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

Wen-Feng Liaw,*,† Chien-Ming Lee,† Lance Horng,§ Gene-Hsiang Lee,‡ and Shie-Ming Peng‡

Department of Chemistry and Department of Physics, National Changhua University of Education, Changhua 50058, Taiwan, and Department of Chemistry and Instrumentation Center, National Taiwan University, Taipei 10764, Taiwan

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Complex *cis*-$[Mn(CO)_4(2\text{-}S\text{-}C_4H_3S)_2]^-$ was employed as a metallo chelating ligand to synthesize $[(CO)_4Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_2Ni(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_2Mn(CO)_4]$ (**1**) with a square planar Ni^{II}-thiolate core. The longer $Ni^{II}\cdots Mn^{I}$ distances and electronic population of nickel(II) (d^8) are adopted to rationalize the construction of complex **1**. Cleavage of the $Mn^{I}-S$ bond in complex **1** by an incoming tridentate metallo ligand *fac*-$[Fe(CO)_3(ER)_3]^-$ ($E = S$, $R = C_4H_3S$; $E = Se$, $R = Ph$), followed by a thiolate group ($[2\text{-}S\text{-}C_4H_3S]^-$) rearranging to bridge two metals, led directly to the anionic $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}ER)_3Fe(CO)_3]^-$ ($E = S$, $R = C_4H_3S$ (**2**); $E = Se$, $R = Ph$ (**3**)) with a homoleptic/heteroleptic hexachalcogenolatonickel(II) core, respectively. Dropwise addition of *cis*-$[Mn(CO)_4(2\text{-}S\text{-}C_4H_3S)_2]^-$ to the anionic **2** in THF resulted in formation of a linear trinuclear complex $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Mn(CO)_3]^{2-}$ (**4**) possessing a homoleptic hexathiolatonickel(II) core. It seems reasonable to conclude that the d^6 Mn(I) $[(2\text{-}S\text{-}C_4H_3S)_3Mn(CO)_3]^{2-}$ fragment is isolobal with the d^6 Fe(II) $[(ER)_3Fe(CO)_3]^-$ fragment in complexes **4**, **3**, and **2**.

Introduction

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

Recent work in this laboratory showed that *cis*-$[Mn(CO)_4(ER)_2]^-$ and *fac*-$[Fe(CO)_3(SePh)_3]^-$ complexes are useful in the syntheses of heterotrimetallic Mn(I)−Co(III)−Mn(I)-chalcogenolate complexes $[(CO)_4Mn(\mu\text{-}ER)_2Co(CO)(\mu\text{-}E'R)_3Mn(CO)_3]$ ($E = E' = Te$, $R = Ph$; $E = Te$, $E' = Se$, $R = Ph$; $E = E' = Se$, $R = Me$) with a unique Co(III)−CO bond,[4] and $[(CO)_3M(\mu\text{-}SePh)_3M'(\mu\text{-}SePh)_3M(CO)_3]^{-1/0}$ ($M = Mn$, $M' = Co$; $M = Fe$, $M' = Fe$, Cd, Zn, Ni) with a homoleptic hexaselenolatometal core.[3b,5] In these reactions, the complexes *fac*-$[Fe(CO)_3(SePh)_3]^-$ and *cis*-$[Mn(CO)_4(ER)_2]^-$ act as potential "chelating metallo ligands" and selenolate ligand-transfer reagents.[5c,6]

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

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† Department of Chemistry, National Changhua University of Education.

§ Department of Physics, National Changhua University of Education.

‡ National Taiwan University.

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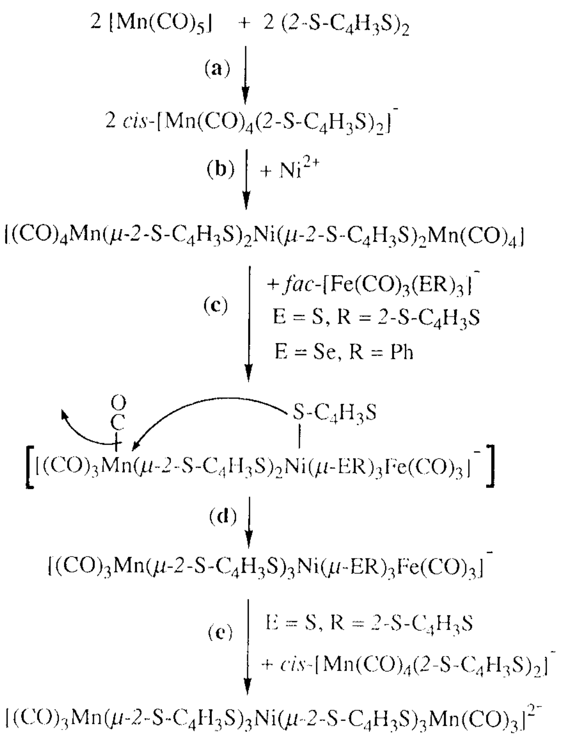
Scheme 1



and CO dehydrogenase,[2] has prompted us to synthesize Ni−Fe-thiolate complexes.[7] Our efforts toward the preparations of Fe^{II}−Ni^{II}-chalcogenolate complexes provide the first example of heterotrimetallic Fe^{II}−Ni^{II}−Mn^{I}-chalcogenolate complexes with a heteroleptic/homoleptic hexachalcogenolatonickel(II) core and Mn^{I}−Ni^{II}−Mn^{I}-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,[8] a rapid reaction ensues over the course of 5 min at ambient temperature to give the yellow *cis*-[PPN][Mn(CO)$_4$(*2*-S-C$_4$H$_3$S)$_2$],[9,10] in 90% isolated yield after removal of [PPN][(CO)$_3$Mn(μ-*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)$_4$(*2*-S-C$_4$H$_3$S)$_2$] and Ni(ClO$_4$)$_2$·6H20 in a 2:1 molar ratio in THF at 10 °C yielded the neutral trinuclear [(CO)$_4$Mn(μ-*2*-S-C$_4$H$_3$S)$_2$Ni(μ-*2*-S-C$_4$H$_3$S)$_2$Mn(CO)$_4$] (**1**) (65% yield) by salt elimination of [PPN][ClO$_4$]. ^{1}H and ^{13}C NMR spectra show the expected signals for the [*2*-S-C$_4$H$_3$S]$^-$ ligands in a diamagneic d^8 Ni^{II} species.

The dark red [PPN][(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-ER)$_3$Fe(CO)$_3$] (E = S, R = C$_4$H$_3$S (**2**); E = Se, R = Ph (**3**)), formed immediately on reaction of complex **1** and *fac*-[Fe(CO)$_3$(ER)$_3$]$^-$ in THF,[5ab,11] was isolated and recrystallized from THF/hexane (85% for **3**) (Scheme 1c,d). The well-known dimer [(CO)$_4$Mn(μ-*2*-S-C$_4$H$_3$S)$_2$Mn(CO)$_4$] was obtained as a byproduct (hexane/THF soluble) during the isolation of complex **3**.[12] IR ν(CO) data (the carbonyl stretching bands 2061 m, 2007 sh cm^{-1} of complex **3**, comparing to ν(CO) (2070 s, 2019 s cm^{-1}) of complex (CO)$_3$Fe(μ-SePh)$_3$Ni^{II}(μ-SePh)$_3$Fe^{II}(CO)$_3$,[5c] were assigned to the Fe^{II}(CO)$_3$ fragment, and the stretching bands 1998 vs, 1904 s cm^{-1}, comparing to the ν(CO) (1994 vs, 1914 s cm^{-1}) in the [(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Mn(CO)$_3$]$^-$, were attributed to the CO stretching bands of the Mn^{I}(CO)$_3$ fragment of complex **3**) suggested its formulation as the PPN$^+$ salt of [(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-SePh)$_3$Fe(CO)$_3$]$^-$ with the central Ni^{II} surrounded by three bridging [S-C$_4$H$_3$S]$^-$ ligands and three bridging [SePh]$^-$ ligands, which was also confirmed by X-ray crystallography. A reasonable reaction sequence accounting for the formation of heterotrinuclear [(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-ER)$_3$Fe(CO)$_3$]$^-$ is shown in Scheme 1c,d. Cleavage of the Mn^{I}−S bond in complex **1** by an incoming tridentate metallo ligand *fac*-[Fe(CO)$_3$(ER)$_3$]$^-$ led to the presumed intermediate [(CO)$_4$Mn(μ-*2*-S-C$_4$H$_3$S)$_2$Ni(*2*-S-C$_4$H$_3$S)(μ-ER)$_3$Fe(CO)$_3$]$^-$, and subsequent rearrangement of the terminal thiolate ligand [*2*-S-C$_4$H$_3$S]$^-$ to bridge two metals (Mn^{I} and Ni^{II}) accompanied by dissociation of a labile carbonyl from Mn^{I} yielded the anionic [(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-ER)$_3$Fe(CO)$_3$]$^-$. These results established that the same stoichiometric quantities of [(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-ER)$_3$Fe(CO)$_3$]$^-$ are formed concurrently with [(CO)$_4$Mn(μ-*2*-S-C$_4$H$_3$S)$_2$Mn(CO)$_4$] 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)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-SePh)$_3$Fe(CO)$_3$]$^-$ 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$_4$H$_3$S)$_2$]$^-$ in THF for 3 h at 22 °C, a dark red-brown solid precipitated, Scheme le. Extracted into CH$_3$CN, and obtained in crystalline form by diethyl ether diffusion into CH$_3$CN solution (56% yield), this compound was analyzed as [PPN]$_2$[(CO)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Ni(μ-*2*-S-C$_4$H$_3$S)$_3$Mn(CO)$_3$] (**4**). The IR ν(CO) bands (1988 vs, 1892 s cm^{-1} (CH$_3$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)$_3$Mn(μ-*2*-S-C$_4$H$_3$S)$_3$Mn(CO)$_3$] (ν(CO) (THF): 1994 vs, 1914 s cm^{-1}). Complex **4** exhibits a diagnostic ^{1}H NMR spectrum with the 2-thienyl proton resonances well removed from the diamagnetic region. The protons resonate downfield, δ 15.20 (br), 13.69 (br) and upfield −12.24 (br) ppm, which is consistent with the central Ni^{II} having a d^8 electronic configuration in an octahedral ligand field. The effective magnetic moment in solid state by SQUID magnetometer was 3.95 and 3.93 μ_B for complexes **3** and **4**, respectively. These values are higher than the spin-only value of 2.83 μ_B, which are attributed to the orbital angular momentum. A plot of χ 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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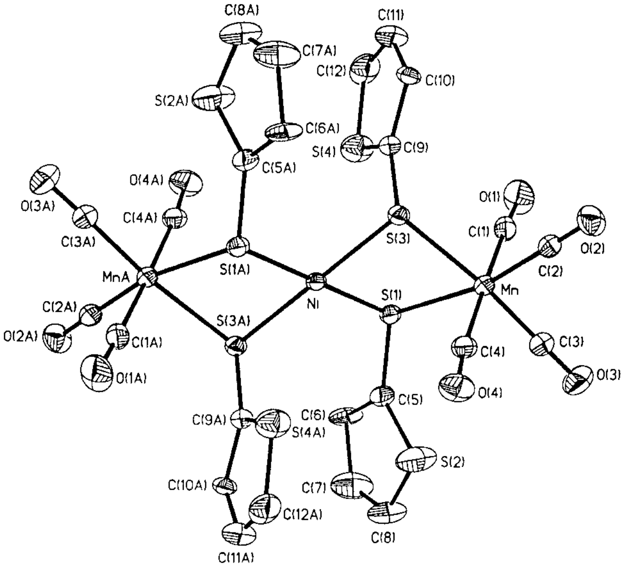

Figure 1. ORTEP drawing and labeling scheme of $[(CO)_4Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_2Ni(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_2Mn(CO)_4]$ with thermal ellipsoids drawn at the 30% probability level.

Further examination shows that there is no significant $Ni^{II}\cdots Mn^{I}$ bonding ($Ni^{II}\cdots Mn^{I}$(A) 3.364 Å and $Ni^{II}\cdots Mn^{I}$-(B) 3.364 Å), and the four-membered NiS_2Mn rings are decidedly bent with a dihedral angle between MnS_2 and NiS_2 planes of 32.74°. In comparison, the heterotrinuclear complex $[\{Cp_2Nb(\mu\text{-}SMe)_2\}_2Ni]^{2+}$ has the Ni^0 atom in an approximately tetrahedral arrangement of the bridging thiolates and Ni^0-Nb^{IV} metal–metal bonds.[13] The dependence of geometry on electron population (d^8 Ni^{II}) and the longer $Ni^{II}\cdots Mn^{I}$ distances are adopted to rationalize the construction of complex **1** with a square planar Ni^{II}-thiolate core. The average $Ni^{II}-S$ bond of length 2.217(8) Å is shorter than the terminal $Ni^{II}-S$ distances in distorted tetrahedral $[Ni(SPh)_4]^{2-}$ (average 2.281(1) Å).[14] 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^{II} atom lies in a slightly distorted octahedral environment of selenium and sulfur atoms (NiS_3Se_3 core) provided by two facially coordinating tridentate $[(PhSe)_3Fe^{II}(CO)_3]$ and $[(2\text{-}S\text{-}C_4H_3S)_3Mn^{I}(CO)_3]$ fragments. The average $Ni^{II}-S$ bond of length 2.451(2) Å is significantly longer than that of complex **1** (average 2.217(8) Å). The $Ni^{II}-Se$ bond lengths range from 2.556(2) to 2.568(2) Å (average = 2.564(2) Å). These are longer than the $Ni^{II}-Se$ distances reported in tetrahedral $[Ni(SePh)_4]^{2-}$ ($Ni-Se_{av}$ = 2.401(3) Å)[15] and distorted square planar $[Ni(CO)(SePh)_3]^-$ ($Ni-Se_{av}$ = 2.317(2) Å).[7] The $Ni^{II}\cdots Fe^{II}$ distance, 3.340 Å, and $Ni^{II}\cdots Mn^{I}$ distance, 3.192 Å, exclude any direct metal–metal interactions. It is noteworthy that $Ni^{II}-S$, $Ni^{II}-Se$, $Ni^{II}\cdots Mn^{I}$, and $Ni^{II}\cdots Fe^{II}$ distances of 2.451(2), 2.564(2), 3.192, and 3.340 Å,[5c] respectively, also support the formation of complex **3** as a heterotrinuclear $Fe^{II}-Ni^{II}-Mn^{I}$-mixed-chalcogenolate complex, consistent with the conclusion in IR ν(CO) data.

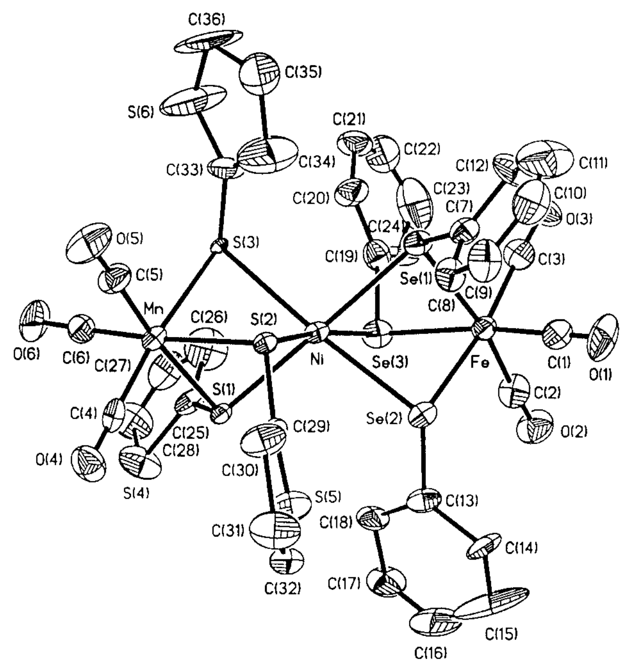

Figure 2. ORTEP drawing and labeling scheme of $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}SePh)_3Fe(CO)_3]^-$ with thermal ellipsoids drawn at the 30% probability level.

Table 1. Crystallographic Data of Complexes (a) 1 and (b) 3·3THF

	1	3·3THF
chem formula	$C_{24}H_{12}O_8Mn_2NiS_8$	$C_{84}H_{78}O_9P_2FeMnNiS_6NSe_3$
fw	853.41	1906.15
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pca2_1$
λ, Å (Mo Kα)	0.7107	0.7107
a, Å	8.4017(1)	24.8147(4)
b, Å	9.2691(1)	12.9101(2)
c, Å	11.3735(1)	27.0074(5)
α, deg	68.345(1)	90
β, deg	79.851(1)	90
γ, deg	78.049(1)	90
V, Å^3	800.51(2)	8652.1(3)
Z	1	4
ρ_{calcd}, g cm^{-3}	1.770	1.463
μ, cm^{-1}	19.25	20.23
F(000)	426	3872
no. of measd reflcns	10 563	50 752
no. of obsd reflcns	3663	15 397
no. of refined params	197	905
T, °C	22	22
R [$I > 2\sigma(I)$]	0.0435[a]	0.0727[a]
R_{wF^2}	0.1320[b]	0.1822[b]

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$, [b] $R_{wF^2} = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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^{II} 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_6 core has

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Table 2. Crystallographic Data of Complex 4·2CH$_3$CN

chem formula	$C_{106}H_{84}N_4O_6P_4Mn_2NiS_{12}$
fw	2187.03
cryst syst	triclinic
space group	$P\bar{1}$
λ, Å (Mo Kα)	0.7107
a, Å	12.575(3)
b, Å	14.176(4)
c, Å	16.156(3)
α, deg	70.37(2)
β, deg	85.54(2)
γ, deg	76.92(2)
V, Å^3	2642.2(11)
Z	1
ρ_{calcd}, g cm^{-3}	1.375
μ, cm^{-1}	7.428
$F(000)$	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
$R_w{}^b$	0.041

[a] $R = \sum|(F_o - F_c)|/\sum F_o$. [b] $R = [\sum(w(F_o - F_c)^2/wF_o{}^2]^{1/2}$.

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 **3**·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)		

$\phi = 54°$ and $s/h = 1.856$ (the six-coordinate polyhedron of D_3 symmetry can be defined by the two parameters ϕ 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),[16] and the staggered conformation of two parallel triangular thiolate faces promises the best minimization of interactions between the thiolates. The $Ni^{II}\cdots Mn^{I}$ distances, average 3.201 Å ($Ni^{II}\cdots Mn^{I}(1)$ 3.201 Å and $Ni^{II}\cdots Mn^{I}(2)$ 3.201 Å), is not short enough to suggest a bonding interaction between the two metals. The mean $Ni^{II}-S$ bond of length 2.443(1) Å and $Ni^{II}\cdots Mn^{I}$ distance of 3.201 Å are comparable with the average $Ni^{II}-S$ bond length of 2.451(2) Å and the $Ni^{II}\cdots Mn^{I}$ 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 prepared by employing *fac*-$[Fe(CO)_3(2\text{-}S\text{-}C_4H_3S)_3]^-$/*cis*-$[Mn(CO)_4(2\text{-}S\text{-}C_4H_3S)_2]^-$ serving as a chelating metallo ligand and intermetal ligand transfer reagent under mild conditions. Also, it seems reasonable to state that the anionic $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}SePh)_3Fe(CO)_3]^-$ bears a close structural resemblance to $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Mn(CO)_3]^{2-}$, in which the d^6 Mn(I) $[(2\text{-}S\text{-}C_4H_3S)_3Mn(CO)_3]^{2-}$ fragment is isolobal with the d^6 Fe(II) $[(ER)_3Fe(CO)_3]^-$ fragment of $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}ER)_3Fe(CO)_3]^-$.

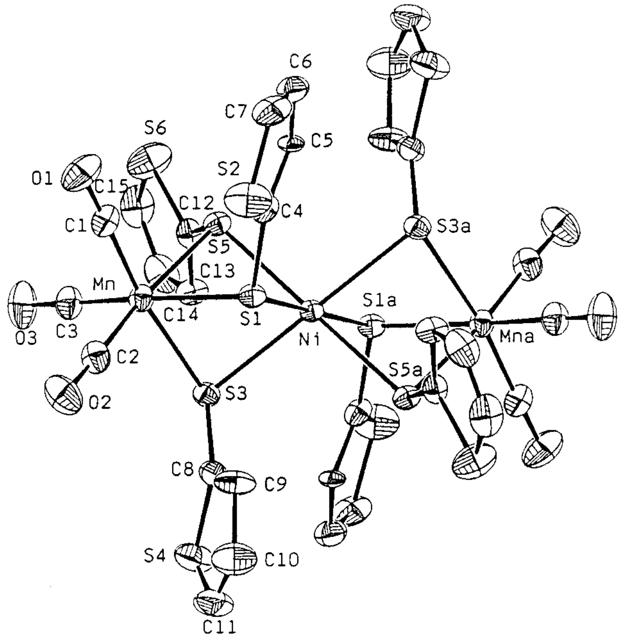

Figure 3. ORTEP drawing and labeling scheme of $[(CO)_3Mn(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Ni(\mu\text{-}2\text{-}S\text{-}C_4H_3S)_3Mn(CO)_3]^{2-}$ with thermal ellipsoids drawn at the 30% probability level.

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_2; acetonitrile from CaH_2/P_2O_5; hexane and tetrahydrofuran (THF) from Na/benzophenone) and stored in dried, N_2-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 N_2 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 ^1H and ^{13}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)$_4$(*2*-SC$_4$H$_3$S)$_2$].[9] [PPN][Mn(CO)$_5$] (0.6 mmol, 0.440 g)[8] dissolved in THF (3 mL) was stirred under N_2, and di(2-thienyl) disulfide (0.6 mmol, 0.138 g) in THF solution was added to the [PPN][Mn(CO)$_5$] solution by cannula under positive N_2 at 10 °C. After stirring of the reaction solution for 5 min, a bright yellow solid precipitated

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[16] (a) Stiefel, E. I.; Brown, G. F. *Inorg. Chem.* **1972**, *11*, 434. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (c) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295. (d) Keppert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 4·2CH_3CN

Ni–S(1)	2.427(1)	Ni–S(3)	2.466(1)
Ni–S(5)	2.437(1)	Mn–S(1)	2.391(1)
Mn–S(3)	2.396(1)	Mn–S(5)	2.419(1)
S(1)–Ni–S(3)	100.18(4)	S(1)–Ni–S(5)	99.41(3)
S(1)–Ni–S(1a)	179.9	S(1)–Ni–S(3a)	79.82(4)
S(1)–Ni–S(5a)	80.59(3)	S(1)–Mn–S(3)	81.98(4)
S(1)–Mn–S(5)	81.69(4)	Ni–S(1)–Mn	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][$Mn(CO)_4$(*2*-S-$C_4H_3S)_2$] partially transformed into [PPN][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Mn(CO)_3$] in THF at ambient temperature, diethyl ether was added to separate *cis*-[PPN][$Mn(CO)_4$(*2*-S-$C_4H_3S)_2$] (soluble in diethyl ether) and [PPN][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Mn(CO)_3$] (insoluble in diethyl ether) characterized by IR (IR (ν_{CO}) (THF): 1994 vs, 1914 s cm^{-1}) 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^3, $F(000) = 2531$, $Z = 4$, $d_{calc} = 1.866$ g cm^{-3}, final $R = 0.039$, and $R_{wF} = 0.040$). The yield of product *cis*-[PPN][$Mn(CO)_4$(*2*-S-$C_4H_3S)_2$] was 0.506 g (90%). IR (ν_{CO}) (THF): 2055 m, 1980 s, 1958 m, 1917 m cm^{-1}. Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 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.

Preparation of [$(CO)_4Mn$(*μ*-2-S-$C_4H_3S)_2Ni$(*μ*-2-S-$C_4H_3S)_2Mn(CO)_4$] (1). The complex *cis*-[PPN][$Mn(CO)_4$(*2*-S-$C_4H_3S)_2$] (0.4 mmol, 0.375 g) dissolved in THF (5 mL) was stirred under N_2, and $Ni(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 0.073 g) in THF solution was added by cannula under positive pressure of N_2 at 10 °C. After stirring for 5 min, hexane (10 mL) was added, and the dark red solution was filtered to remove [PPN][ClO_4]. The filtrate (in THF + hexane) was dried under vacuum, and diethyl ether was added to separate product [$(CO)_4Mn$(*μ*-$SC_4H_3S)_2Ni$(*μ*-$SC_4H_3S)_2Mn(CO)_4$] (**1**) (diethyl ether soluble) and the [$(CO)_3Mn$(*μ*-$SC_4H_3S)_3Mn(CO)_3$]$^-$ (IR (ν_{CO}) (THF): 1914 s, 1994 vs cm^{-1}; diethyl ether insoluble).[10] 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 (ν_{CO}): 2082 m, 2010 s, 2001 sh, 1966 m cm^{-1} (THF); 2082 m, 2013 s, 2001 m, 1969 m cm^{-1} (diethyl ether). ^1H NMR (C_4D_8O): δ 7.46 (d), 7.45 (d), 7.26 (d), 7.25 (d), 6.36 (d), 6.34 (d) ppm (SC_4H_3S). ^{13}C NMR (C_4D_8O): δ 127.90, 129.37, 135.04 ppm (SC_4H_3S). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 449(6921), 523(4013). Anal. Calcd for $C_{24}H_{12}O_8Mn_2NiS_8$: C, 33.78; H, 1.42. Found: C, 33.62; H, 1.39. The analogue [$(CO)_4Mn$(*μ*-SPh)$_2$Ni(*μ*-SPh)$_2$Mn($CO)_4$] (IR (ν_{CO}) (THF): 2079 m, 2002 vs, 1990 sh, 1960 m cm^{-1}) is extremely unstable and decomposes under prolonged vacuum. The IR spectrum revealed that the neutral [$(CO)_4Mn$(*μ*-SPh)$_2$Ni(*μ*-SPh)$_2$Mn($CO)_4$] converted to the well-known [$(CO)_3Mn$(*μ*-SPh)$_3$Mn($CO)_3$]$^-$ (IR (ν_{CO}) (THF): 1907 vs, 1987 s cm^{-1}) and insoluble solid.[10]

Preparation of [PPN][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ*-ER)$_3$Fe($CO)_3$] (E = S, R = C_4H_3S (2); E = Se, R = Ph (3)). Compound **1** (0.094 g, 0.1 mmol) dissolved in THF (2 mL) was stirred under N_2, and *fac*-[PPN][$Fe(CO)_3(SePh)_3$] (0.115 g, 0.1 mmol; or *fac*-[PPN][$Fe(CO)_3$(2-S-$C_4H_3S)_3$], 0.102 g, 0.1 mmol)[5] 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][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ*-SePh)$_3$Fe($CO)_3$] (**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 (ν_{CO}) (THF): 2061 m, 2007 sh, 1998 vs, 1904 s cm^{-1}. ^1H NMR (C_4D_8O): δ 16.35 (br), 12.84 (br) ppm (SC_4H_3S); 14.87 (br), 7.62−6.80 ppm (Ph). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 674(210). Anal. Calcd for $C_{72}H_{54}NO_6P_2S_6Se_3NiMnFe$: C, 51.18; H, 3.22; N, 0.83. Found: C, 51.35; H, 3.37; N, 1.00. The compound [PPN][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ-2*-S-$C_4H_3S)_3Fe(CO)_3$] (**2**) (IR (ν_{CO}) (THF): 2073 m, 2017 sh, 1998 vs, 1906 s cm^{-1}) 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]$_2$[$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ-2*-S-$C_4H_3S)_3Mn(CO)_3$] (4). *cis*-[PPN][$Mn(CO)_4$(*2*-S-$C_4H_3S)_2$] (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_2 at room temperature. The reaction solution was stirred for 3 h, and the dark red-brown product [PPN]$_2$[$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ-2*-S-$C_4H_3S)_3Mn(CO)_3$] (**4**) precipitated. The brown solution was removed under positive N_2, 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_3CN at −15 °C for 3 weeks led to dark red-brown crystals suitable for X-ray crystallography. IR (ν_{CO}) (CH_3CN): 1988 vs, 1892 s cm^{-1}. ^1H NMR (CD_3CN): δ 15.20 (br), 13.69 (br), −12.24 (br) ppm (SC_4H_3S); 7.60−7.04 ppm (Ph). Absorption spectrum (CH_3CN) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 405(8417), 494(2728). Anal. Calcd for $C_{106}H_{84}N_4O_6P_4S_{12}Mn_2Ni$: 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_3CN 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 × 0.20 × 0.10 mm; **3**, dark red, 0.40 × 0.40 × 0.10 mm; **4**, dark red brown, 0.50 × 0.50 × 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 (λ 0.7107 Å) with graphite-monochromated Mo Kα radiation (λ 0.7107 Å) with θ 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 2θ 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 Kα radiation (λ 0.7107 Å) employing the $\theta-2\theta$ scan mode.[17] A ψ-scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[18,19] Selected bond distances and angles are listed in Tables 3 and 4.

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Supporting Information Available: An X-ray crystallographic file for the structure determinations of [$(CO)_4Mn$(*μ-2*-S-$C_4H_3S)_2Ni$(*μ-2*-S-$C_4H_3S)_2Mn(CO)_4$], [PPN][$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ*-SePh)$_3$Fe($CO)_3$], and [PPN]$_2$[$(CO)_3Mn$(*μ-2*-S-$C_4H_3S)_3Ni$(*μ-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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