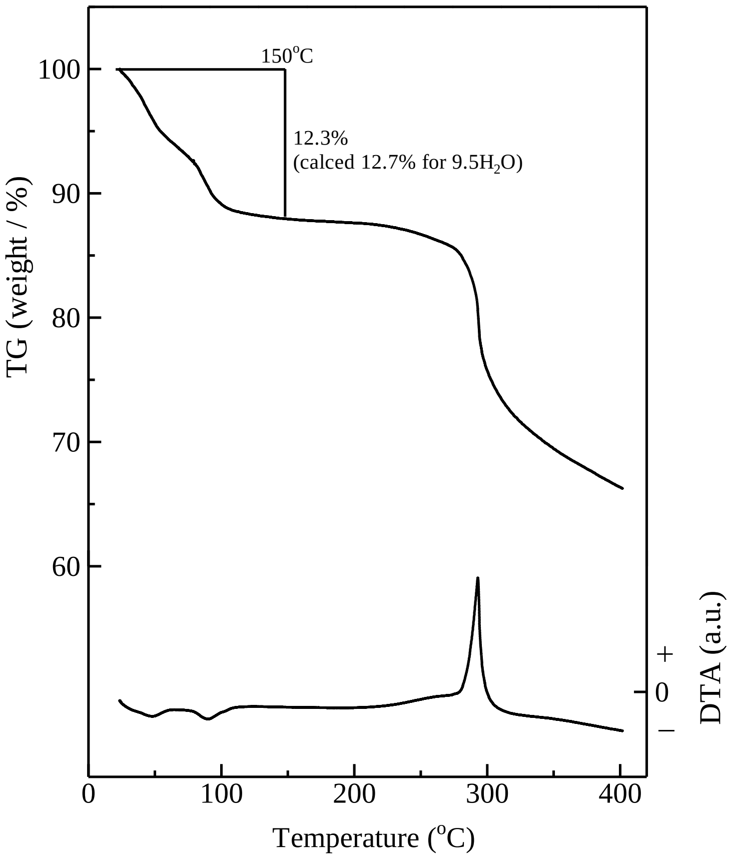


Figure S12. The thermal gravity (TG) and the differential thermal analysis (DTA) curves of Mg[**2**].

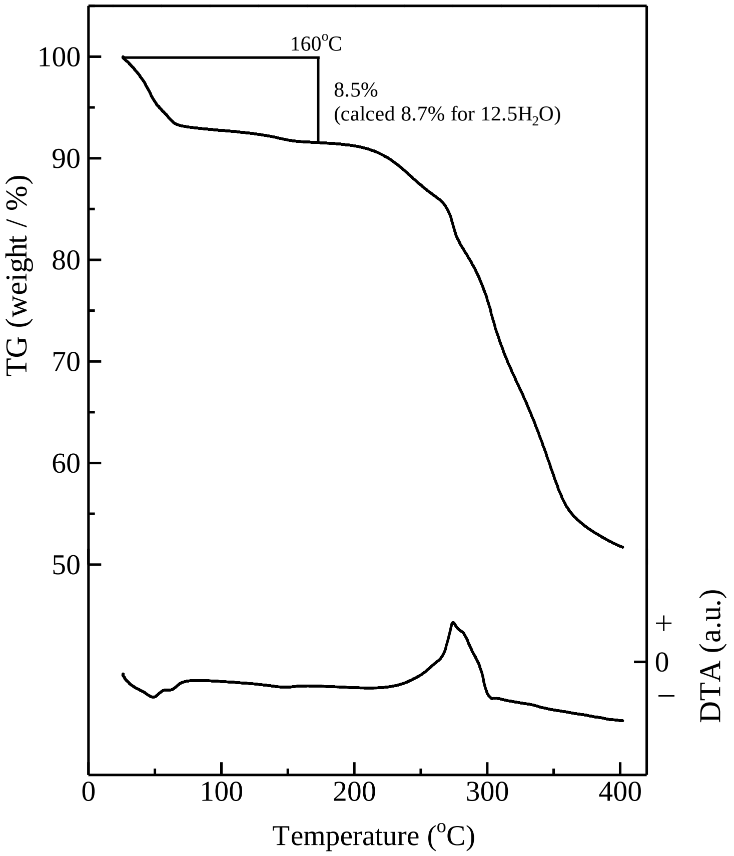


Figure S13. The thermal gravity (TG) and the differential thermal analysis (DTA) curves of [**3**].