

Control of S-Based Aggregation: Designed Synthesis of NiM₂ and Ni₂M Trinuclear Complexes

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Modification of the nickel dithiolate metalloligand, Ni(bme-daco) [where bme-daco = bis(mercaptoethyl)-diazacyclooctane] or **Ni-1**, by oxygenation of one thiolate into a sulfinato, Ni(mese-daco) [where mese-daco = (mercaptoethyl)(sulfinatoethyl)diazacyclooctane] or **Ni-2**, restricts the ligating ability to monodentate and is expected to reduce the donor ability of the remaining thiolate S. Nevertheless, the **Ni-2** complex forms a stable thiolate S-bound adduct of W⁰(CO)₅, (**Ni-2**)W(CO)₅, a complex whose $\nu(\text{CO})$ IR spectrum reports insignificant differences in the donor abilities of **Ni-1** and **Ni-2** in $(\eta^1\text{-Ni}_2\text{S}_2)\text{W}(\text{CO})_5$ complexes. In the presence of the strong sulfophile Cu^I, a CuNi₂ trimetallic, (**Ni-2**)₂CuBr, was isolated. Another trimetallic, $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$, demonstrated the Ni(bme-daco), **Ni-1**, unit to bridge low-valent metals in a transoid configuration, yielding W–W distances of over 5 Å.

Introduction

S-based aggregation in transition-metal thiolate complexes has been well documented in the chemical literature.¹ Recent accounts have described the syntheses of a myriad of polymetallic complexes based on NiN₂S₂ units as building blocks in a variety of molecular constructions.^{2–6} Some of these were designed as biomimics of the acetyl-coA synthase (ACS) active site containing a tripeptide N₂S₂^{4–} square-planar binding site for Ni^{II}, which S-bridges in bidentate fashion to a second catalytic Ni of variable oxidation state. A further cysteinyl thiolate S bridge connects this unit into a 4Fe4S cluster.^{7–10} At the chemist's bench, simple bimetallic com-

plexes of NiN₂S₂ metalloligands are obtained only in the cases of steric blocks on the second metal or in the presence of metals with a low affinity for S.^{11–14}

Our work with the metallodithiolate ligand (bis(mercaptoethyl)diazacyclooctane)nickel, Ni(bme-daco) or **Ni-1**,¹⁵ has attempted to establish its overall characteristics as an innocent mono- or bidentate ligand.^{3,13} Some of its structural versatility is shown in Figure 1. Complexes a and b are aggregates of Cu^I, a potent sulfophile, which in the case of the hexametalllic Ni₂Cu₄S₄ species connects two NiN₂S₂ units to four Cu^I, producing the overall topology of adamantane. In complex b, two Cu^I are bridged by three NiN₂S₂ moieties, producing a C₃ paddlewheel-type structure. Structure c of Figure 1 demonstrates the ability of NiN₂S₂ as a bidentate ligand to bind to a single metal, in this case W⁰(CO)₄. Under mild conditions, one thiolate S was replaced by CO, producing a very stable monodentate $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ adduct. To be described below is an extension of this adduct in which a

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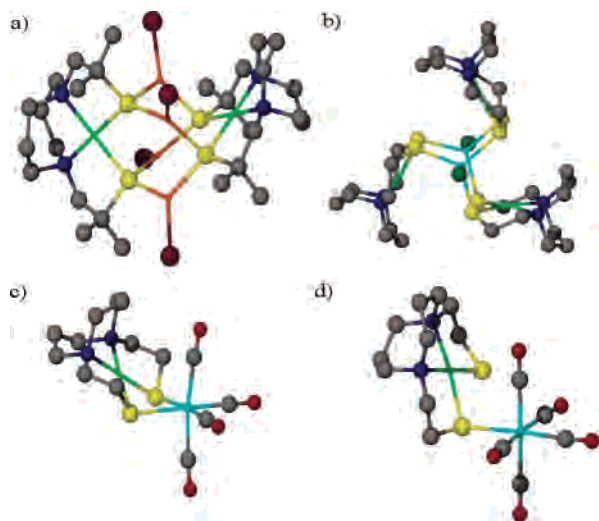
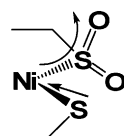


Figure 1. Ball-and-stick representation of the molecular structures of (a) $(\text{Ni-1}^*)_2(\text{CuCl})_4$,¹⁹ (b) $(\text{Ni-1})_3(\text{CuBr})_2$,²⁰ (c) $(\text{Ni-1})\text{W}(\text{CO})_4$,¹³ and (d) $(\text{Ni-1})\text{W}(\text{CO})_5$.¹³

second $[\text{W}^0(\text{CO})_5]$ moiety is added to the empty thiolate, producing a NiW_2 trimetallic cluster, $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$.

flow of electron density



The S-oxygenated compound ((mercaptoethyl)(sulfinatoethyl)diazacyclooctane)nickel, Ni(mese-daco) or **Ni-2**, has a Ni^{II} reduction potential some 300 mV more positive than its dithiolate parent.^{16,17} This reduced electron density at Ni results in diminished nucleophilicity of the thiolate S. Kinetic studies of alkylation of the unmodified thiolate S by MeI show that the nucleophilic reactivity is reduced by an order of magnitude in comparison to the **Ni-1** dithiolate.¹⁸ Thus, a priori one expects that the formation of aggregates via thiolate interaction with exogenous metals would be limited for **Ni-2**. Nevertheless, herein we report that a **Ni-2** complex of $\text{W}(\text{CO})_5$ has been isolated and its donor ability compared to that of the analogous $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ adduct. In the presence of $\text{Cu}^{\text{I}}\text{Br}$, two **Ni-2** complexes assemble into $(\text{Ni-2})_2\text{CuBr}$. These new trimetallic complexes, CuNi_2 and NiW_2 , are characterized and described.

Experimental Section

Methods and Materials. Unless specifically stated, all syntheses and manipulations were performed using standard Schlenk-line and syringe/rubber septa techniques under N_2 or in an Ar atmosphere glovebox. Solvents were reagent grade, purified according to published procedures, and freshly distilled under N_2 prior to use.²¹

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Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Delta, British Columbia, Canada. IR spectra were recorded on a Matteson Galaxy series 6021 Fourier transform IR (FTIR) spectrometer or a Bruker Tensor 27 spectrometer in CaF_2 solution cells of 0.1-mm path length. Solid-state IR spectra for $(\text{Ni-1})\text{W}(\text{CO})_5$ and $(\text{Ni-2})\text{W}(\text{CO})_5$ were taken using attenuated reflectance FTIR spectroscopy carried out on a Bruker Tensor 27 spectrometer fitted with a Pike MIRacle attachment from Pike Technology. Photolysis experiments were performed using a 450-W UV mercury arc vapor immersion lamp purchased from the Ace Glass Co.

The **Ni-1**,¹⁵ $(\text{Ni-1})\text{W}(\text{CO})_5$,¹³ and **Ni-2**¹⁶ complexes were synthesized according to previously published procedures. Anhydrous dimethylformamide (DMF; 99.9%) was purchased from Acros Chemical Co. and used as received.

X-ray Structure Analysis. Low-temperature (110 K) X-ray diffraction data were collected on a Bruker SMART 1000 CCD-based diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) for the $(\text{Ni-2})_2\text{CuBr}$ complex.²² For the $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ and $(\text{Ni-2})\text{W}(\text{CO})_5$ complexes, data were obtained on a Bruker D8 GADDS general-purpose three-circle X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$), also operating at 110 K.

The structures were solved by direct methods. H atoms were added at idealized positions and refined with fixed isotropic displacement parameters equal to 1.2 times the isotropic displacement parameters of the atoms to which they were attached. Anisotropic displacement parameters were determined for all non-H atoms. Programs used were as follows: data collection and cell refinement, *SHELXTL*;²³ absorption correction, *SADABS*; structure solution, *SHELXS-97* (Sheldrick);²⁴ structure refinement, *SHELXL-97* (Sheldrick),²⁵ and molecular graphics and preparation of material for publication, *SHELXTL-PLUS*, version 5.1 or later (Bruker). X-seed was employed for the final data presentation and structure plots.²⁶ The crystallographic data for all compounds are given in Table 1.

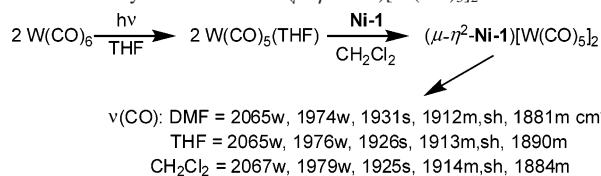
Preparation of $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$. To a Schlenk flask containing 20 mL of tetrahydrofuran (THF) was added $\text{W}(\text{CO})_6$ (0.241 g, 0.68 mmol). This clear solution was transferred to a water-cooled Pyrex photolysis cell and photolyzed using a Hg lamp for approximately 1 h. The IR spectrum of the resulting yellow solution showed bands as follows: $\nu(\text{CO})$ 2075w, 1975s, 1930m, 1892w cm^{-1} . This solution was transferred via cannula to a Schlenk flask containing a purple solution of **Ni-1** (0.100 g, 0.343 mmol) in 10 mL of CH_2Cl_2 . The solution turned dark red-brown upon mixing and was further vigorously stirred for 1 day at ambient temperature. Following in vacuo reduction of the volume to half, hexanes were added to precipitate a dark red-brown solid. The supernatant solution was decanted, and the residue was washed with hexanes ($3 \times 15 \text{ mL}$). Crystals were obtained by dissolving the solid in CH_2Cl_2 and layering with hexanes. Large, dark reddish-brown crystals formed in approximately 1 week. Yield: 0.184 g (57.3%). It should be

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Table 1. Crystallographic Experimental Data for the Complexes

	$(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$	$(\text{Ni-2})_2\text{CuBr}$	$(\text{Ni-2})\text{W}(\text{CO})_5$
formula	$\text{C}_{20}\text{H}_{20}\text{N}_2\text{NiO}_{10}\text{S}_2\text{W}_2$	$\text{C}_{20}\text{H}_{40}\text{BrCuN}_4\text{Ni}_2\text{O}_4\text{S}_4$	$\text{C}_{15}\text{H}_{20}\text{N}_2\text{NiO}_7\text{S}_2\text{W}$
fw	937.89	789.72	647.01
T (K)	110(2)	110(2)	110(2)
wavelength (\AA)	1.541 78	0.710 73	0.710 73
Z	1	8	4
D_{calcd} (Mg/cm^3)	2.366	1.916	2.108
μ (mm^{-1})	18.591	3.932	6.804
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/m$
unit cell			
a (\AA)	10.4829(7)	8.467(5)	7.4188(13)
b (\AA)	10.5887(7)	11.600(7)	13.712(2)
c (\AA)	13.7992(8)	27.870(16)	20.111(4)
α (deg)	106.304(5)	90	90
β (deg)	96.606(4)	90	94.620(3)
γ (deg)	112.242(4)	90	90
V (\AA^3)	1317.83(15)	2737(3)	2039.2(6)
GOF	1.079	1.019	1.047
$R1,^a$ $wR2^b$ (%) [$I > 2\sigma(I)$]	0.0376, 0.0849	0.1353, 0.1682	0.0496, 0.1192
$R1,^a$ $wR2^b$ (%) (all data)	0.0562, 0.0942	0.077, 0.1451	0.616, 0.1192

$$^a R1 = \sum ||F_o| - |F_c|| / \sum F_o, \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Scheme 1. Synthetic Route to $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ 

noted that the crystals used for the X-ray diffraction analysis originated from stability studies of $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ in the presence of PPh_3 at 60 °C in a DMF solvent. IR ($\nu(\text{CO})$, cm^{-1}): values given in Scheme 1. UV-vis (nm, CH_2Cl_2): 247vs, 290sh, 380m, 440vw, 550vw. UV-vis (nm, THF): 246vs, 297w, 380m, 550w. UV-vis (nm, DMF): 267vs, 326m, 380m, 431vw, 546vw. Elem. anal. Calcd (found) for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_{10}\text{NiW}_2$: C, 25.1 (25.6); H, 1.97 (2.15); N, 2.94 (2.98).

Preparation of $(\eta^1\text{-Ni-2})\text{W}(\text{CO})_5$. A solution of $\text{W}(\text{CO})_6$ (0.543 g, 1.54 mmol in 15 mL of THF) was transferred via cannula to a Schlenk flask containing an orange solution of **Ni-2** (0.050 g, 0.154 mmol) in 15 mL of MeCN. The solution was stirred for 24 h at 22 °C. During this time, IR monitoring showed no change in the reactants. The flask was then placed in direct sunlight for 6 days, resulting in the formation of dark-red crystals on the side of the flask. The solution was filtered, and the crystals were washed with hexanes, THF, and methanol. Yield: 0.023 g (23.2%). Elem. anal. Calcd (found) for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_7\text{NiW}$: C, 27.9 (27.8); H, 3.12 (3.17); N, 4.34 (4.39). MS (ESI): m/z 645–651 isotopic bundle ($\text{C}_{15}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_7\text{NiW}$). An alternate route, using photolysis as described above to produce $(\text{THF})\text{W}(\text{CO})_5$, followed by the addition of a CH_3CN solution of **Ni-2**, produced a powdered form of the highly insoluble $(\text{Ni-2})\text{W}(\text{CO})_5$.

Preparation of $(\text{Ni-2})_2\text{CuBr}$. An orange-brown solution of **Ni-2** (0.032 g, 0.099 mmol in 20 mL CH_3CN) was transferred via cannula over a period of 15 min to a flask containing a colorless solution of CuBr (0.005 g, 0.035 mmol) dissolved in 20 mL of MeCN. The resulting orange solution was stirred for 3 h at room temperature. The solution was concentrated in vacuo prior to the addition of 10 mL of hexanes and 50 mL of Et_2O , yielding a red-orange solid, which was isolated and washed with Et_2O . Diffraction-quality red crystals formed over several days from a MeOH solution layered with Et_2O . Yield: 0.048 g (86%). Elem. anal. Calcd (found) for $\text{C}_{20}\text{H}_{40}\text{N}_4\text{S}_4\text{O}_4\text{Ni}_2\text{CuBr}$: C, 30.4 (30.6); H, 5.11 (5.24); N, 7.10 (6.91).

Results and Discussion

Synthesis and $\nu(\text{CO})$ IR Spectral Analysis. The preparation of $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$, rather than $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$, is controlled by stoichiometry (Scheme 1). Its molecular structure, to be described below, finds each $\text{W}(\text{CO})_5$ unit in C_{4v} local symmetry (i.e., neglecting the asymmetry in the nickel thiolate ligand) as found in the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex.¹³ The solution-phase $\nu(\text{CO})$ IR spectrum of the trimetallic $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ revealed a five-band pattern, as shown in Figure 2a. In comparison, the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex has a four-band $\nu(\text{CO})$ IR spectrum typical of C_{4v} $\text{LW}(\text{CO})_5$ (Figure 2b). The average positions of the $\nu(\text{CO})$ bands of the $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ complex are from 3 to 10 cm^{-1} higher than those of the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex (see Figure 2b). This result indicates a decrease in the donor ability of the **Ni-1** complex when both thiolates are engaged in bonding to electron-withdrawing $\text{W}(\text{CO})_5$ groups. It also indicates that $\text{W}(\text{CO})_5$ dissociation to produce mixtures of $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ and $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ is not occurring. In fact, deliberate attempts to produce the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex from $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ by the addition of excess **Ni-1** to solutions of $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ held at 60 °C in DMF solvent resulted in no reaction over periods as long as 24 h.

The $\nu(\text{CO})$ IR spectra of the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ and $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ complexes were recorded in three solvents, DMF, CH_2Cl_2 , and THF (Figure 2). Notably, the four-band pattern of the pseudo- C_{4v} NiW bimetallic is largely unchanged with the solvent; the most intense E band precisely retains its position and shape. Minor shifts in the A_1 bands occur; however, the pattern is maintained with solvent changes. Greater solvent dependencies are observed for the NiW₂ trimetallic complex. The intense E band is broad and less symmetric than that in $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ and clearly splits into two bands in THF and DMF. The breadth and shape of the highest-energy A_1^1 band are also solvent-dependent, as is the position of the low-frequency A_1^2 band.

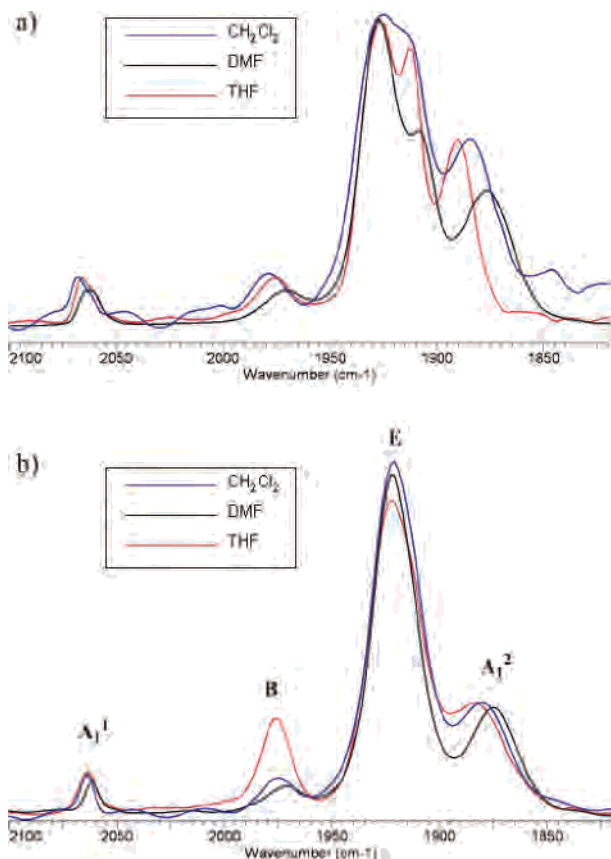


Figure 2. Overlaid $\nu(\text{CO})$ IR spectra of (a) $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ and (b) $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$.

Spectra identical with those displayed in Figure 2a were obtained on a second, highly pure sample in which solvents were stripped off and the same sample was redissolved in each solvent successively in the order CH_2Cl_2 , DMF, and THF. From this experiment, it is concluded that the pattern changes or shifts are a true solvent effect rather than a result of sample degradation.

The nature of the solvent effect on $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ and the differences between the IR spectra of $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ and $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ are not easily rationalized. It is known that complexes with two $\text{W}(\text{CO})_5$ groups bound to diphosphines or hydrocarbon-bridged dithiolates as bidentate bridging ligands produce $\nu(\text{CO})$ patterns consistent with analogous monometallic $\text{LW}(\text{CO})_5$ complexes and the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex shown in Figure 2.^{27,28} On the other hand, the coupling of CO vibrational levels across the hydride bridge in $(\mu\text{-H})[\text{Mo}(\text{CO})_5]_2^-$ accounts for the $\nu(\text{CO})$ IR band pattern of $(\mu\text{-H})[\text{Mo}(\text{CO})_5][\text{Mo}^{13}\text{CO}(\text{CO})_4]^-$.²⁹ That the electron-rich $\mu\text{-}\eta^2\text{-NiS}_2$ bridge might serve to transmit electronic information between two exogenous S-bound metal centers as hydride does is an interesting, albeit speculative, possibility for which proof is beyond the scope

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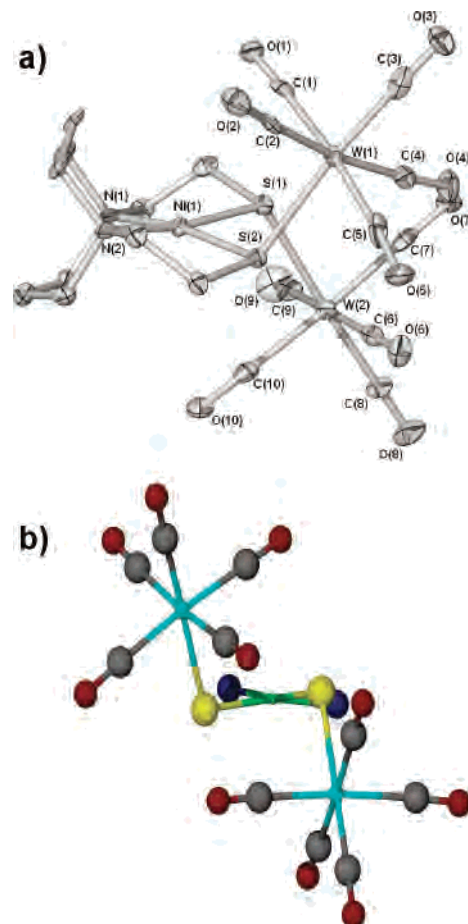


Figure 3. $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ complex shown as (a) a thermal ellipsoid plot (50% probability) with select atoms labeled and (b) a ball-and-stick representation viewed down the bisector of $\angle\text{S-Ni-S}$ with hydrocarbons omitted.

of this study. Should such a coupling occur across the NiS_2 bridge, one might expect that interactions with solvents of different polarity could lead to conformational or structural modifications, resulting in changes in the $\nu(\text{CO})$ IR band pattern display.

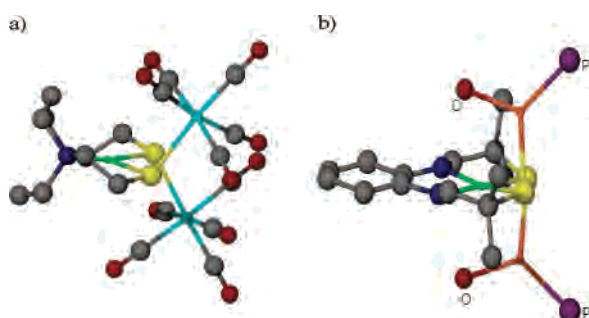
Structural Description of Ni-1 as a Monodentate Ligand to Two $\text{W}(\text{CO})_5$ Moieties. The molecular structure of $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ is given in Figure 3a. Selected metric data are listed in Table 2 and compared to those of the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ and free **Ni-1** complexes. The $(\mu\text{-}\eta^2\text{-Ni-1})[\text{W}(\text{CO})_5]_2$ trimetallic species finds that each NiN_2S_2 serves as a bidentate bridge through S donors to two $\text{W}(\text{CO})_5$ moieties that are oriented in a transoid fashion with respect to the NiN_2S_2 plane. The Ni–W distances average to 4.021 Å, and the W atoms are 5.583 Å apart. Additional views of the compound are shown in the Supporting Information. When the stereodirecting effect of the remaining lone pair on each S is emphasized, the Ni–S–W angles are $113.9(1)^\circ$ and $117.5(1)^\circ$.³⁰ The S–Ni–S angle of $89.25(9)^\circ$ in the NiW_2 complex is essentially unchanged from that of free **Ni-1**, $89.4(1)^\circ$; in the $(\eta^1\text{-Ni-1})\text{W}(\text{CO})_5$ complex, this angle is slightly compressed to $88.4(1)^\circ$. All other structural features in the NiN_2S_2 unit, including the 13.7° tetrahedral twist at

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Table 2. Selected Metric Data for (μ - η^2 -Ni-1)[W(CO)₅]₂ with (μ -Ni-1)W(CO)₅ and Ni-1 Shown for Comparison [Distances (Å); Angles (deg)]

	(Ni-1)[W(CO) ₅] ₂	(Ni-1)W(CO) ₅ ¹³	Ni-1 ¹⁵
Ni–W(avg)	4.021	3.894	
W–C _{ax} (avg)	1.975(13)	1.955(13)	
W–C _{eq} (avg)	2.048(12)	2.038(11)	
W(1)–S(1)	2.572(3)	2.577(3)	
W(2)–S(2)	2.571(2)		
Ni–S(1)	2.186(3)	2.176(3) ^a	2.159(3)
Ni–S(2)	2.170(2)	2.164(3)	2.159(3)
Ni–N(1)	1.984(7)	1.985(8) ^b	1.979(7)
Ni–N(2)	1.984(8)	1.982(8)	1.979(7)
W(1)–S(1)–Ni(1)	113.39(10)	109.8(11)	
W(2)–S(2)–Ni(1)	117.47(11)		
S(1)–Ni–S(2)	89.25(9)	88.45(11)	89.4(1)
N(1)–Ni–N(2)	90.9(3)	89.5(3)	89.8(3)
NiN ₂ S ₂ T _d twist	13.8	8.6	13.1

^a S(1) defined as W(μ -S)Ni; S(2) is a dangling thiolate S. ^b N(1) is that N trans to S(2); N(2) is that N trans to S(1).

**Figure 4.** Ball-and-stick representations of (a) (μ - η^2 -Ni-1)[W(CO)₅]₂ and (b) (μ - η^2 -NiN₂S₂)[Cu(OPh)(PPh₃)₂] with phenyl groups omitted. \angle Ni–S–W(avg) = 115.43(1)°; \angle Ni–S–Cu(avg) = 79.04(8)°.^{2a}

Ni and the staggered N to S thiolate arms, are largely identical in free Ni-1 and (μ - η^2 -Ni-1)[W(CO)₅]₂. Because of asymmetry, there are greater disparities in the (η^1 -Ni-1)W(CO)₅ metric data as compared to free Ni-1.

The W–C–O units are substantially linear. The closest intermolecular CO contacts are in the range of 3.01–3.30 Å, which is slightly beyond the overlap of the van der Waals radii of 3.22 Å.³¹ The metric differences between the W(CO)₅ units are statistically insignificant.

An analogous formulation and structure has been reported by Holm et al. in the form of a (μ - η^2 -(NiN₂S₂))[Cu(PPh₃)(OPh)]₂ complex based on Schugar's dianionic ligand *trans-rac-N,N'*-bis(2-mercapto-2-methylprop-1-yl)-1,2-cyclohexanediamine).^{2,32} The major difference in the trimetallic structures is emphasized in the views and caption presented in Figure 4. Whereas the Ni–S–W angles of the bis-W(CO)₅ adduct are obtuse, the Ni–S–Cu angles in the bis-Cu(PPh₃)(OPh) adduct are acute (Figure 4 caption).

Another structural analogue is found in the electrophile/NiN₂S₂ complex adduct which features reversible SO₂ uptake by (bis(mercaptoethyl)diazacycloheptane)nickel, Ni(bmedach) or Ni-1'.³³ As found in the (μ - η^2 -Ni-1)[W(CO)₅]₂ complex, the square-planar NiN₂S₂ unit in (μ - η^2 -Ni-1')(SO₂)

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Table 3. ν (CO) IR Values (cm⁻¹) for NiN₂S₂ Adducts of W(CO)₅

N ₂ S ₂ complex	medium	ν (CO) IR bands, cm ⁻¹
Ni-1	DMF	2065(w), 1974(w), 1923(s), 1879(m)
Ni-2	DMF	2066(w), 1977(w), 1924(s), 1876(m)
Ni-1	solid state ^a	2063(w), 1977(w), 1926(sh), 1902(s), 1861(ms)
Ni-2	solid state ^a	2066(w), 1984(w), 1924(sh), 1907(s), 1855(ms)

^a Attenuated reflectance FTIR on a powdered sample. ^b w: weak. m: medium. ms: medium strong. s: strong. sh: shoulder.

has each thiolato S bound to SO₂ molecules, oriented transoid to each other with the SO₂ S atoms 6.035 Å apart. Coincidentally, the S–SO₂ distances of 2.660(1) and 2.557(1) Å are comparable to the W–S distances found in the NiW₂ trimetallic, 2.572(3) and 2.571(2) Å. Despite the large steric bulk of the W(CO)₅ units, the Ni–S–W angles [113.4(1)° and 117.5(1)°] are only slightly larger than the Ni–S–SO₂ angles [105.2(3)° and 102.4(3)°].

Synthesis of (η^1 -Ni-2)W(CO)₅, IR Analysis, and Structure. The crystalline material used in the X-ray diffraction study of (Ni-2)W(CO)₅ was obtained from the reaction of W(CO)₆ and Ni-2 dissolved in a 1:1 THF/CH₃CN mixture and allowed to stand for 1 week under mild photolytic conditions (sunlight/window sill). Because of slow product formation and its insolubility, a crystalline (Ni-2)W(CO)₅ adduct formed on the walls of the flask. These crystals are insoluble in all common organic solvents including MeOH. The compound is slightly soluble in DMF, in which the ν (CO) IR studies were performed.

Table 3 lists ν (CO) IR values for (Ni-2)W(CO)₅ in a DMF solution as well as values from the solid-state IR spectrum obtained by attenuated reflectance measurements. The solution-phase spectra of the two complexes show the same four-band pattern as was expected for pseudo-C_{4v} symmetry. The insignificant differences in ν (CO) values for the (Ni-1)W(CO)₅ and (Ni-2)W(CO)₅ complexes show that the donor ability of the thiolate S is unaffected by the sulfinato group.

The attenuated reflectance IR spectra on powdered samples have greater complexity in contrast to the solution IR data; the weak, higher wave number bands show greater differences between the dithiolate and thiolate–sulfinato complexes, with the latter shifted to more positive values. In each complex, a shoulder develops on the strong bands at 1902 and 1907 cm⁻¹, while the lowest wavenumber bands are significantly increased in intensity and are shifted negatively by some 20 cm⁻¹ relative to the solution analogues. The IR spectrum also shows a positive shift for the two weak bands corresponding to the ν (SO) stretches at 1191 and 1059 cm⁻¹ for the (Ni-2)W(CO)₅ complex as compared to the values of 1181 and 1053 cm⁻¹ reported for free Ni-2.¹⁶

In Figure 5, the molecular structure of (Ni-2)W(CO)₅ is displayed as a thermal ellipsoid plot. The NiN₂S₂ moiety binds through the thiolate S to W(CO)₅, resulting in pseudooctahedral coordination about W. The W–S(2) bond distance of 2.584(2) Å is largely the same as the W–S distance in (Ni-1)W(CO)₅ [2.577(3) Å]. Within the metallo Ni-2 ligand, the Ni–S_{sulfinato} distance in (Ni-2)W(CO)₅ is, at

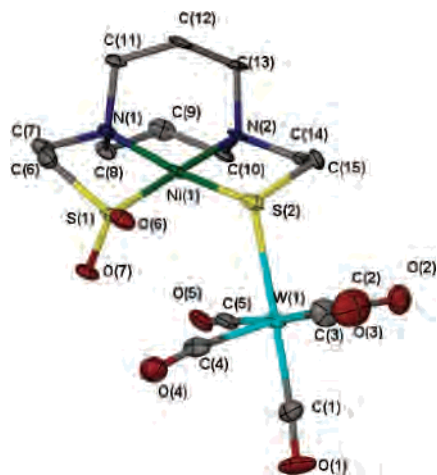


Figure 5. Thermal ellipsoid plot (50% probability) of the molecular structure of $(\text{Ni-2})\text{W}(\text{CO})_5$. Selected distances (Å): Ni–W 3.929; W–C_{eq}(avg) 2.034(3); W–C(1) 1.971(8); W–S(2) 2.5843(19); Ni–S(1) 2.124(2); Ni–S(2) 2.172(2); Ni–N(1) 1.982(7); Ni–N(2) 1.985(6); S(1)–O(6) 1.448(6); S(1)–O(7) 1.483(4). Selected bond angles (deg): W–S(2)–Ni 111.12(8); S(1)–Ni–S(2) 90.66(9); N(1)–Ni–N(2) 90.8(3). Tetrahedral twist = 9.7°.

2.124(2) Å, very slightly shorter than that of the Ni–S_{thiolate} distance, 2.172(2) Å. These individual distances are not significantly altered from those in the isolated **Ni-2** complex.¹⁶ An approximate tetrahedral twist angle has been defined in the Ni₂S₂ complexes as the angle of intersection of the NiN₂ and NiS₂ planes.¹⁶ Its value of 18.3° in **Ni-2** is the largest of all of the daco-derived Ni₂S₂ complexes. It is diminished to 9.7° in the $(\text{Ni-2})\text{W}(\text{CO})_5$ complex.

While the axial CO and three of the equatorial CO's in $(\text{Ni-2})[\text{W}(\text{CO})_5]$ are linear, the carbonyl closest to the sulfonato O atoms is significantly bent, $\angle\text{W}-\text{C}(4)-\text{O}(4) = 171.5^\circ$. Overlay of the Ni–S(1) bond with the W–C(4) bond vector finds that the O(4)–C(4)–W vector bisects the O(6)–S(1)–O(7) angle (Figure 6a,b) and the sulfonato O atoms flank the bent carbonyl. The distances of the sulfonato O atoms to carbonyl O, O(4), are 3.163 and 3.279 Å, averaging to 3.22 Å. As given in Figure 6c, distances between the sulfonato O atoms and C(4) average to 3.14 Å and are slightly less than the sum of the van der Waals radii for those atoms, 3.22 Å.³¹ The closest intermolecular contact between the sulfonato O atoms and carbonyl O atoms is 3.838 Å (sulfonato O and an equatorial carbonyl O on an adjacent molecule).

The deviation from linearity of ca. 10° of the W–C–O unit most closely aligned with the nickel sulfonato group is likely a result of close proximity and steric repulsion. As can be seen in Figure 6c, any increase in the W–C(4)–O(4) angle or twist in the W–S(2) bond would result in the energetically unfavorable contacts, within van der Waals radii, of sulfonato O atoms and carbonyl C and O atoms. This rigidity might also explain the low solubility of the $(\text{Ni-2})\text{W}(\text{CO})_5$ complex as compared to other NiN₂S₂–W complexes.¹³

Synthesis and Structure of the Ni₂Cu Trimetallic. In a further probe of the ability of **Ni-2** to bind metal ions, the compound was mixed with copper(I) bromide in a 2:1 ratio. Consistent with the well-known affinity of nickel thiolates for copper, the red-orange crystals obtained from this reaction revealed a trimetallic compound in which copper bromide

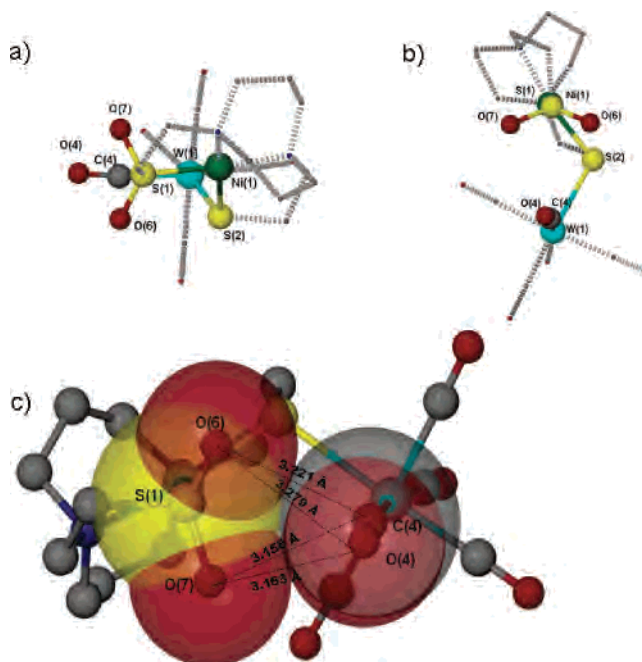


Figure 6. $(\text{Ni-2})[\text{W}(\text{CO})_5]$ as viewed from the C(4)–W–Ni–S(1) plane showing (a) an eclipsed view of the bisecting carbonyl (b) a rotated view of that in part a, and (c) sulfinato/carbonyl contact distances with van der Waals radii spheres superimposed.

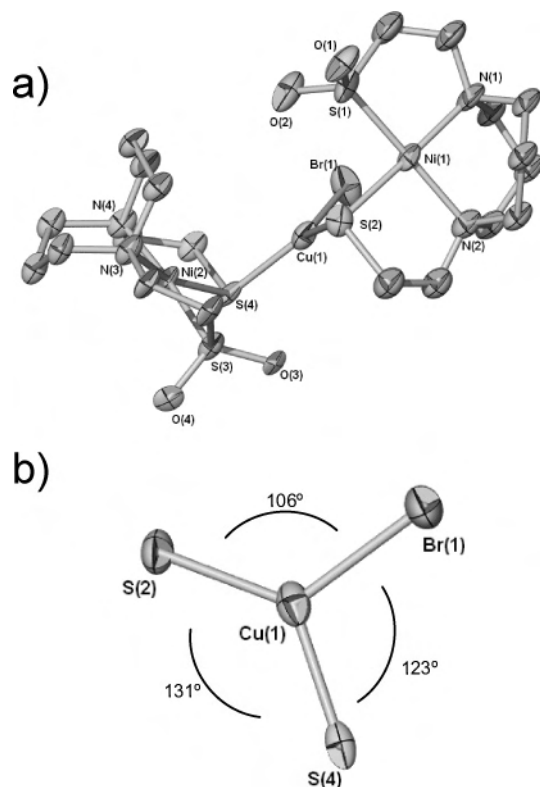


Figure 7. Thermal ellipsoid plot (50% probability), with select atoms labeled, of (a) $(\text{Ni-2})_2\text{CuBr}$ and (b) the trigonal-planar S_2CuBr unit.

is ligated by two **Ni-2** units via its non-oxygenated S atom. The molecular structure of $(\text{Ni-2})_2\text{CuBr}$ is shown in Figure 7 as a thermal ellipsoid plot. Selected metric data are given in Table 4.

The trimetallic $(\text{Ni-2})_2\text{CuBr}$ complex features two **Ni-2** units, each with one of its S atoms doubly oxygenated into

Table 4. Selected Metric Data for (Ni-2)₂CuBr [Distances (Å); Angles (deg)]

Ni(1)–S(1)	2.102(5)	Ni(2)–S(3)	2.101(5)
Ni(1)–S(2)	2.159(6)	Ni(2)–S(4)	2.152(4)
Ni(1)–N(1)	1.967(15)	Ni(2)–N(3)	1.994(12)
Ni(1)–N(2)	1.959(15)	Ni(2)–N(4)	1.908(15)
S(1)–O(1)	1.456(11)	S(3)–O(3)	1.478(11)
S(1)–O(2)	1.465(14)	S(3)–O(4)	1.493(13)
Cu(1)–S(4)	2.248(5)	Ni(1)–Cu(1)	3.301
Cu(1)–S(2)	2.245(5)	Ni(2)–Cu(1)	3.257
Cu(1)–Br(1)	2.421(3)	Ni(1)–Ni(2)	6.021
S(1)–Ni(1)–S(2)	88.9(2)	S(2)–Cu(1)–S(4)	130.80(19)
N(1)–Ni(1)–N(2)	91.9(6)	S(2)–Cu(1)–Br(1)	123.23(17)
S(3)–Ni(2)–S(4)	90.75(18)	S(4)–Cu(1)–Br(1)	105.97(14)
N(3)–Ni(2)–N(4)	91.6(6)	Ni(1)–S(2)–Cu(1)	95.65(19)
O(1)–S(1)–O(2)	113.7(7)	Ni(2)–S(4)–Cu(1)	97.32(17)
O(3)–S(3)–O(4)	114.5(7)		

a sulfinate. A molecule of copper(I) bromide is bound by the remaining thiolate S atoms, resulting in a trigonal-planar S₂Br coordination environment. The average deviation in the CuBrS₂ unit from the best least-squares plane is 0.0009 Å, and the angle defined by the Ni(1), S(2), Cu(1), and Br(1) atoms displays a maximum torsion of 0.7°. A similar structural unit is found in the (Ni-1*)₂(CuCl)₄ complex cluster, Ni-1* = (bis(mercaptoethyl-2-methylpropyl)(diazacyclooctane))nickel, which contains four trigonal-planar CuClS₂ units in an adamantane-like Ni₂S₄Cu₄ core (Figure 1a).¹⁹ In that structure, both lone pairs on each S donor are engaged in bonding to CuCl.

While one of the NiN₂S₂ units in the CuNi₂ complex is rigorously square-planar, the second is highly distorted in that the thiolate S deviates from the best N₂S_{sulfinate} plane by 0.7620 Å. The NiN₂S₂ planes are tilted with respect to each other and have a best planes angle of intersection of ca. 110°. The Ni–S_{sulfinate} distances [Ni(1)–S(1) = 2.102(5) Å and Ni(2)–S(3) = 2.101(5) Å] for each Ni-2 are shorter in CuNi₂ than in the unbound form [2.140(1) Å], whereas the Ni–S_{thiolate} distances [Ni(1)–S(2) = 2.141 Å and Ni(2)–S(4) = 2.168 Å] are largely unchanged. Additional views of this compound are given in the Supporting Information.

Concluding Comments

As monitored by the $\nu(\text{CO})$ stretching frequencies, the presence of the sulfinato group had little effect on the donor ability of (Ni-2)W(CO)₅ in contrast to the dithiolate complex, (Ni-1)W(CO)₅. In question is the sensitivity of the W(CO)₅ spectral probe because other measures, nucleophilicity and Ni^{III} reduction potential, suggest a greater electron-rich character of the Ni-1 complex over the Ni-2 complex. Consistent with the spectroscopic results were insignificant differences in W–S_{thiolate} distances in the two complexes. We conclude that modification of the thiolate S to sulfinato can serve as a block to bidentate coordination that prevails in the nickel dithiolato complexes without significantly

altering the monodentate ligation and donor ability of such metalloligands.

The close proximity of the sulfinato O atoms to one carbonyl group in (Ni-2)W(CO)₅ appears to account for the distinct nonlinearity of one W–C–O linkage. The implications of this interaction for distinguishing equatorial carbonyl groups in solution or for enhancing the CO lability await further studies.

As a bidentate bridging ligand in the C₃ and C₄ paddle-wheel complexes, the cisoid arrangements of the exogenous metals bound to NiN₂S₂ metalloligands lead to M–M distances ranging from 2.14 to 4.35 Å.^{3,20,35} The NiW₂ complex of this study finds the W(CO)₅ moieties in a transoid configuration with respect to the NiN₂S₂ plane, thus separating the W atoms by 5.58 Å. Even so, IR spectral studies suggest at least some communication between the W(CO)₅ moieties.

A second trimetallic complex discovered in this study is made up of two Ni-2 complexes S-bound to Cu^IBr. While the aggregative ability of the S-oxygenated complex is restricted because of the availability of a single thiolate, the synthesis of mixed-metal clusters can be designed with the sulfinato thiolate as a monodentate metalloligand.

Prior to this study, we assumed that previous work of ourselves and others, as well as the extensive results of Holm et al.,^{2a} had largely established the limit of structural variations for this unusual class of ligand. While surprises arose in this work and will probably do so in the future, one should, on the whole, expect that designed syntheses using the known bonding principles associated with metal-bound thiolate S donors will have predictable results.

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Supporting Information Available: Alternative views of the (μ - η^2 -Ni-1)W(CO)₅)₂ and (Ni-2)₂CuBr structures and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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