Coordination Modes

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A Nickel(II) Gold(I) D-Penicillaminate Coordination System with Multiple Switching in Color, Magnetism, and Chirality**

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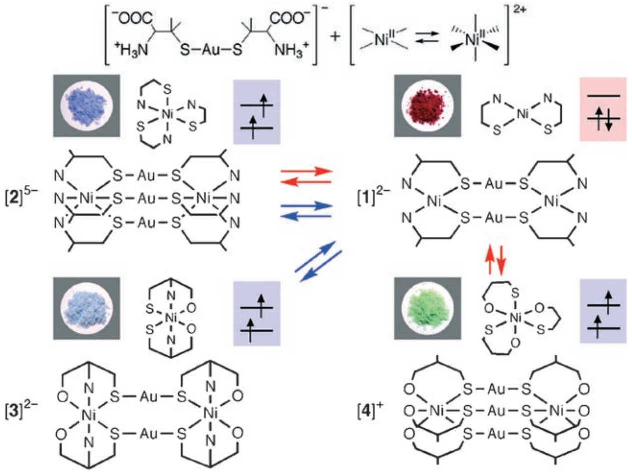
The design and creation of molecular systems that show chemical and physical changes in response to external stimuli is a topic of current interest because of their potential applications as sensing and switching devices.[1] A common approach to create such systems is to combine multifunctional organic or inorganic ligands or both with transition-metal ions that adopt flexible geometrical and electronic structures.[2] The Ni^{2+} ion is promising as a metal component of switching systems because it can adopt several coordination geometries such as octahedral and square-planar, which are interconvertible with concomitant changes in spin state and color. In fact, there are a number of reports on the chromotropic behavior of Ni^{II} complexes based on geometrical changes.[3] However, most systems contain a single Ni^{II} center; therefore, the level of switching in such systems is limited. Herein we report a unique dinickel(II) coordination system derived from the combination of Ni^{II} and $[Au(\text{D-Hpen-}S)_2]^-$ ions ($\text{D-H}_2\text{pen}$ = D-penicillamine). The anion serves as a chiral multidentate metalloligand by exploiting free amine and carboxylate groups in addition to coordinated thiolate groups.[4] This system involved four different S-bridged $Ni^{II}Au^{I}$ structures that are interconvertible in response to several external factors; changes in structure are accompanied by changes in color, magnetism, and chirality (Scheme 1). To our knowledge, such a multiple reversible switching system is unprecedented.



Scheme 1. Four S-bridged $Ni^{II}Au^{I}$ structures constructed from $[Au(\text{D-Hpen-}S)_2]^-$ and Ni^{2+} ions, and their interconversion as a consequence of changes in the solution pH (red arrows) and the Ni/Au ratio (blue arrows). The coordination environments and electronic configurations of the Ni^{II} centers are highlighted. Photographs of the isolated salts of these ionic structures show their different colors.

The reaction of an aqueous solution of $NH_4[Au(\text{D-Hpen-}S)_2]$, neutralized by K_2CO_3, with $Ni(NO_3)_2$ in a 1:1 ratio gave a red solution, from which red crystals of K_2[**1**] were isolated. X-ray fluorescence spectroscopy suggested that K_2[**1**] contains Ni and Au atoms in a 1:1 ratio and its elemental-analysis data were in agreement with a 1:1 adduct of $[Au(\text{D-pen})_2]^{3-}$ and Ni^{2+} ions. The structure of K_2[**1**] was determined by single-crystal X-ray analysis.[5] As shown in Figure 1 a, the $[\mathbf{1}]^{2-}$ ion has an expected S-bridged $Ni^{II}{}_2Au^{I}{}_2$ structure in $[Au_2\{Ni(\text{D-pen-}N,S)_2\}_2]^{2-}$, in which two square-planar $[Ni(\text{D-pen-}N,S)_2]^{2-}$ units bearing two bidentate *N*,*S*-D-pen moieties are linked by two linearly coordinated Au^{I} centers in a twisted chairlike form.[6] The two bridging S atoms in each square-planar $[Ni(\text{D-pen-}N,S)_2]^{2-}$ unit commonly adopt the opposite (*R* and *S*) configurations. The Vis/near-IR spectrum of K_2[**1**] in the solid state is dominated by a visible-light band at 488 nm, which is assigned to the $^3A_2 \leftarrow {}^3T_1$ transition for Ni^{II} centers with square-planar environments.[7]

The reaction of $NH_4[Au(\text{D-Hpen-}S)_2]$ with $Ni(NO_3)_2$ in a 3:2 ratio under similar conditions yielded a blue solution from which purple-blue crystals of K_5[**2**] were isolated. X-ray fluorescence and elemental-analysis data imply that this compound contains $[Au(\text{D-pen})_2]^{3-}$ and Ni^{2+} ions in a 3:2 ratio. While the overall IR spectrum of K_5[**2**] is very similar to that of K_2[**1**], its Vis/near-IR spectrum is different.[8] K_5[**2**] gives a broad near-IR band (902 nm) and a visible-light band (577 nm) in the solid state, which are characteristic of octahedral Ni^{II} complexes as a result of $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ transitions.[7] Based on these results, K_5[**2**] is assumed to contain octahedrally coordinated Ni^{II} centers surrounded by three bidentate D-pen-*N*,*S* moieties. Indeed, X-ray analysis demonstrated that $[\mathbf{2}]^{5-}$ has an S-bridged $Ni^{II}{}_2Au^{I}{}_3$ structure, in which two octahedral $[Ni(\text{D-pen-}N,S)_3]^{4-}$ units are linked by three Au^{I} atoms with linear

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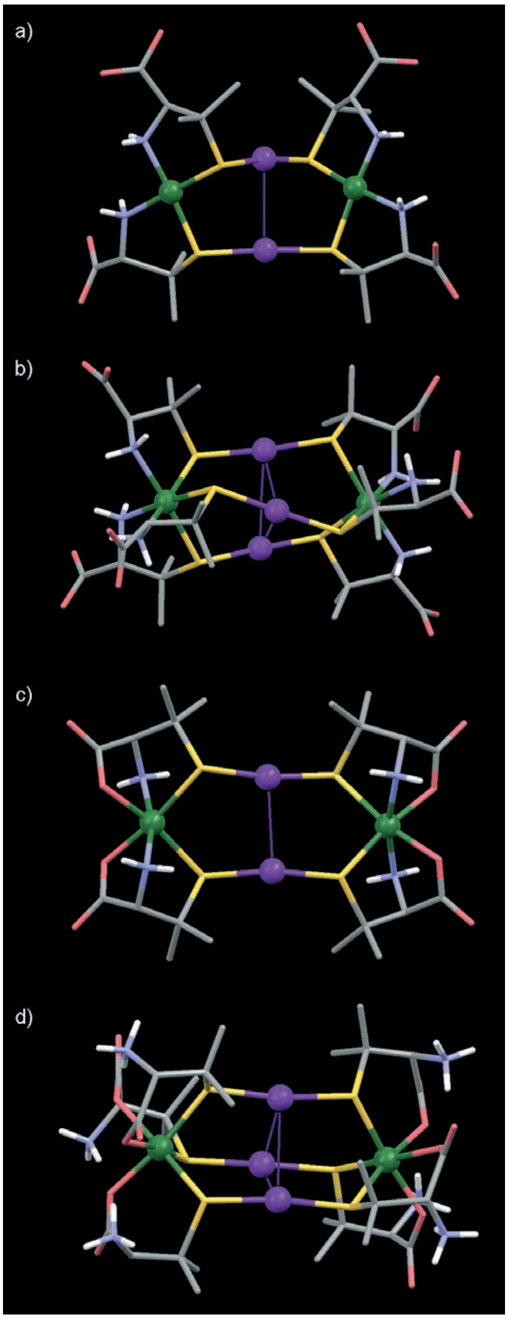

Figure 1. Perspective views of a) [**1**]$^{2-}$, b) [**2**]$^{5-}$, c) [**3**]$^{2-}$, and d) [**4**]$^{+}$. Ni green, Au violet, C gray, H white (C-bound H omitted), N blue, O red, S yellow.

coordination environments (Figure 1b).[5] As there are two kinds of chiralities, Δ or Λ, for the two octahedrally coordinated Ni^{II} atoms, and *R* or *S* configurations for the six bridging S atoms, a total of 21 stereoisomers are possible. However, the [**2**]$^{5-}$ ion gave only the (Λ)$_2$(*R*)$_6$ isomer that forms a triple helix from S–Au–S linkages.

Prompted by the formation of the different Ni^{II}Au^{I} structures when changing the molar ratio from 1:1 to 3:2, we investigated the reaction of NH_4[Au(D-Hpen-*S*)$_2$] and $Ni(NO_3)_2$ with a molar ratio of 2:3 under similar conditions. As with the 1:1 reaction, the resulting solution was red and light blue crystals of [$Ni(H_2O)_6$][**3**], which is insoluble in water, were grown from the red solution with a weakening of its color. X-ray fluorescence and elemental-analysis data imply that [$Ni(H_2O)_6$][**3**] contains [Au(D-pen)$_2$]$^{3-}$ and Ni^{2+} ions in a 2:3 ratio, which is consistent with the reaction stoichiometry. The presence of octahedral Ni^{II} centers in [$Ni(H_2O)_6$][**3**] is indicated by the appearance of a broad near-IR band (1094 nm) and a visible-light band (638 nm) in the solid-state spectrum. The crystal structure of [$Ni(H_2O)_6$][**3**], determined by X-ray analysis,[5] revealed the presence of a Ni$^{II}_2$Au$^{I}_2$ tetranuclear anion, [**3**]$^{2-}$, and an [$Ni(H_2O)_6$]$^{2+}$ ion (Figure 1c). In the [**3**]$^{2-}$ ion, two [Ni(D-pen-*N*,*O*,*S*)$_2$]$^{2-}$ units are linked by two linearly coordinated Au^{I} centers to form an S-bridged Ni$^{II}_2$Au$^{I}_2$ structure. Each Ni^{II} center in the [**3**]$^{2-}$ ion has an octahedral coordination geometry, as with the [**2**]$^{5-}$ ion, but each center is surrounded by two tridentate D-pen-*N*,*O*,*S* moieties such that two *N*,*S*-chelate rings selectively form a Λ configurational skew pair with four bridging S atoms being fixed to the *R* configuration. It should be noted that in the crystal, each [$Ni(H_2O)_6$]$^{2+}$ ion is spanned by two neighboring cations by strong O–H···O hydrogen bonds (O···O 2.61(3) Å–2.81(3) Å), thus creating a rare example of a 1D chain composed of hexa-aqua metal species.[8]

To investigate the influence of solution pH on the formation of Ni^{II}Au^{I} structures, an aqueous solution of NH_4[Au(D-Hpen-*S*)$_2$] (pH ≈ 3.5) was treated with $Ni(NO_3)_2$ in a 1:1 or 3:2 ratio without the addition of K_2CO_3. Interestingly, a green reaction solution resulted, from which yellow-green crystals of [**4**]NO_3 were isolated, which are poorly soluble in water. Although the solid-state spectrum of this compound, which is dominated by a broad near-IR band (1102 nm) and a visible-light band (672 nm), is similar to that of the [**2**]$^{5-}$ ion, each band is considerably red-shifted, thus indicating a weaker ligand field around the octahedral Ni^{II} centers. X-ray analysis for [**4**]Br, prepared by using $NiBr_2$ instead of $Ni(NO_3)_2$, demonstrated that the [**4**]$^{+}$ ion has an S-bridged Ni$^{II}_2$Au$^{I}_3$ structure in [Au$_3${Ni(D-Hpen-*O*,*S*)$_3$}$_2$]$^{+}$ consisting of two octahedrally-coordinated [Ni(D-Hpen-*O*,*S*)$_3$]$^{-}$ units linked by three Au^{I} centers with linear coordination environments (Figure 1d).[5] This S-bridged structure in the [**4**]$^{+}$ ion resembles that in the [**2**]$^{5-}$ ion except that each D-Hpen moiety in the former coordinates to a Ni^{II} center through carboxylate and thiolate groups and a protonated NH_3^{+} group does not participate in the coordination. In the [**4**]$^{+}$ ion, the two octahedral Ni^{II} units selectively take the Λ configuration, with six bridging S atoms being fixed to the *R* configuration as in the [**2**]$^{5-}$ ion. However, the three S–Au–S linkages in the [**4**]$^{+}$ ion are almost parallel to each other because of the steric demand of the O,S-chelating mode.

As expected, magnetic measurements indicate that K_5[**2**], [$Ni(H_2O)_6$][**3**], and [**4**]Br with octahedral Ni^{II} centers are all paramagnetic, while K_2[**1**] with square-planar Ni^{II} centers is diamagnetic. From the temperature dependence of the magnetic susceptibility (2–300 K), a very weak antiferromagnetic interaction between two Ni^{II} centers was revealed for the [**2**]$^{5-}$ ($J = -4.3(1)\ \mathrm{cm^{-1}}$ and $g = 2.04(1)$) and [**3**]$^{2-}$ ions ($J = -1.1(1)\ \mathrm{cm^{-1}}$ and $g = 2.16(1)$), which is compatible with the large Ni···Ni separation (6.808(2) Å in [**2**]$^{5-}$ and 7.351(3) Å in [**3**]$^{2-}$).[8] However, for the [**4**]$^{+}$ ion, an appreciable antiferromagnetic interaction was recognized between the two Ni^{II}

centers ($J = -11.6(1)$ cm^{-1} and $g = 2.19(1)$) despite the Ni···Ni separation (7.025(4) Å) being comparable with those in the [**2**]$^{5-}$ and [**3**]$^{2-}$ ions.[8] The presence of a relatively large M···M magnetic interaction through closed-shell d^{10} Au^{I} centers bridged by thiolate groups is noteworthy and is related to the parallel arrangement of S–Au–S linkages in the [**4**]$^{+}$ ion, which is distinct from the skewed arrangement in the [**2**]$^{5-}$ and [**3**]$^{2-}$ ions.

The most striking feature of this Ni^{II}Au^{I} coordination system is the facile interconversion between the four S-bridged structures, accompanied by color change (Scheme 1).[8,9] When 0.5 molar equivalents of $Ni(NO_3)_2$ were added to a blue aqueous solution of K$_5$[**2**], the solution immediately turned red, and the absorption spectrum coincided with that of the [**1**]$^{2-}$ ion; further addition of $Ni(NO_3)_2$ led to the precipitation of a light blue powder, [Ni(H$_2$O)$_6$][**3**]. In reverse, treatment of an aqueous suspension of [Ni(H$_2$O)$_6$] [**3**] with 0.5 molar equivalents of [Au(D-pen-*S*)$_2$]$^{3-}$ produced a red solution ([**1**]$^{2-}$), which turned blue ([**2**]$^{5-}$) on further addition of [Au(D-pen-*S*)$_2$]$^{3-}$ ions. Furthermore, the addition of 0.1 M of aqueous HNO_3 to a blue aqueous solution of K$_5$[**2**] (pH ≈ 8.5) induced a change to red ([**1**]$^{2-}$) in a pH range of about 7 to 5, and this red solution turned green ([**4**]$^{+}$) on lowering the pH to about 3.5 by further addition of 0.1 M aqueous HNO_3. The green solution of [**4**]$^{+}$ ions reverted back to a blue solution of [**2**]$^{5-}$ ions by way of a red solution on raising the pH to about 8.5 with aqueous NH_3. Notably, the [**1**]$^{2-}$ and [**2**]$^{5-}$ ions are also interconvertible in response to solvent and temperature, thus demonstrating solvatochromism and thermochromism.[10]

In summary, we have shown that four different, chiral-selective polynuclear structures are constructed from only Ni^{II} and [Au(D-Hpen-*S*)$_2$]$^{-}$ ions because of the flexible geometries of the Ni^{II} center and the versatile coordination modes of D-penicillaminate bound to a Au^{I} center (N,S-bidentate, O,S-bidentate, and N,O,S-tridentate). Complexes [**2**]$^{5-}$, [**1**]$^{2-}$, and [**3**]$^{2-}$ are interconvertible in response to the Ni^{II}/[Au(D-pen-*S*)$_2$]$^{3-}$ ratio, whereas [**2**]$^{5-}$, [**1**]$^{2-}$, and [**4**]$^{+}$ are interconvertible in response to solution pH. Note that [**1**]$^{2-}$ has Ni^{II} centers with a square-planar, achiral coordination environment and with a low-spin d^{8} configuration, while [**2**]$^{5-}$, [**3**]$^{2-}$, and [**4**]$^{+}$ have Ni^{II} centers with an octahedral, chiral coordination environment and with a high-spin configuration. Thus, [**1**]$^{2-}$ is triply reversible with [**2**]$^{5-}$, [**3**]$^{2-}$, and [**4**]$^{+}$; the interconversion is accompanied not only by the readily detectable color change, but also by the drastic switching in magnetism and chirality. The creation of other dynamic switching systems through the use of multifunctional chiral metalloligands, such as [Au(D-pen-*S*)$_2$]$^{3-}$ ions, in combination with two or more transition-metal ions with manifold geometrical and electronic properties is promising.

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[5] Crystal data for K$_2$[**1**]·6H$_2$O: Bruker SMART CCD diffractometer, $T = 210$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SIR97 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[11] $C_{80}H_{184}Au_8K_8N_{16}Ni_8O_{52}S_{16}$, $M_r = 5073.60$, crystal size $0.26 \times 0.07 \times 0.07$ mm^3, trigonal, space group *R*3, $a = 36.132(8)$, $c = 37.686(11)$ Å, $V = 42607(19)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.780$ g cm^{-3}, $\mu = 7.362$ mm^{-1}, ω–2θ scan mode, $2\theta_{max} = 55.0°$, 102126 reflections collected, 42850 independent reflections, 25612 observed reflections ($I > 2\sigma(I)$), 1568 parameters, semiempirical absorption corrections with SADABS, max./min. transmission 0.563/0.445, $R1$ ($I > 2\sigma(I)$) = 0.0458, $wR2$ (all data) = 0.0957, Flack parameter −0.023(4), residual electron density 2.380/−0.894 e Å^{-3}. Crystal data for K$_5$[**2**]·23H$_2$O·KNO$_3$: Bruker SMART CCD diffractometer, $T = 220$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SIR97 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[11] $C_{30}H_{100}Au_3K_6N_7Ni_2O_{38}S_6$, $M_r = 2302.45$, crystal size $0.25 \times 0.20 \times 0.10$ mm^3, trigonal, space group $P3_2$, $a = 11.6927(13)$, $c = 48.269(89)$ Å, $V = 5715.1(13)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.007$ g cm^{-3}, $\mu = 6.819$ mm^{-1}, ω–2θ scan mode, $2\theta_{max} = 50.0°$, 25529 reflections collected, 11364 independent reflections, 10445 observed reflections ($I > 2\sigma(I)$), 812 parameters, semiempirical absorption corrections with SADABS, max./min. transmission 0.562/0.406, $R1$ ($I > 2\sigma(I)$) = 0.0338, $wR2$ (all data) = 0.0615, Flack parameter −0.019(5), residual electron density 1.460/−1.075 e Å^{-3}. Crystal data for [Ni(H$_2$O)$_6$][**3**]·3.5H$_2$O: Bruker SMART CCD diffractometer, $T = 200$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by the Patterson method with DIRDIF99[12] (PATTY) and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[11] $C_{20}H_{55}Au_2N_4Ni_3O_{17.5}S_4$, $M_r = 1329.98$, crystal size $0.39 \times 0.12 \times 0.05$ mm^3, monoclinic, space group *C*2, $a = 22.307(6)$, $b = 5.5472(14)$, $c = 17.234(4)$ Å, $\beta = 133.135(5)°$, $V = 1961.1(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.252$ g cm^{-3}, $\mu = 9.153$ mm^{-1}, ω–2θ scan mode, $2\theta_{max} = 55.0°$, 6803 reflections collected, 3202 independent reflections, 2936 observed reflections ($I > 2\sigma(I)$), 227 parameters, absorption corrections (numerical integration), max./min. transmission 0.629/0.191, $R1$ ($I > 2\sigma(I)$) = 0.0361, $wR2$ (all data) = 0.0897, Flack parameter −0.021(10), residual electron density 2.224/−1.711 e Å^{-3}. Crystal structure analysis for [**4**]Br·9H$_2$O: Bruker SMART CCD diffractometer, $T = 200$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct method with SIR97 and refined by full-matrix least-squares techniques on F^2 by using SHELXL-97.[11] $C_{30}H_{78}Au_3BrN_6Ni_2O_{21}S_6$, $M_r = 1839.57$, crystal

size $0.40 \times 0.08 \times 0.08$ mm^3, hexagonal, space group $P6_522$, $a = 11.8102(6)$, $c = 76.306(6)$ Å, $V = 9217.3(9)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.988$ g cm^{-3}, $\mu = 8.659$ mm^{-1}, ω–2θ scan mode, $2\theta_{max} = 55.0°$, 100847 reflections collected, 7074 independent reflections, 6295 observed reflections ($I > 2\sigma(I)$), 317 parameters, semiempirical absorption corrections with SADABS, max./min. transmission 0.603/0.435, $R1$ ($I > 2\sigma(I)$) = 0.0722, $wR2$ (all data) = 0.1571, Flack parameter 0.067(18), residual electron density 1.207/−2.983 e Å^{-3}. CCDC-627744–627747 (**1**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[6] The structure of K_2[**1**] is very similar to that of the previously reported $Na_2[Au_2\{Ni(D\text{-pen-}N,S)_2\}_2]$, which was isolated from a mixture of D-H_2pen, $NiCl_2 \cdot 6H_2O$, and $[Au(tu)_2Cl]$ (tu = thiourea) in aqueous sodium acetate buffer. P. J. M. L. Birker, G. C. Verschoor, *Inorg. Chem.* **1982**, *21*, 990–995.

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[9] Compounds K_2[**1**], K_5[**2**], $[Ni(H_2O)_6]$[**3**], and [**4**]X (X = NO_3, Br) are all optically active, and their absorption and CD spectra in water, except those of insoluble $[Ni(H_2O)_6]$[**3**], are essentially the same as those in the solid state, which is indicative of the retention of their chiral structures in water.

[10] Dissolution of K_5[**2**] in methanol gave a red solution characteristic of the presence of [**1**]$^{2-}$ ions, although its aqueous solution is blue. In addition, a blue aqueous solution of K_5[**2**] turned red when heated to 60 °C and reverted back to blue on cooling to room temperature.

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