## Heterotrimetallic Iron(II)–Nickel(II)–Manganese(I) Chalcogenolate Complexes Containing a Heteroleptic Hexachalcogenolatonickel(II)/Homoleptic Hexathiolatonickel(II) Core

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Received October 5, 1998

Complex *cis*-[Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>]<sup>-</sup> was employed as a metallo chelating ligand to synthesize [(CO)<sub>4</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>Ni( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>Mn(CO)<sub>4</sub>] (**1**) with a square planar Ni<sup>II</sup>-thiolate core. The longer Ni<sup>II</sup>····Mn<sup>I</sup> distances and electronic population of nickel(II) (d<sup>8</sup>) are adopted to rationalize the construction of complex **1**. Cleavage of the Mn<sup>I</sup>–S bond in complex **1** by an incoming tridentate metallo ligand *fac*-[Fe(CO)<sub>3</sub>(ER)<sub>3</sub>]<sup>-</sup> (E = S, R = C<sub>4</sub>H<sub>3</sub>S; E = Se, R = Ph), followed by a thiolate group ([2-S-C<sub>4</sub>H<sub>3</sub>S)<sup>-</sup>) rearranging to bridge two metals, led directly to the anionic [(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -ER)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> (E = S, R = C<sub>4</sub>H<sub>3</sub>S (**2**); E = Se, R = Ph (**3**)) with a homoleptic/heteroleptic hexachalcogenolatonickel(II) core, respectively. Dropwise addition of *cis*-[Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>]<sup>-</sup> to the anionic **2** in THF resulted in formation of a linear trinuclear complex [(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>]<sup>2-</sup> (**4**) possessing a homoleptic hexathiolatonickel(II) core. It seems reasonable to conclude that the d<sup>6</sup> Mn(I) [(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>]<sup>2-</sup> fragment is isolobal with the d<sup>6</sup> Fe(II) [(ER)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> fragment in complexes **4**, **3**, and **2**.

## Introduction

The study of nickel thiolate and selenolate chemistry has been actively pursued,<sup>1</sup> motivated primarily by the relevance of such biomimetic nickel/nickel-iron complexes to [NiFe] hydrogenases and CO dehydrogenase.<sup>2</sup> To our knowledge, a few examples of complexes containing a homoleptic hexathiolatometal core or hexaselenolatometal core are reported and characterized by X-ray crystallography.<sup>3</sup>

Recent work in this laboratory showed that *cis*-[Mn-(CO)<sub>4</sub>(ER)<sub>2</sub>]<sup>-</sup> and *fac*-[Fe(CO)<sub>3</sub>(SePh)<sub>3</sub>]<sup>-</sup> complexes are useful in the syntheses of heterotrimetallic Mn(I)–Co-(III)–Mn(I)-chalcogenolate complexes [(CO)<sub>4</sub>Mn( $\mu$ -ER)<sub>2</sub>-Co(CO)( $\mu$ -E'R)<sub>3</sub>Mn(CO)<sub>3</sub>] (E = E' = Te, R = Ph; E = Te, E' = Se, R = Ph; E = E' = Se, R = Me) with a unique Co(III)–CO bond,<sup>4</sup> and [(CO)<sub>3</sub>M( $\mu$ -SePh)<sub>3</sub>M'( $\mu$ -SePh)<sub>3</sub>M-(CO)<sub>3</sub>]<sup>-1/0</sup> (M = Mn, M' = Co; M = Fe, M' = Fe, Cd, Zn, Ni) with a homoleptic hexaselenolatometal core.<sup>3b,5</sup> In these reactions, the complexes *fac*-[Fe(CO)<sub>3</sub>(SePh)<sub>3</sub>]<sup>-</sup> and *cis*-[Mn(CO)<sub>4</sub>(ER)<sub>2</sub>]<sup>-</sup> act as potential "chelating metallo ligands" and selenolate ligand-transfer reagents.<sup>5c,6</sup>

A recent report on distorted square planar [Ni(CO)- $(SPh)_n(SePh)_{3-n}$ ]<sup>-</sup> (n = 0, 1, 2), in preparations of the biomimetic nickel-site structure of [NiFe] hydrogenases

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Scheme 1  

$$2 [Mn(CO)_{5}] + 2 (2 \cdot S \cdot C_{4}H_{3}S)_{2}$$
(a)  

$$2 cis \cdot [Mn(CO)_{4}(2 \cdot S \cdot C_{4}H_{3}S)_{2}]^{-}$$
(b)  

$$| + Ni^{2+}$$

$$[(CO)_{4}Mn(\mu \cdot 2 \cdot S \cdot C_{4}H_{3}S)_{2}Ni(\mu \cdot 2 \cdot S \cdot C_{4}H_{3}S)_{2}Mn(CO)_{4}]$$

(c) 
$$\begin{array}{c} +fac-[Fe(CO)_{3}(ER)_{3}]^{T} \\ E = S, R = 2-S-C_{4}H_{3}S \\ E = Se, R = Ph \\ \hline \\ 0 \\ E = Se, R = Ph \\ \hline \\ [(CO)_{3}Mn(\mu-2-S-C_{4}H_{3}S)_{2}Ni(\mu-ER)_{3}Fe(CO)_{3}]^{T} \\ \hline \\ (d) \\ \hline \\ [(CO)_{3}Mn(\mu-2-S-C_{4}H_{3}S)_{3}Ni(\mu-ER)_{3}Fe(CO)_{3}]^{T} \\ \hline \\ (e) \\ E = S, R = 2-S-C_{4}H_{3}S \\ + cis-[Mn(CO)_{4}(2-S-C_{4}H_{3}S)_{2}]^{T} \\ \hline \\ [(CO)_{3}Mn(\mu-2-S-C_{4}H_{3}S)_{3}Ni(\mu-2-S-C_{4}H_{3}S)_{3}Mn(CO)_{3}]^{2T} \\ \end{array}$$

and CO dehydrogenase,<sup>2</sup> has prompted us to synthesize Ni-Fe-thiolate complexes.7 Our efforts toward the preparations of Fe<sup>II</sup>-Ni<sup>II</sup>-chalcogenolate complexes provide the first example of heterotrimetallic Fe<sup>II</sup>-Ni<sup>II</sup>-Mn<sup>I</sup>-chalcogenolate complexes with a heteroleptic/ homoleptic hexachalcogenolatonickel(II) core and Mn<sup>I</sup>-Ni<sup>II</sup>-Mn<sup>I</sup>-thiolate complexes with a homoleptic hexathiolatonickel(II) core.

## **Results and Discussion**

When a THF solution of di(2-thienyl) disulfide and  $[PPN][Mn(CO)_5]$  are stirred under  $N_2$ ,<sup>8</sup> a rapid reaction ensues over the course of 5 min at ambient temperature to give the yellow cis-[PPN][Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>],<sup>9,10</sup> in 90% isolated yield after removal of [PPN][(CO)<sub>3</sub>Mn- $(\mu - 2 - S - C_4 H_3 S)_3 Mn(CO)_3$  by diethyl ether and recrystallization with THF/hexane (Scheme 1a). As illustrated in Scheme 1b, the reaction of *cis*-[PPN][Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>] and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H20 in a 2:1 molar ratio in THF at 10 °C yielded the neutral trinuclear [(CO)<sub>4</sub>Mn- $(\mu - 2 - S - C_4 H_3 S)_2 Ni(\mu - 2 - S - C_4 H_3 S)_2 Mn(CO)_4]$  (1) (65% yield) by salt elimination of [PPN][ClO<sub>4</sub>]. <sup>1</sup>H and <sup>13</sup>C NMR spectra show the expected signals for the  $[2-S-C_4H_3S]^$ ligands in a diamagneic d<sup>8</sup> Ni<sup>II</sup> species.

The dark red [PPN][(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -ER)<sub>3</sub>- $Fe(CO)_3$ ] (E = S, R = C<sub>4</sub>H<sub>3</sub>S (2); E = Se, R = Ph (3)), formed immediately on reaction of complex 1 and fac-

[Fe(CO)<sub>3</sub>(ER)<sub>3</sub>]<sup>-</sup> in THF,<sup>5ab,11</sup> was isolated and recrystallized from THF/hexane (85% for 3) (Scheme 1c,d). The well-known dimer  $[(CO)_4Mn(\mu-2-S-C_4H_3S)_2Mn(CO)_4]$  was obtained as a byproduct (hexane/THF soluble) during the isolation of complex **3**.<sup>12</sup> IR  $\nu$ (CO) data (the carbonyl stretching bands 2061 m, 2007 sh  $cm^{-1}$  of complex 3, comparing to  $\nu$ (CO) (2070 s, 2019 s cm<sup>-1</sup>) of complex (CO)<sub>3</sub>Fe(*u*-SePh)<sub>3</sub>Ni<sup>II</sup>(*u*-SePh)<sub>3</sub>Fe<sup>II</sup>(CO)<sub>3</sub>, <sup>5c</sup> were assigned to the  $Fe^{II}(CO)_3$  fragment, and the stretching bands 1998 vs, 1904 s cm  $^{-1}$ , comparing to the  $\nu(\rm CO)$  (1994 vs, 1914 s cm<sup>-1</sup>) in the  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Mn(CO)_3]^-$ , were attributed to the CO stretching bands of the Mn<sup>I</sup>- $(CO)_3$  fragment of complex **3**) suggested its formulation as the PPN<sup>+</sup> salt of  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu SePh_{3}Fe(CO)_{3}$  with the central Ni<sup>II</sup> surrounded by three bridging  $[S-C_4H_3S]^-$  ligands and three bridging [SePh]<sup>-</sup> ligands, which was also confirmed by X-ray crystallography. A reasonable reaction sequence accounting for the formation of heterotrinuclear [(CO)<sub>3</sub>Mn- $(\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni $(\mu$ -ER)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> is shown in Scheme 1c,d. Cleavage of the Mn<sup>I</sup>-S bond in complex **1** by an incoming tridentate metallo ligand fac-[Fe(CO)<sub>3</sub>(ER)<sub>3</sub>]led to the presumed intermediate  $[(CO)_4Mn(\mu-2-S C_4H_3S_2Ni(2-S-C_4H_3S)(\mu-ER)_3Fe(CO)_3]^-$ , and subsequent rearrangement of the terminal thiolate ligand [2-S-C<sub>4</sub>H<sub>3</sub>S]<sup>-</sup> to bridge two metals (Mn<sup>I</sup> and Ni<sup>II</sup>) accompanied by dissociation of a labile carbonyl from Mn<sup>I</sup> yielded the anionic  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu-ER)_3Fe(CO)_3]^-$ . These results established that the same stoichiometric quantities of  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu-ER)_3Fe(CO)_3]^$ are formed concurrently with  $[(CO)_4Mn(\mu-2-S-C_4H_3S)_2-$ Mn(CO)<sub>4</sub>] dimer. When attempting to isolate complex **2** by drying under vacuum and extracting with THF, we isolated only an insoluble solid. We conclude that the replacement of the selenolate ligands with thiolate ligands in complex [(CO)<sub>3</sub>Mn(µ-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni(µ-SePh)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> has a significant effect on its thermal stability.

On stirring a 1:1 mixture of complex 2 and cis-[Mn- $(CO)_4(2$ -S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>]<sup>-</sup> in THF for 3 h at 22 °C, a dark redbrown solid precipitated, Scheme le. Extracted into CH<sub>3</sub>CN, and obtained in crystalline form by diethyl ether diffusion into CH<sub>3</sub>CN solution (56% yield), this compound was analyzed as [PPN]<sub>2</sub>[(CO)<sub>3</sub>Mn(u-2-S- $C_4H_3S_3Ni(\mu - 2 - S - C_4H_3S_3Mn(CO)_3]$  (4). The IR  $\nu(CO)$ bands (1988 vs, 1892 s  $cm^{-1}$  (CH<sub>3</sub>CN)) in the solution spectrum of **4** are indicative of  $C_{3v}$  symmetry about Mn  $(2A_1 + E)$ , as observed in the complex [PPN][(CO)<sub>3</sub>Mn-(μ-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>] (ν(CO) (THF): 1994 vs, 1914 s cm<sup>-1</sup>). Complex **4** exhibits a diagnostic <sup>1</sup>H NMR spectrum with the 2-thienyl proton resonances well removed from the diamagnetic region. The protons resonate downfield,  $\delta$  15.20 (br), 13.69 (br) and upfield -12.24 (br) ppm, which is consistent with the central Ni<sup>II</sup> having a d<sup>8</sup> electronic configuration in an octahedral ligand field. The effective magnetic moment in solid state by SQUID magnetometer was 3.95 and 3.93  $\mu_{\rm B}$ for complexes 3 and 4, respectively. These values are higher than the spin-only value of 2.83  $\mu_{\rm B}$ , which are attributed to the orbital angular momentum. A plot of  $\chi$  versus T (5–300 K) indicated no antiferromagnetic interaction for complexes **3** and **4**, respectively.

The structure of **1** is depicted in Figure 1. The geometry around the Ni atom is distorted square planar.

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**Figure 1.** ORTEP drawing and labeling scheme of  $[(CO)_4Mn(\mu-2-S-C_4H_3S)_2Ni(\mu-2-S-C_4H_3S)_2Mn(CO)_4]$  with thermal ellipsoids drawn at the 30% probability level.

Further examination shows that there is no significant Ni<sup>II</sup>····Mn<sup>I</sup> bonding (Ni<sup>II</sup>····Mn<sup>I</sup>(A) 3.364 Å and Ni<sup>II</sup>····Mn<sup>I</sup>-(B) 3.364 Å), and the four-membered NiS<sub>2</sub>Mn rings are decidedly bent with a dihedral angle between MnS<sub>2</sub> and NiS<sub>2</sub> planes of 32.74°. In comparison, the heterotrinuclear complex  $[{Cp_2Nb(\mu-SMe)_2}_2Ni]^{2+}$  has the Ni<sup>0</sup> atom in an approximately tetrahedral arrangement of the bridging thiolates and Ni<sup>0</sup>-Nb<sup>IV</sup> metal-metal bonds.<sup>13</sup> The dependence of geometry on electron population (d<sup>8</sup> Ni<sup>II</sup>) and the longer Ni<sup>II</sup>...Mn<sup>I</sup> distances are adopted to rationalize the construction of complex 1 with a square planar Ni<sup>II</sup>-thiolate core. The average Ni<sup>II</sup>-S bond of length 2.217(8) Å is shorter than the terminal Ni<sup>II</sup>-S distances in distorted tetrahedral [Ni(SPh)<sub>4</sub>]<sup>2-</sup> (average 2.281(1) Å).<sup>14</sup> The intramolecular S···S contact distances in 1 are in the range 2.980–3.059 Å, indicative of the absence of direct S-S bonding.

The molecular structure of **3** is shown in Figure 2, with selected bond distances and angles collected in Table 3. Complex 3 has a linear chain of one nickel(II), one iron(II), and one manganese(I) atom; the central Ni<sup>II</sup> atom lies in a slightly distorted octahedral environment of selenium and sulfur atoms (NiS<sub>3</sub>Se<sub>3</sub> core) provided by two facially coordinating tridentate [(PhSe)<sub>3</sub>Fe<sup>II</sup>- $(CO)_3$  and  $[(2-S-C_4H_3S)_3Mn^{I}(CO)_3]$  fragments. The average Ni<sup>II</sup>-S bond of length 2.451(2) Å is significantly longer than that of complex 1 (average 2.217(8) Å). The Ni<sup>II</sup>–Se bond lengths range from 2.556(2) to 2.568(2) Å (average = 2.564(2) Å). These are longer than the Ni<sup>II</sup>-Se distances reported in tetrahedral [Ni(SePh)<sub>4</sub>]<sup>2-</sup> (Ni- $Se_{av} = 2.401(3)$  Å)<sup>15</sup> and distorted square planar  $[Ni(CO)(SePh)_3]^-$  (Ni-Se<sub>av</sub> = 2.317(2) Å).<sup>7</sup> The Ni<sup>II</sup>... Fe<sup>II</sup> distance, 3.340 Å, and Ni<sup>II</sup>····Mn<sup>I</sup> distance, 3.192 Å, exclude any direct metal-metal interactions. It is noteworthy that Ni<sup>II</sup>-S. Ni<sup>II</sup>-Se. Ni<sup>II</sup>···Mn<sup>I</sup>. and Ni<sup>II</sup>···



**Figure 2.** ORTEP drawing and labeling scheme of  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu-SePh)_3Fe(CO)_3]^-$  with thermal ellipsoids drawn at the 30% probability level.

Table 1. Crystallographic Data of Complexes (a) 1and (b) 3.3THF

	1	<b>3</b> •3THF
chem formula	C24H12O8Mn2NiS8	C <sub>84</sub> H <sub>78</sub> O <sub>9</sub> P <sub>2</sub> FeMnNiS <sub>6</sub> NSe <sub>3</sub>
fw	853.41	1906.15
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pca2_1$
λ, Å (Μο Κα)	0.7107	0.7107
<i>a,</i> Å	8.4017(1)	24.8147(4)
<i>b,</i> Å	9.2691(1)	12.9101(2)
<i>c</i> , Å	11.3735(1)	27.0074(5)
α, deg	68.345(1)	90
$\beta$ , deg	79.851(1)	90
γ, deg	78.049(1)	90
V, Å <sup>3</sup>	800.51(2)	8652.1(3)
Ζ	1	4
$ ho_{ m calcd}$ , g cm $^{-3}$	1.770	1.463
$\mu$ , cm <sup>-1</sup>	19.25	20.23
F(000)	426	3872
no. of measd reflcns	10 563	50 752
no. of obsd	3663	15 397
reflcns		
no. of refined params	197	905
T. °C	22	22
$R[I > 2\sigma(I)]$	0.0435 <sup>a</sup>	0.0727 <sup>a</sup>
$R_{\mathrm{w}F^2}$	0.1320 <sup>b</sup>	0.1822 <sup>b</sup>
$a R = \sum  \langle  F_0  -$	$- F_c ) /\Sigma F_o , \ ^{b}R_{wF^2} =$	$\{\sum w(F_0^2 - F_c^2)^2 / \sum [w(F_0^2)^2]\}^{1/2}$

•Fe<sup>II</sup> distances of 2.451(2), 2.564(2), 3.192, and 3.340 Å, <sup>5c</sup> respectively, also support the formation of complex **3** as a heterotrinuclear Fe<sup>II</sup>–Ni<sup>II</sup>–Mn<sup>I</sup>-mixed-chalcogeno-late complex, consistent with the conclusion in IR  $\nu$ (CO) data.

The X-ray structural analysis (Figure 3) of complex 4, isostructural with complex 3, reveals a centrosymmetric trinuclear manganese–nickel–manganese-thiolate complex in which the Ni<sup>II</sup> is in a distorted octahedral arrangement with the sulfur atoms of thiolates in two parallel faces of the octahedron capped by tricarbonylmanganese(I) fragments. The NiS<sub>6</sub> core has

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Table 2.	<b>Crystallographic Data of Complex</b>	2
	4·2CH <sub>3</sub> CN	

- 0 -	
chem formula fw cryst syst space group $\lambda$ , Å (Mo K $\alpha$ ) a, Å b, Å c, Å $\alpha$ , deg	$\begin{array}{c} C_{106}H_{84}N_4O_6P_4Mn_2NiS_{12}\\ 2187.03\\ triclinic\\ P\bar{1}\\ 0.7107\\ 12.575(3)\\ 14.176(4)\\ 16.156(3)\\ 70.37(2) \end{array}$
$\beta$ , deg	85.54(2)
$\gamma$ , deg	76.92(2)
V, Å <sup>3</sup>	2642.2(11)
Z	1
$ ho_{ m calcd}$ , g cm $^{-3}$	1.375
$\mu$ , cm <sup>-1</sup>	7.428
<i>F</i> (000)	1129
no. of measd reflcns	9288
no. of obsd reflcns $(I > 2\sigma(I))$	7002
no. of refined params	611
T, °C	25
$R^a$	0.043
$R_{\rm w}{}^{\scriptscriptstyle D}$	0.041

<sup>a</sup>  $R = \sum |(F_0 - F_c)| / \sum F_0$ . <sup>b</sup>  $R = [\sum (w(F_0 - F_c)^2 / wF_0^2]^{1/2}.$ 

Table 3. Selected Bond Distances (Å) and Angles(deg) for (a) Complex 1 and (b) Complex 3.3THF

(a) Complex 1						
Ni-S(1)	2.217(1)	Ni-S(3)	2.216(1)			
Mn-S(1)	2.382(1)	Mn-S(3)	2.391(1)			
S(3A)-Ni-S(3)	180.0	S(1)-Mn-S(3)	77.28(3)			
S(3)-Ni-S(1)	84.47(3)	Ni-S(1)-Mn	93.93(3)			
S(3)-Ni-S(1A)	95.53(3)	Ni-S(3)-Mn	93.72(3)			
S(4)-C(9)-S(3)	124.7(2)	S(2)-C(5)-S(1)	125.2(2)			
(b) Complex <b>3</b> ·3THF						
Ni-S(1)	2.430(2)	Ni-S(2)	2.424(2)			
Ni-S(3)	2.499(2)	Ni-Se(1)	2.556(2)			
Ni-Se(2)	2.568(2)	Ni-Se(3)	2.567(2)			
Fe-Se(1)	2.436(2)	Fe-Se(2)	2.438(2)			
Fe-Se(3)	2.422(2)	Mn-S(1)	2.419(2)			
Mn-S(2)	2.409(2)	Mn-S(3)	2.453(2)			
S(1)-Ni-S(2)	81.18(7)	S(1)-Ni-S(3)	81.67(7)			
S(1)-Ni-Se(1)	175.07(7)	S(1)-Ni-Se(2)	102.91(6)			
S(1)-Ni-Se(3)	98.96(7)	Se(1)-Ni-Se(2)	79.07(5)			
Se(1)-Ni-Se(3)	77.00(5)	Fe-Se(1)-Ni	83.95(5)			
Mn-S(1)-Ni	82.33(7)	Se(1)-Fe-Se(2)	84.01(5)			
S(1)-Mn-S(2)	81.72(8)					

 $\phi = 54^{\circ}$  and s/h = 1.856 (the six-coordinate polyhedron of  $D_3$  symmetry can be defined by the two parameters  $\phi$  and s/h, i.e. the twist angle between two parallel triangular faces of the polyhedron and the ratio of the side of the triangle to the distance between the triangles),<sup>16</sup> and the staggered conformation of two parallel triangular thiolate faces promises the best minimization of interactions between the thiolates. The Ni<sup>II</sup>····Mn<sup>I</sup> distances, average 3.201 Å (Ni<sup>II</sup>····Mn<sup>I</sup>(1) 3.201 Å and Ni<sup>II</sup>····Mn<sup>I</sup>(2) 3.201 Å), is not short enough to suggest a bonding interaction between the two metals. The mean Ni<sup>II</sup>-S bond of length 2.443(1) Å and Ni<sup>II</sup>····Mn<sup>I</sup> distance of 3.201 Å are comparable with the average Ni<sup>II</sup>-S bond length of 2.451(2) Å and the Ni<sup>II</sup>····Mn<sup>I</sup> distance of 3.192 Å in complex **3**, respectively.

In summary, the heterotrimetallic complexes **1**, **2**, **3**, and **4** possessing a homoleptic hexathiolatonickel(II)/ heteroleptic hexachalcogenolatonickel(II) core have been



**Figure 3.** ORTEP drawing and labeling scheme of  $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu-2-S-C_4H_3S)_3Mn(CO)_3]^2$  with thermal ellipsoids drawn at the 30% probability level.

prepared by employing fac-[Fe(CO)<sub>3</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>]<sup>-</sup>/cis-[Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>]<sup>-</sup> serving as a chelating metallo ligand and intermetal ligand transfer reagent under mild conditions. Also, it seems reasonable to state that the anionic [(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -SePh)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> bears a close structural resemblance to [(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mi( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mi( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mi( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>]<sup>2-</sup>, in which the d<sup>6</sup> Mn(I) [(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>]<sup>2-</sup> fragment is isolobal with the d<sup>6</sup> Fe(II) [(ER)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup> fragment of [(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni( $\mu$ -ER)<sub>3</sub>Fe(CO)<sub>3</sub>]<sup>-</sup>.

## **Experimental Section**

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH<sub>2</sub>; acetonitrile from CaH<sub>2</sub>/P<sub>2</sub>O<sub>5</sub>; hexane and tetrahydrofuran (THF) from Na/benzophenone) and stored in dried, N<sub>2</sub>-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use, and transfers to reaction vessels were via stainless-steel cannula under N2 at a positive pressure. The reagents dimanganese decacarbonyl, iron pentacarbonyl, bis(triphenylphosphoranylidene)ammonium chloride, di(2-thienyl) disulfide, diphenyl diselenide, and nickel perchlorate (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-185) with sealed solution cells (0.1 mm) and KBr windows. UV-visible spectra were recorded on a GBC 918 spectrophotometer. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of <sup>1</sup>H and <sup>13</sup>C are relative to tetramethylsilane. Magnetic susceptibilities were carried out in the temperature range 300-5 K on a Quantum Design MPMS-5S SQUID magnetometer. Magnetic data were corrected for diamagnetic contribution. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

**Preparation of** *cis*-**[PPN][Mn(CO)<sub>4</sub>(2-SC<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>].<sup>9</sup>** [PPN]-[Mn(CO)<sub>5</sub>] (0.6 mmol, 0.440 g)<sup>8</sup> dissolved in THF (3 mL) was stirred under N<sub>2</sub>, and di(2-thienyl) disulfide (0.6 mmol, 0.138 g) in THF solution was added to the [PPN][Mn(CO)<sub>5</sub>] solution by cannula under positive N<sub>2</sub> at 10 °C. After stirring of the reaction solution for 5 min, a bright yellow solid precipitated

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Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 4·2CH<sub>3</sub>CN

Ni-S(1)	$\begin{array}{c} 2.427(1) \\ 2.437(1) \\ 2.396(1) \end{array}$	Ni-S(3)	2.466(1)
Ni-S(5)		Mn-S(1)	2.391(1)
Mn-S(3)		Mn-S(5)	2.419(1)
$\begin{array}{l} S(1)-Ni-S(3)\\ S(1)-Ni-S(1a)\\ S(1)-Ni-S(5a)\\ S(1)-Mn-S(5) \end{array}$	100.18(4) 179.9 80.59(3) 81.69(4)	$\begin{array}{l} S(1)-Ni-S(5)\\ S(1)-Ni-S(3a)\\ S(1)-Mn-S(3)\\ Ni-S(1)-Mn \end{array}$	99.41(3) 79.82(4) 81.98(4) 83.29(4)

on addition of hexane (15 mL) at 10 °C. The solid was isolated by removing the solvent. Since the thermally unstable cis-[PPN][Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>] partially transformed into [PPN]-[(CO)<sub>3</sub>Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>] in THF at ambient temperature, diethyl ether was added to separate cis-[PPN][Mn(CO)<sub>4</sub>(2- $S-C_4H_3S_2$  (soluble in diethyl ether) and [PPN][(CO)\_3Mn( $\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>] (insoluble in diethyl ether) characterized by IR (IR ( $\nu_{CO}$ ) (THF): 1994 vs, 1914 s cm<sup>-1</sup>) and X-ray crystallography (the complex crystallized in orthorhombic space group  $Pna2_1$  with a = 29.371(4) Å, b = 10.904(2) Å, c =18.179(3) Å, V = 5821.9(16) Å<sup>3</sup>, F(000) = 2531, Z = 4,  $d_{calc} =$ 1.866 g cm<sup>-3</sup>, final R = 0.039, and  $R_{wF} = 0.040$ ). The yield of product cis-[PPN][Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>] was 0.506 g (90%). IR  $(\nu_{CO})$  (THF): 2055 m, 1980 s, 1958 m, 1917 m cm<sup>-1</sup>. Absorption spectrum (THF) [ $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)]: 266(13638), 274- $(12202), 289(9252), 303(8853), 410(958).^9$ 

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive; only small amounts of material should be prepared and handled with great caution.

of Preparation  $[(CO)_4Mn(\mu-2-S-C_4H_3S)_2Ni(\mu-2-S-$ **C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>Mn(CO)<sub>4</sub>] (1).** The complex *cis*-[PPN][Mn(CO)<sub>4</sub>(2-S- $C_4H_3S)_2]\ (0.4\ mmol,\ 0.375\ g)\ dissolved\ in\ THF\ (5\ mL)\ was$ stirred under N<sub>2</sub>, and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 mmol, 0.073 g) in THF solution was added by cannula under positive pressure of N<sub>2</sub> at 10 °C. After stirring for 5 min, hexane (10 mL) was added, and the dark red solution was filtered to remove [PPN]-[ClO<sub>4</sub>]. The filtrate (in THF + hexane) was dried under vacuum, and diethyl ether was added to separate product  $[(CO)_4Mn(\mu-SC_4H_3S)_2Ni(\mu-SC_4H_3S)_2Mn(CO)_4]$  (1) (diethyl ether soluble) and the  $[(CO)_3Mn(\mu-SC_4H_3S)_3Mn(CO)_3]^-$  (IR  $(\nu_{CO})$ (THF): 1914 s, 1994 vs cm<sup>-1</sup>; diethyl ether insoluble).<sup>10</sup> The yield of dark red complex 1 was 0.111 g (65%). The dark red complex 1, dissolved in diethyl ether solution and stored for 3 weeks at -15 °C, led to formation of dark red crystals of 1 suitable for X-ray crystallography. IR ( $\nu_{\text{CO}}$ ): 2082 m, 2010 s, 2001 sh, 1966 m cm<sup>-1</sup> (THF); 2082 m, 2013 s, 2001 m, 1969 m cm<sup>-1</sup> (diethyl ether). <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O):  $\delta$  7.46 (d), 7.45 (d), 7.26 (d), 7.25 (d), 6.36 (d), 6.34 (d) ppm (SC<sub>4</sub>H<sub>3</sub>S). <sup>13</sup>C NMR (C<sub>4</sub>D<sub>8</sub>O): δ 127.90, 129.37, 135.04 ppm (SC<sub>4</sub>H<sub>3</sub>S). Absorption spectrum (THF)  $[\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1})]$ : 449(6921), 523(4013). Anal. Calcd for C24H12O8Mn2NiS8: C, 33.78; H, 1.42. Found: C, 33.62; H, 1.39. The analogue [(CO)<sub>4</sub>Mn(*u*-SPh)<sub>2</sub>Ni(*u*-SPh)<sub>2</sub>Mn- $(CO)_4$ ] (IR ( $\nu_{CO}$ ) (THF): 2079 m, 2002 vs, 1990 sh, 1960 m cm<sup>-1</sup>) is extremely unstable and decomposes under prolonged vacuum. The IR spectrum revealed that the neutral [(CO)<sub>4</sub>Mn(µ-SPh)<sub>2</sub>Ni(*µ*-SPh)<sub>2</sub>Mn(CO)<sub>4</sub>] converted to the well-known [(CO)<sub>3</sub>- $Mn(\mu$ -SPh)<sub>3</sub> $Mn(CO)_3$ ]<sup>-</sup> (IR ( $\nu_{CO}$ ) (THF): 1907 vs, 1987 s cm<sup>-1</sup>) and insoluble solid.10

Preparation of [PPN][(CO)<sub>3</sub>Mn(µ-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni(µ- $ER_{3}Fe(CO_{3}] (E = S, R = C_{4}H_{3}S (2); E = Se, R = Ph (3)).$ Compound 1 (0.094 g, 0.1 mmol) dissolved in THF (2 mL) was stirred under N<sub>2</sub>, and fac-[PPN][Fe(CO)<sub>3</sub>(SePh)<sub>3</sub>] (0.115 g, 0.1 mmol; or fac-[PPN][Fe(CO)<sub>3</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>], 0.102 g, 0.1 mmol)<sup>5</sup> in THF solution was slowly added to compound 1 solution by cannula under positive  $N_2$  at 10 °C. After stirring of the reaction solution for 30 min, a dark red product [PPN]- $[(CO)_3Mn(\mu-2-S-C_4H_3S)_3Ni(\mu-SePh)_3Fe(CO)_3]$  (3) precipitated on addition of hexane (15 mL) at 10 °C. The product 3 was isolated by removing the solvent and recrystallizing from THF/ hexane (0.145 g, 85%). Complex 3: IR (v<sub>CO</sub>) (THF): 2061 m, 2007 sh, 1998 vs, 1904 s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O):  $\delta$  16.35 (br), 12.84 (br) ppm (SC<sub>4</sub>H<sub>3</sub>S); 14.87 (br), 7.62-6.80 ppm (Ph). Absorption spectrum (THF)  $[\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1})]$ : 674(210). Anal. Calcd for C<sub>72</sub>H<sub>54</sub>NO<sub>6</sub>P<sub>2</sub>S<sub>6</sub>Se<sub>3</sub>NiMnFe: C, 51.18; H, 3.22; N, 0.83. Found: C, 51.35; H, 3.37; N, 1.00. The compound [PPN][(CO)<sub>3</sub>Mn(*µ*-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni(*µ*-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Fe(CO)<sub>3</sub>] (2) (IR  $(\nu_{CO})$  (THF): 2073 m, 2017 sh, 1998 vs, 1906 s cm<sup>-1</sup>) is unstable in THF solution and decomposes over a period of several hours at room temperature. When attempting to isolate complex 2 by drying under vacuum and extracting with THF, we isolated only the decomposition solid.

Preparation of [PPN]<sub>2</sub>[(CO)<sub>3</sub>Mn(µ-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni(µ-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn(CO)<sub>3</sub>] (4). cis-[PPN][Mn(CO)<sub>4</sub>(2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>] (0.094 g, 0.1 mmol) in THF solution was added to compound 2 (0.156 g, 0.1 mmol) in THF solution dropwise under N<sub>2</sub> at room temperature. The reaction solution was stirred for 3 h, and the dark red-brown product [PPN]<sub>2</sub>[(CO)<sub>3</sub>Mn(*µ*-2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Ni- $(\mu$ -2-S-C<sub>4</sub>H<sub>3</sub>S)<sub>3</sub>Mn( $\overline{CO}$ )<sub>3</sub>] (**4**) precipitated. The brown solution was removed under positive N<sub>2</sub>, then complex 4 was washed with THF twice and dried under vacuum (0.123 g, 56%). Diffusion of diethyl ether into a solution of complex 4 in CH<sub>3</sub>-CN at -15 °C for 3 weeks led to dark red-brown crystals suitable for X-ray crystallography. IR ( $\nu_{CO}$ ) (CH<sub>3</sub>CN): 1988 vs, 1892 s cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  15.20 (br), 13.69 (br), -12.24 (br) ppm (SC<sub>4</sub>H<sub>3</sub>S); 7.60-7.04 ppm (Ph). Absorption spectrum  $(CH_3CN)$   $[\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1})]$ : 405(8417), 494(2728). Anal. Calcd for C<sub>106</sub>H<sub>84</sub>N<sub>4</sub>O<sub>6</sub>P<sub>4</sub>S<sub>12</sub>Mn<sub>2</sub>Ni: C, 58.22; H, 3.87; N, 2.56. Found: C, 58.09; H, 3.88; N, 2.66. The compound 4 is unstable in CH<sub>3</sub>CN solution and decomposes overnight at room temperature.

Crystallography. Crystallographic data for complexes 1, 3. and 4 are collected in Tables 1 and 2, and in the Supporting Information. All crystals were chunky: 1, dark red, ca. 0.22  $\times$  0.20  $\times$  0.10 mm; 3, dark red, 0.40  $\times$  0.40  $\times$  0.10 mm; 4, dark red brown,  $0.50 \times 0.50 \times 0.50$  mm. Each was mounted on a glass fiber and quickly coated in epoxy resin. Diffraction measurements for complexes 1 and 3 were carried out at 25 °C on a Siemens SMART CCD diffractometer ( $\lambda$  0.7107 Å) with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  0.7107 Å) with  $\theta$  between 1.94° and 27.48° for complex 1, 1.51° <  $\theta$  < 25.09° for complex 3. A SADABS absorption correction was made. The SHELXTL program was employed. In the structure determination, the positions of Fe and Mn atoms are determined on the basis of the synthetic route, not from the X-ray diffraction data for complex 3. The unit-cell parameters were obtained by the least-square refinement from 25 reflections with  $2\theta$ between 14.68° and 26.84° for 4. Diffraction measurements for complex 4 was carried out at 25 °C on a Nonius CAD 4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  0.7107 Å) employing the  $\theta$ -2 $\theta$  scan mode.<sup>17</sup> A  $\psi$ -scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.<sup>18,19</sup> Selected bond distances and angles are listed in Tables 3 and 4.

Acknowledgment. The support of the National Science Council (Taiwan) is gratefully acknowledged.

Supporting Information Available: An X-ray crystallographic file for the structure determinations of [(CO)<sub>4</sub>Mn- $(\mu - 2 - S - C_4 H_3 S)_2 Ni(\mu - 2 - S - C_4 H_3 S)_2 Mn(CO)_4], [PPN][(CO)_3 Mn(\mu - 2 - Mn(CO)_4)], [PPN][(CO)_3 Mn(\mu - 2 - Mn(CO)_4)]], [PPN][(CO)_3 Mn(\mu - 2 - Mn(CO)_4)]]$  $S-C_4H_3S_3Ni(\mu-SePh)_3Fe(CO)_3]$ , and  $[PPN]_2[(CO)_3Mn(\mu-2-S C_4H_3S_3Ni(\mu-2-S-C_4H_3S_3Mn(CO)_3]$ . This material is available free of charge via the Internet at http://pubs.acs.org.

OM980833M

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