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Cyclization of Thiocarbonyl Groups in Binuclear Homoleptic Nickel Thiocarbonyls To Give Ligands Derived from Sulfur Analogues of Croconic and Rhodizonic Acids

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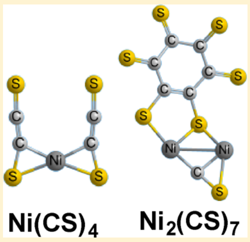
S *Supporting Information*

ABSTRACT: The sulfur analogue of the well-known $Ni(CO)_4$, namely, $Ni(CS)_4$, has been observed spectroscopically in low temperature matrices but is not known as a stable species under ambient conditions. Theoretical studies show that $Ni(CS)_4$ with monomeric CS ligands and tetrahedrally coordinated nickel is disfavored by ~17 kcal/mol relative to unusual isomeric $Ni(C_2S_2)_2$ structures. In the latter structures the CS ligands couple pairwise through C−C bond formation to give dimeric S═C═C═S ligands, which bond preferentially to the nickel atom through their C═S bonds rather than their C═C bonds. Coupling of CS ligands in the lowest energy binuclear $Ni_2(CS)_n$ (n = 7, 6, 5) structures results in cyclization to give remarkable C_nS_n (n = 5, 6) ligands containing five- and six-membered carbocyclic rings. Such ligands, which are the sulfur analogues of the well-known croconate (n = 5) and rhodizonate (n = 6) oxocarbon ligands, function as bidentate ligands to the central Ni_2 unit. Higher energy $Ni_2(CS)_n$ (n = 7, 6, 5) structures contain dimeric C_2S_2 ligands, which can bridge the central Ni_2 unit. Dimeric C_2S_2 ligands rather than tetrathiosquare C_4S_4 ligands are found in the lowest energy $Ni_2(CS)_4$ structures.



1. INTRODUCTION

The chemistry of homoleptic metal carbonyls dates back to the 1890 synthesis of $Ni(CO)_4$ by Mond, Langer, and Quincke using the reaction of finely divided nickel with CO at atmospheric pressure.[1] Shortly thereafter, a number of other homoleptic metal carbonyls, including $Fe(CO)_5$, $Co_2(CO)_8$, and $Mo(CO)_6$, were synthesized using reactions of free metals with carbon monoxide at elevated pressures. The syntheses of additional homoleptic metal carbonyls of the first row transition metals such as $V(CO)_6$, $Cr(CO)_6$, and $Mn_2(CO)_{10}$ required more sophisticated reductive carbonylation methods and occurred much later. Such syntheses of these and other binary metal carbonyls were feasible since carbon monoxide is a stable, readily available gas that can be manipulated at high pressures when necessary.

A question of long-standing interest is whether homoleptic metal thiocarbonyls $M_y(CS)_x$ can be synthesized as stable compounds. However, synthetic methods analogous to those used for the binary metal carbonyls $M_y(CO)_x$ are not available since carbon monosulfide, CS, unlike CO, is unstable at temperatures above −100 °C and is primarily observed in experiments at low temperatures (e.g., −190 °C).[2,3] However, use of indirect methods with reagents such as CS_2 and Cl_2CS as sources of the thiocarbonyl group has provided syntheses of a wide variety of metal thiocarbonyl derivatives.[4−8] Most thiocarbonyls synthesized by such methods contain only one CS group per metal atom. Nevertheless, $(\eta^5\text{-}C_5H_5)Mn(CS)_3$ has been synthesized by a long synthetic sequence involving stepwise replacement of CO groups in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ with CS groups through cyclooctene metal complex intermediates.[9,10] A CS_2/PPh_3 reagent was the source of the CS groups.

The existence of $(\eta^5\text{-}C_5H_5)Mn(CS)_3$ as a stable compound appears to suggest that binary $M_x(CS)_y$ derivatives might prove to be stable compounds if methods could be found for their syntheses circumventing the difficulties arising from the instability of free CS. The nickel derivative $Ni(CS)_4$ appears to be a good candidate for an accessible binary metal thiocarbonyl for a number of reasons. First, only four CS groups are required to give the favored 18-electron configuration for the nickel atom. In addition, the synthesis of $Ni(CO)_4$ requires the mildest reaction conditions of the syntheses of binary metal carbonyls in that it proceeds readily with finely divided nickel and carbon monoxide at atmospheric pressure. Finally the reaction of nickel atoms with CS in a low temperature matrix has been reported to give $Ni(CS)_4$ identified by its infrared and mass spectra.[11]

Density functional theory (DFT) is a useful method to obtain information on molecules that are difficult to access experimentally. This certainly is the case with homoleptic metal thiocarbonyls such as $Ni(CS)_4$. We report such computational studies designed to explore the structures and thermochemistry of both mononuclear homoleptic nickel thiocarbonyls $Ni(CS)_x$ (x = 4, 3, 2, 1) and binuclear homoleptic nickel thiocarbonyls $Ni_2(CS)_x$ (x = 7, 6, 5, 4). The corresponding binuclear

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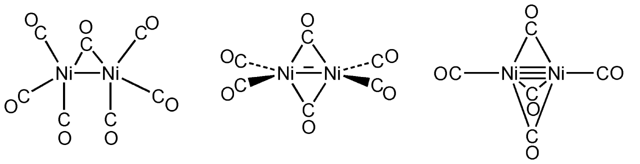
homoleptic nickel carbonyls $Ni_2(CO)_x$ are not known experimentally in contrast to the stable well-known binuclear metal carbonyls $Co_2(CO)_8$, $Fe_2(CO)_9$, and $Mn_2(CO)_{10}$. However, they have been studied theoretically using DFT methods.[12] These studies predict a systematic progression of structures for the binuclear $Ni_2(CO)_n$ (n = 7, 6, 5) derivatives with both the formal Ni−Ni bond order and the number of bridging CO groups increasing as CO groups are lost in going from $Ni_2(CO)_7$ to $Ni_2(CO)_6$ and then $Ni_2(CO)_5$ (Figure 1).



$Ni_2(CO)_7$ **[= $Ni_2(CO)_6(\mu\text{-}CO)$]** **$Ni_2(CO)_6$** **[= $Ni_2(CO)_4(\mu\text{-}CO)_2$]** **$Ni_2(CO)_5$** **[= $Ni_2(CO)_2(\mu\text{-}CO)_3$]**

Figure 1. Progression of structures in the series $Ni_2(CO)_7$ → $Ni_2(CO)_6$ → $Ni_2(CO)_5$ predicted by density functional theory.

The results from the present theoretical study show the nickel thiocarbonyl systems $Ni(CS)_x$ and $Ni_2(CS)_x$ to be very different from the corresponding nickel carbonyl systems $Ni(CO)_x$ and $Ni_2(CO)_x$. In particular, the CS groups in $Ni(CS)_x$ and $Ni_2(CS)_x$ are shown to couple in the lowest energy isomers to give C_2S_2 ligands in the mononuclear derivatives. The binuclear derivatives also provide examples of coupling of multiple CS ligands to give cyclic C_nS_n (n = 3, 5, 6) ligands including the perthio analogues of the oxocarbon croconic (n = 5) and rhodizonic (n = 6) acids.[13,14] These results suggest that complexation to nickel cannot protect monomeric CS ligands from oligomerization to more complicated C_nS_n ligands. They further suggest that synthesis of a stable $Ni(CS)_4$ species under ambient conditions analogous to $Ni(CO)_4$ is not promising even if indirect methods can be found to circumvent the instability of free CS.[1,15]

2. THEORETICAL METHODS

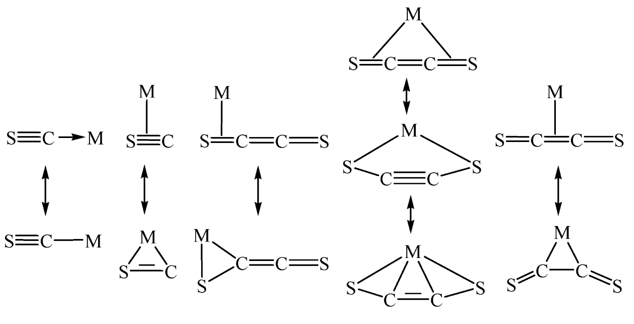
Electron correlation effects were considered using DFT methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[16−22] Two DFT methods were adopted in this study. The first method uses the popular B3LYP functional, which is a hybrid HF/DFT functional using a combination of the three-parameter Becke exchange functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[23,24] The other DFT method used in the present Article is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional (P86).[25,26] The geometric parameters predicted by these two methods are usually in reasonable agreement despite the fact that the two methods are rather different conceptually. The BP86 method generally predicts vibrational frequencies closer to experimental values.

The DZP basis sets used for carbon and sulfur add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(S) = 0.70$ to the standard Huzinaga−Dunning−Hay contracted DZ sets.[27−29] The DZP basis set for carbon is designated (9s5p1d/4s2p1d) and that for sulfur is designated (12s8p1d/6s4p1d). For nickel, in our loosely contracted DZP basis set, the Wachters primitive set[30] is used augmented by two sets of p functions and one set of d functions, and contracted following Hood, Pitzer, and Schaefer.[31] This basis set is designated as (14s11p6d/10s8p3d). For $Ni_2(CS)_7$, $Ni_2(CS)_6$, $Ni_2(CS)_5$, and $Ni_2(CS)_4$, there are 364, 326, 288, and 250 contracted Gaussian functions, respectively.

The geometries of all structures were fully optimized. Vibrational frequencies and their corresponding infrared intensities were determined analytically. All of the optimizations were carried out using the Gaussian 09 program with the (75, 302) default fine grid.[32]

In the search for minima using currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in all conventional DFT computations.[33] Thus, all imaginary vibrational frequencies with magnitudes less than 100i cm^{-1} are considered questionable and are given less weight in the analysis.[34,35] Therefore, we do not always follow such low imaginary vibrational frequencies. The optimized structures are designated as **ab-c** where **a** is the number of nickel atoms, **b** is the number of CS groups, and **c** is the relative energy order determined using the B3LYP method. Thus, the lowest energy structure of $Ni_2(CS)_7$ is designated **27-1**.

In the $Ni(CS)_x$ and $Ni_2(CS)_x$ structures, monomeric CS ligands were found to bond to a nickel atom in two different ways (**1a** and **1b** in Figure 2). In **1a**, the metal−carbon bond can be viewed as a dative bond similar to the Ni−CO bond in $Ni(CO)_4$.[12] In **1b**, the CS ligand coordinates to the metal atom though the C−S π bond.



1a **1b** **2a** **2b** **2c**

Figure 2. Types of CS and SCCS coordination to nickel in $Ni(CS)_x$ and $Ni_2(CS)_x$ structures.

Previous studies found that carbon monosulfide is intrinsically unstable readily undergoing polymerization.[36,37] The dimer SCCS obtained by coupling two CS units can bond to a metal in three different ways, namely, as a dihapto ligand by using one C−S π bond (**2a** in Figure 2), as a tetrahapto ligand using both carbon and sulfur atoms (**2b** in Figure 2), or as a dihapto ligand through both carbon atoms by using the C−C π bond (**2c** in Figure 2). Among these three bonding modes, the most favorable is **2a** which has two advantages. One is that the orbital of the C−S π bond lies higher in energy than that of the C−C π bond; i.e., the electrons populated in this orbital can more readily coordinate to the metal atom than the corresponding orbital of the C−C π bond. In addition, the ligand arrangement in **2a** allows an optimal metal−ligand interaction.

3. RESULTS AND DISCUSSION

3.1. Mononuclear Derivatives.

3.1.1. $Ni(CS)_4$ Structures. Eight structures were found for $Ni(CS)_4$. However, only the six structures lying within 45 kcal/mol of the lowest energy structure are discussed in this Article (Figure 3 and Table 1). The two lowest energy structures **14-1** and **14-2** are cis and trans $(\eta^2\text{-SCCS})_2Ni$ isomers with each dihapto SCCS ligand bonded to the nickel atom through the π orbital of a C═S bond (**2a** in Figure 2). The two stereoisomers **14-1** and **14-2** have similar energies, i.e., the trans isomer **14-2** lies only 1.2 kcal/mol (B3LYP) or 0.7 kcal/mol (BP86) above the cis isomer **14-1**. The isomer **14-3**, lying 1.3 kcal/mol (B3LYP) or 6.9 kcal/mol (BP86) in energy above **14-1**, is a $(\eta^2\text{-SCCS})Ni(CS)_2$ structure with one dihapto SCCS ligand similar to the two ligands in **14-1** and **14-2** and two simple

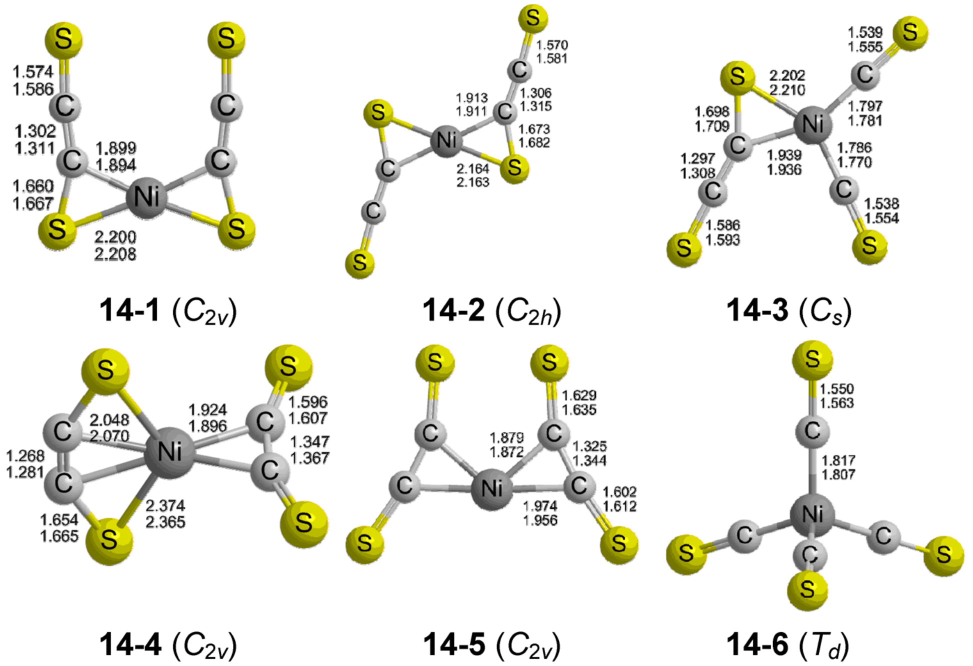


Figure 3. Optimized $Ni(CS)_4$ structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

Table 1. Total Energies (*E*, hartrees) and Relative Energies (Δ*E*, kcal/mol) for the $Ni(CS)_4$ Structures[a]

		14-1	14-2	14-3	14-4	14-5	14-6
B3LYP	$-E$	3253.48041	3253.47851	3253.47828	3253.45650	3253.45256	3253.45239
	ΔE	0.0	1.2	1.3	15.0	17.5	17.6
BP86	$-E$	3253.85281	3253.85167	3253.84188	3253.82491	3253.83724	3253.82801
	ΔE	0.0	0.7	6.9	17.5	9.8	15.6

[a]None of these structures has any imaginary vibrational frequencies.

thiocarbonyl ligands, bonded to the nickel atom exclusively through their carbon atoms.

The remaining $Ni(CS)_4$ structures (Figure 3 and Table 1) are considerably higher energy structures. Structure **14-4**, lying 15.0 kcal/mol (B3LYP) or 17.5 kcal/mol (BP86) in energy above **14-1**, is an (η^2-SCCS)(η^4-SCCS)Ni structure with the two SCCS ligands perpendicular to each other. The dihapto η^2-SCCS ligand in **14-4** is of a different type than the dihapto η^2-SCCS ligands in **14-1**, **14-2**, and **14-3** since in **14-4** the η^2-SCCS ligand is bonded to the nickel atom through the two carbon atoms (**2c** in Figure 2) rather than through a carbon and a sulfur atom (**2a** in Figure 2). Structure **14-5**, lying 17.5 kcal/mol (B3LYP) or 9.8 kcal/mol (BP86) in energy above **14-1**, is an $(\eta^2\text{-SCCS})_2$Ni structure in which both η^2-SCCS ligands are bonded to the nickel atom through their carbon atoms (**2c** in Figure 2). The corresponding D_{2h} isomer of **14-5** with parallel SCCS ligands was found to lie 14.5 kcal/mol (B3LYP) higher in energy than **14-5** and has three imaginary vibrational frequencies. Thus, it is not considered in detail in this Article.

The beautiful $Ni(CS)_4$ structure **14-6** has four separate CS ligands coordinated to the central nickel atom with tetrahedral nickel geometry similar to the well-known $Ni(CO)_4$ structure (Figure 3).[12] Structure **14-6**, however, is a moderately high energy structure, lying 17.6 kcal/mol (B3LYP) or 15.6 kcal/mol (BP86) above **14-1**. The relatively high energy of **14-6** with separate CS ligands is related to the exergonic dimerization of two isolated CS fragments by 61.4 kcal/mol (B3LYP) or 65.4 kcal/mol (BP86). Thus, structure **14-6** is energetically disfavored, compared with structures from **14-1** to **14-5**.

3.1.2. $Ni(CS)_3$ Structures. A total of six structures have been found for $Ni(CS)_3$. However, only the five structures lying within 45 kcal/mol of the lowest energy structure are discussed in this Article (Figure 4 and Table 2). The lowest energy structure **13-1** is an (η^4-SCCS)Ni(CS) structure with a tetrahapto η^4-SCCS ligand bonded to the nickel through carbon and sulfur (**2b** in Figure 2) and a simple CS ligand (**1a** in Figure 2).

The next $Ni(CS)_3$ structure **13-2**, lying 7.2 kcal/mol (B3LYP) or 1.5 kcal/mol (BP86) above **13-1**, has a trigonal planar nickel atom coordinated to three separate CS ligands through their carbon atoms (**1a** in Figure 2). It is thus analogous to the lowest energy $Ni(CO)_3$ structure.[12] The relatively high energy $Ni(CS)_3$ structure **13-5**, lying 26.0 kcal/mol (B3LYP) or 21.5 kcal/mol (BP86) above **13-1**, also has three separate CS ligands (Figure 4 and Table 2). However, in **13-5**, one of the CS ligands is a dihapto η^2-CS ligand bonded to the nickel atom through both the carbon and sulfur atoms (Figure 4 and Table 2).

The remaining two of the five lowest energy $Ni(CS)_3$ structures have one SCCS ligand and one CS ligand (Figure 4 and Table 2). In **13-3**, lying 15.3 kcal/mol (B3LYP) or 7.2 kcal/mol (BP86) above **13-1**, the SCCS ligand is a trihapto ligand. However, in **13-4**, lying 16.7 kcal/mol (B3LYP) or 10.8 kcal/mol (BP86) above **13-1**, the SCCS ligand is a dihapto

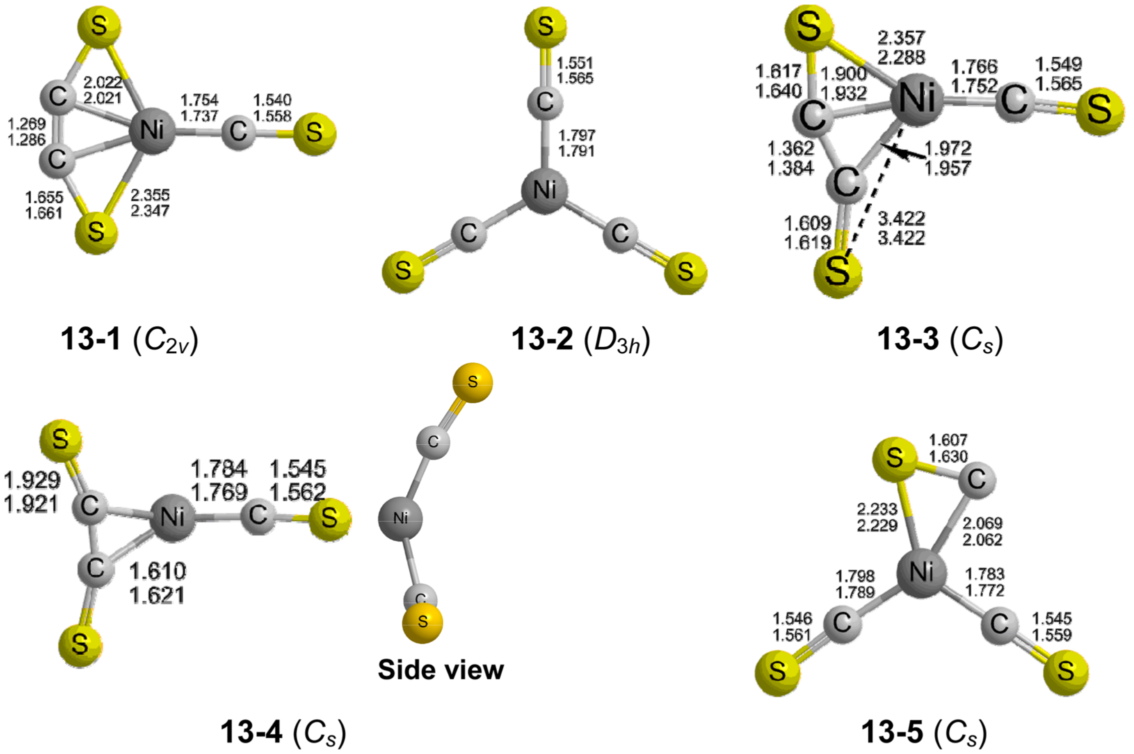


Figure 4. Optimized $Ni(CS)_3$ structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

Table 2. Total Energies (*E*, hartrees) and Relative Energies (Δ*E*, kcal/mol)[a]

		13-1	13-2	13-3	13-4	13-5
B3LYP	−*E*	2817.20191	2817.19040	2817.17760	2817.17534	2817.16040
	Δ*E*	0.0	7.2	15.3	16.7	26.0
BP86	−*E*	2817.52822	2817.52577	2817.51674	2817.51101	2817.49401
	Δ*E*	0.0	1.5	7.2	10.8	21.5

[a] None of the structures has any imaginary vibrational frequencies.

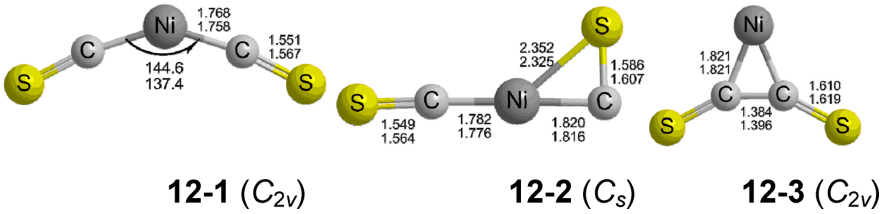


Figure 5. Optimized $Ni(CS)_2$ structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

ligand, bonded to the nickel atom through its two carbon atoms (**2c** in Figure 2).

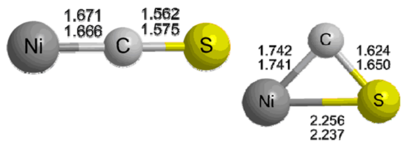
3.1.3. $Ni(CS)_2$ Structures. Three structures were found for $Ni(CS)_2$ (Figure 5 and Table 3). The lowest energy structure **12-1** has separate CS ligands bonded to the nickel atom only through the carbon atoms (**1a** in Figure 2) analogous to the lowest energy structure of $Ni(CO)_2$.[12] Structure **12-1** is a favorable structure, since it lies ~17 kcal/mol below the next lowest energy $Ni(CS)_2$ structure **12-2**, which, like **12-1**, has two separate CS ligands. However, in **12-2** one of the CS ligands is a dihapto η^2-CS ligand bonded to the nickel atom through both the carbon and sulfur atoms. In the third $Ni(CS)_2$ structure **12-3**, with an almost identical energy to **12-2**, the two CS ligands are coupled to form a dihapto η^2-SCCS ligand bonded to the nickel atom through its two carbon atoms (**2c** in Figure 2).

Table 3. Total Energies (*E*, hartrees) and Relative Energies (Δ*E*, kcal/mol) for the $Ni(CS)_2$ Structures

		12-1	12-2	12-3
B3LYP	−*E*	2380.91224	2380.88500	2380.88484
	Δ*E*	0.0	17.1	17.2
BP86	−*E*	2381.21098	2381.18185	2381.18359
	Δ*E*	0.0	18.3	17.2

3.1.4. Ni(CS) Structures. The lowest energy Ni(CS) structure **11-1** has the CS group bonded to the nickel atom solely through the carbon atom (**1a** in Figure 2) and thus is analogous to the lowest energy structure of the corresponding

Ni(CO)[12] (Figure 6 and Table 4). The Ni(CS) structure **11-2** with a η^2-CS ligand bonded to the nickel atom through both the carbon and sulfur atoms (**1b** in Figure 2) is predicted to be a relatively high energy structure, lying 18.6 kcal/mol (B3LYP) or 20.7 kcal/mol(BP86) above **11-1**.



11-1 ($C_{\infty v}$) **11-2** (C_s)

Figure 6. Optimized Ni(CS) structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

Table 4. Total Energies (E, hartrees) and Relative Energies (ΔE, kcal/mol) for the Ni(CS) Structures[a]

		11-1	11-2
B3LYP	$-E$	1944.57968	1944.60924
	ΔE	0.0	18.6
BP86	$-E$	1944.83615	1944.86917
	ΔE	0.0	20.7

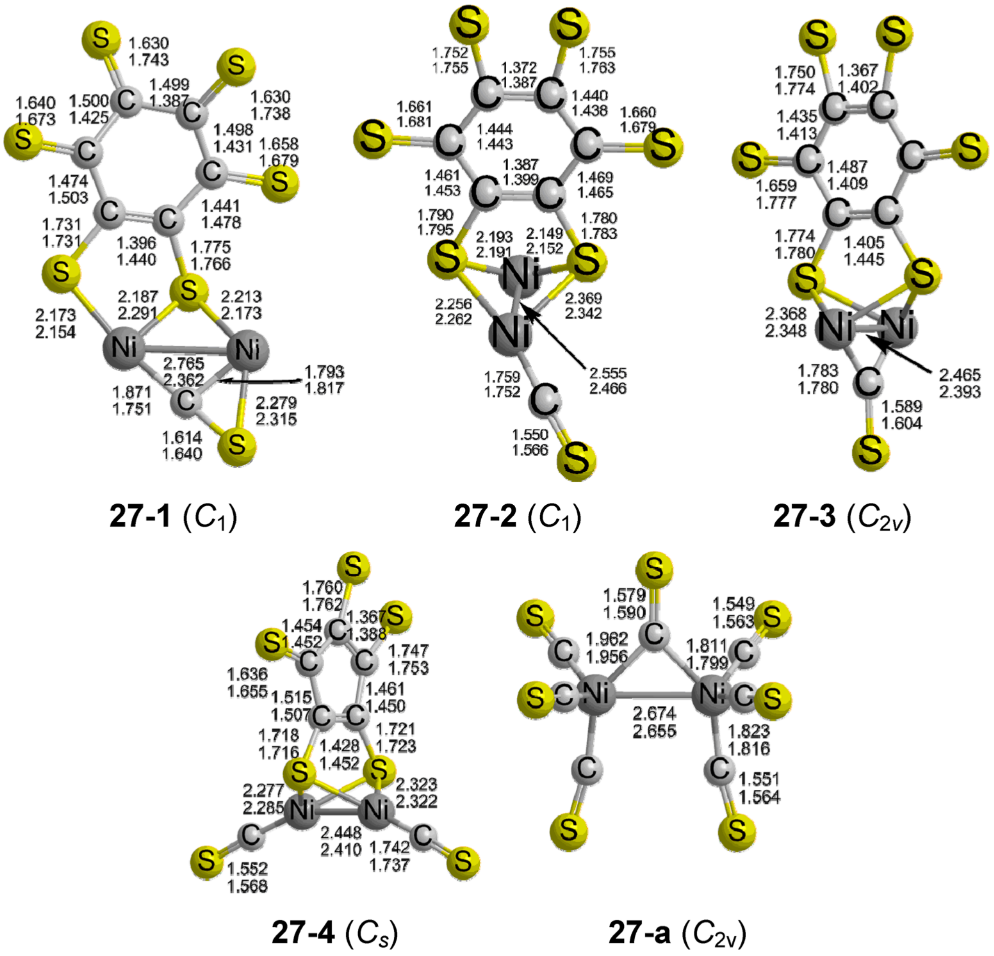
[a] Neither structure has any imaginary vibrational frequencies.

3.2. Binuclear Derivatives.

3.2.1. $Ni_2(CS)_7$ Structures.

A total of 22 structures have been optimized for $Ni_2(CS)_7$. However, only the four structures lying in energy within 18 kcal/mol of the lowest energy structure are discussed in this Article (Figure 7 and Table 5). The three lowest energy structures **27-1**, **27-2**, and **27-3** have related geometries. All of them are (η^2-C_6S_6)Ni(CS) structures, in which six of the CS groups are coupled to form a remarkable six-membered hexathiorhodizonate (cyclohexanehexathione) ring bridging the two nickel atoms through formation of Ni−S bonds. Structure **27-1** has a four-electron donor η^2-μ-CS group, structure **27-2** has a terminal CS group, and structure **27-3** has a bridging two-electron donor CS group. The Ni−Ni distances of ~2.5 Å in **27-1**, **27-2**, and **27-3** can correspond to formal single bonds. The B3LYP method predicts **27-2** and **27-3** to lie 0.9 and 11.9 kcal/mol in energy, respectively, above **27-1**. However, the BP86 method predicts **27-2** and **27-3** to be significantly higher energy structures, lying 11.0 and 26.2 kcal/mol, respectively, above **27-1**.

Structure **27-4** is an (η^2-C_5S_5)Ni$(CS)_2$ structure in which five of the CS groups have coupled to form an unprecedented pentathiocroconate (cyclopentanepentathione) ring bridging the two nickel atoms through formation of Ni−S bonds. This



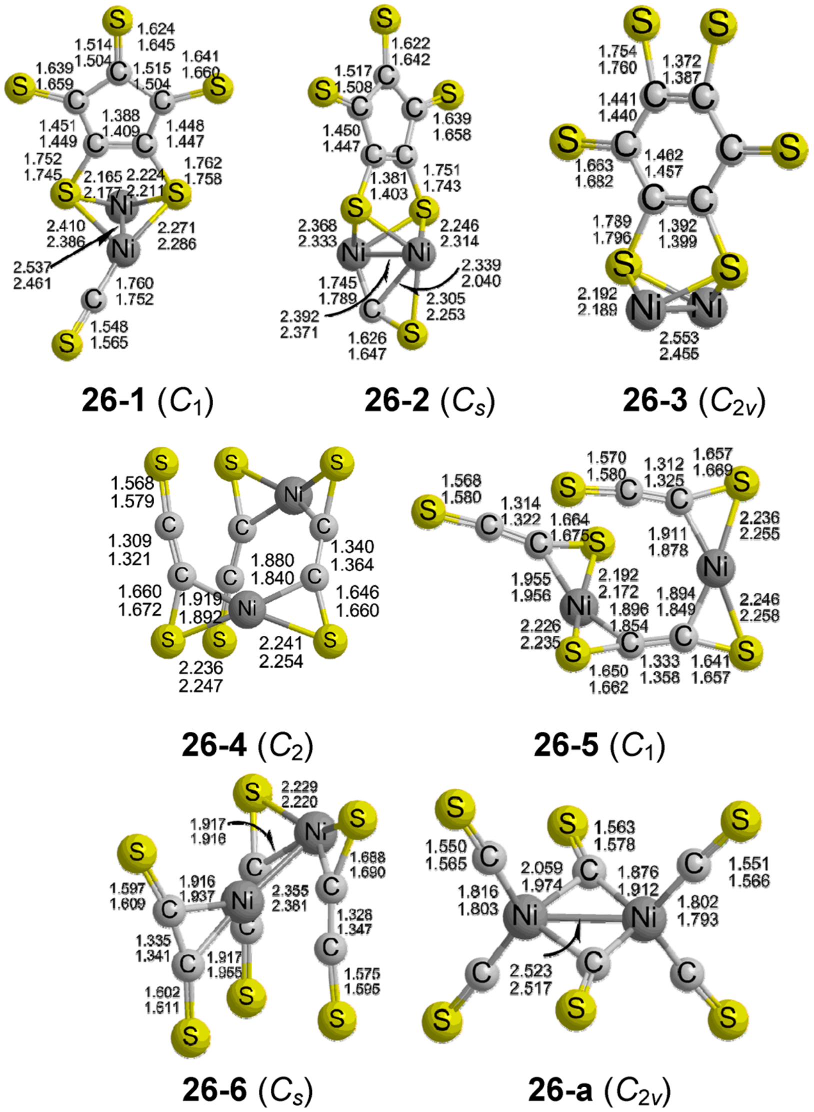
27-1 (C_1) **27-2** (C_1) **27-3** (C_{2v})

27-4 (C_s) **27-a** (C_{2v})

Figure 7. Four lowest energy $Ni_2(CS)_7$ structures and the model system **27-a**. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by B3LYP method and the lower distances by the BP86 method.

Table 5. Total Energies (E, hartrees), Relative Energies (ΔE, kcal/mol), and Numbers of Imaginary Vibrational Frequencies (N_{imag}) for the $Ni_2(CS)_7$ Structures

		27-1	27-2	27-3	27-4	27-a
B3LYP	$-E$	6070.78192	6070.780475	6070.762941	6070.759228	6070.646912
	ΔE	0.0	0.9	11.9	14.2	84.7
	N_{imag}	0	0	0	0	0
BP86	$-E$	6071.493746	6071.476212	6071.45196	6071.466452	6071.370481
	ΔE	0.0	11.0	26.2	17.1	77.4
	N_{imag}	0	0	1 (45*i*)	0	0



26-1 (C_1) **26-2** (C_s) **26-3** (C_{2v})

26-4 (C_2) **26-5** (C_1)

26-6 (C_s) **26-a** (C_{2v})

Figure 8. Optimized $Ni_2(CS)_6$ structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distance is predicted by the B3LYP method and the lower distance by the BP86 method.

bridging pentathiocroconate group, considered as a neutral ligand, donates a total of six electrons to the central Ni_2 unit. Each nickel atom is coordinated to one of the remaining CS groups, and the (SC)Ni–Ni(CS) plane is perpendicular to the five-membered ring. Interpreting the Ni–Ni distance of 2.448 Å (B3LYP) or 2.410 Å (BP86) as a formal single bond gives each nickel atom a 16-electron configuration.

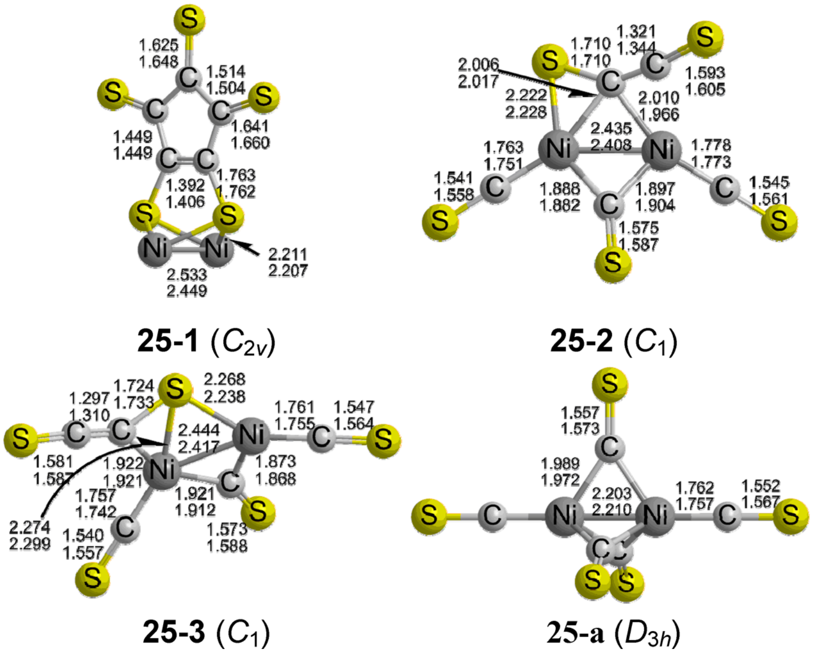
In order to compare the $Ni_2(CS)_7$ and $Ni_2(CO)_7$[12] systems, a special $Ni_2(CS)_7$ structure **27-a** with seven separate CS ligands analogous to the previously found[12] lowest energy $Ni_2(CO)_7$ structure was also optimized (Figure 7 and Table 5). However, structure **27-a** was found to be a very high energy structure, lying 84.7 kcal/mol (B3LYP) or 77.4 kcal/mol (BP86) above **27-1** and thus is highly unlikely to be observed experimentally. The thermodynamic instability of the sulfur analogue of $Ni_2(CO)_7$ is again related to the exergonic coupling reaction of CS molecules leading ultimately to pentathiocroconate. This result illustrates dramatically the enormous difference between CO and CS ligands.

3.2.2. *$Ni_2(CS)_6$ Structures.*

Seventeen structures were optimized for $Ni_2(CS)_6$. However, only the six structures lying in energy within 30 kcal/mol of the lowest energy

Table 6. Total Energies (*E*, hartrees), Relative Energies (Δ*E*, kcal/mol), and Numbers of Imaginary Vibrational Frequencies (N_{imag}) for the $Ni_2(CS)_6$ Structures

		26-1	26-2	26-3	26-4	26-5	26-6	26-a
B3LYP	−*E*	5634.48449	5634.47733	5634.47994	5634.46502	5634.45338	5634.44630	5634.39697
	Δ*E*	0.0	4.5	2.9	12.2	19.5	24.0	54.9
	N_{imag}	0	1 (16*i*)	0	0	0	0	0
BP86	−*E*	5635.14631	5635.14917	5635.13577	5635.13143	5635.12171	5635.14144	5635.09035
	Δ*E*	0.0	−1.8	6.6	9.3	15.4	3.1	35.1
	N_{imag}	0	0	0	0	0	0	0



25-1 (C_{2v})

25-2 (C_1)

25-3 (C_1)

25-a (D_{3h})

Figure 9. Optimized $Ni_2(CS)_5$ structures. The distances (Å) are predicted by the B3LYP and BP86 methods. The upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

structure are discussed in this Article (Figure 8 and Table 6). The two lowest energy structures **26-1** and **26-2** have related geometries and similar relative energies. The B3LYP method predicts **26-2** to lie 4.5 kcal/mol in energy above **26-1** whereas the BP86 method predicts **26-1** to lie 1.8 kcal/mol in energy above **26-2**. This suggests that these two structures are nearly degenerate in energy implying a possible fluxional system. Both **26-1** and **26-2** are (η^2-C_5S_5)Ni(CS) with a pentathiocroconate five-membered ring and are closely related to the lowest energy (η^2-C_5S_5)$Ni(CS)_2$ structure **27-4**. Structure **26-1** has a terminal CS group and can be derived from **27-4** by loss of a terminal CS group. However, **26-2** has a four-electron donor η^2-μ-CS group, instead of a terminal CS group. The Ni−Ni distances in **26-1** and **26-2** of ~2.4 Å are similar to those in **27-4**. Interpreting the Ni−Ni bonds as short formal single bonds in **26-1** gives the Ni atom bearing a CS group a 16-electron configuration and the other Ni atom a 14-electron configuration. In **26-2** each Ni atom has a 16-electron configuration.

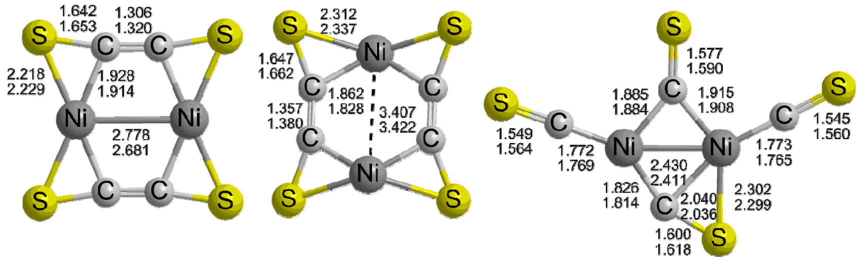
The $Ni_2(CS)_6$ structure **26-3** has a six-membered ring bridging the two Ni atoms through the formation of four Ni−S bonds (Figure 8 and Table 6). Structure **26-3** can be derived from the $Ni_2(CS)_7$ structure **27-2** by removal of the terminal CS group. The Ni−Ni bond distance of 2.553 Å (B3LYP) or 2.455 Å (BP86) can be interpreted as a formal single bond. This gives each nickel atom in **26-3** a 14-electron configuration. The $Ni_2(CS)_6$ structures **26-4** and **26-5** have similar geometries. Both structures have two terminal η^2-SCCS groups bonded to a nickel atom through their C−S bonds (**2a** in Figure 2), as well as one bridging η^2,η^2-SCCS group bonded to each nickel atom through C−S bonds (Figure 8 and Table 6). In **26-4**, lying 12.2 kcal/mol (B3LYP) or 9.3 kcal/mol (BP86) in energy above **26-1**, the two terminal η^2-SCCS groups are oriented in opposite directions. However, in **26-5**, lying 19.5 kcal/mol (B3LYP) or 15.4 kcal/mol (BP86) in energy above **26-1**, the two terminal η^2-SCCS groups are oriented in the same direction. The $Ni_2(CS)_6$ structure **26-6**, lying 24.0 kcal/mol (B3LYP) or 3.1 kcal/mol (BP86) above **26-1**, has three terminal η^2-SCCS groups (Figure 8 and Table 6). Two of them are bonded to one of the nickel atoms through their C−S bonds (**2a** in Figure 2), whereas the other η^2-SCCS group is bonded to the other nickel atom through its C−C bond (**2c** in Figure 2). This structure can be regarded as two fragments, Ni(SCCS) and $Ni(SCCS)_2$, linked solely by a Ni═Ni bond of predicted length of 2.355 Å (B3LYP) or 2.381 Å (BP86). This Ni═Ni bond is ~0.1 Å shorter than the Ni−Ni bonds in the other $Ni_2(CS)_7$ and $Ni_2(CS)_6$ structures and thus may be interpreted as a formal double bond.

In order to compare the $Ni_2(CS)_6$ and $Ni_2(CO)_6$ systems,[12] a special $Ni_2(CS)_6$ structure **26-a** with six separate CS ligands analogous to the previously found[12] lowest energy $Ni_2(CO)_6$ structure was optimized (Figure 8 and Table 6). However, structure **26-a** was predicted to be a very high energy structure,

Table 7. Total Energies (E, hartrees) and Relative Energies (ΔE, kcal/mol) for the $Ni_2(CS)_5$ Structures[a]

		25-1	25-2	25-3	25-a
B3LYP	$-E$	5198.18384	5198.17478	5198.16826	5198.13388
	ΔE	0.0	5.7	9.8	31.4
BP86	$-E$	5198.80576	5198.82062	5198.80993	5198.79668
	ΔE	9.3	0.0	6.7	15.0

[a] None of the structures has any imaginary vibrational frequencies.



24-1 (C_{2h}) **24-2** (C_{2h}) **24-3** (C_s)

Figure 10. Optimized $Ni_2(CS)_4$ structures. The distances (Å) and the relative energies (kcal/mol) are predicted by the B3LYP and BP86 methods. The upper distance is obtained by the B3LYP method and the lower distance by the BP86 method.

lying 54.9 kcal/mol (B3LYP) or 35.1 kcal/mol (BP86) above **26-1**.

3.2.3. $Ni_2(CS)_5$ Structures. A total of eight structures were optimized for $Ni_2(CS)_5$. However, only the three structures within 10 kcal/mol of the lowest energy structure are discussed in this Article (Figure 9 and Table 7). The B3LYP method predicts **25-1** to be the lowest energy structure with **25-2** lying 5.7 kcal/mol in energy above **25-1**. However, the BP86 method predicts **25-2** to be the global minimum with **25-1** lying 9.3 kcal/mol above **25-2**. Structure **25-1** has a five-membered pentathiocroconate ring bridging the two Ni atoms through the formation of four Ni—S bonds. Structure **25-1** can be derived from the $Ni_2(CS)_6$ structure **26-1** by removal of the terminal CS group. The pentathiocroconate five-membered ring in this structure donates six electrons to the Ni_2 unit through two S atoms. The Ni—Ni bond distance of 2.533 Å (B3LYP) or 2.449 Å (BP86) is slightly longer by ~0.08 Å than that in **26-1** but can still be interpreted as a formal single bond. This gives each nickel atom in **25-1** a 14-electron configuration.

The $Ni_2(CS)_5$ structure **25-2** has two terminal CS groups, one bridging CS group, and one bridging SCCS group (Figure 9 and Table 7). Each CS group is a two-electron donor. The bridging η^2-μ-SCCS group is a four-electron donor bonded to the Ni_2 unit through a C—S bond with the carbon atom bridging the two nickel atoms. Interpreting the Ni—Ni distance of 2.435 Å (B3LYP) or 2.408 Å (BP86) as a formal single bond gives each nickel atom a 16-electron configuration. Structure **25-3**, lying 9.8 kcal/mol above **25-1** (B3LYP) or 6.7 kcal/mol above **25-2** (BP86), is similar to **25-2** in geometry, but the sulfur atom rather than the carbon atom in the η^2-μ-SCCS group bridges the two nickel atoms.

In order to compare the $Ni_2(CS)_5$ and $Ni_2(CO)_5$ systems,[12] a special $Ni_2(CS)_5$ structure **25-a** with three bridging CS groups, two terminal CS groups, and D_{3h} symmetry analogous to the previously found[12] lowest energy $Ni_2(CO)_5$ structure was optimized (Figure 9 and Table 7). However, this beautifully symmetric structure was found to lie at the significantly higher energy of 31.4 kcal/mol above **25-1** (B3LYP) or 15.0 kcal/mol above **25-2** (BP86). The predicted Ni≡Ni distance of ~2.21 Å in **25-a** is the shortest among those in all of the $Ni_2(CS)_n$ (n = 4, 5, 6, 7) complexes and thus can be considered as a formal triple bond. This gives each nickel atom in **25-a** the favored 18-electron configuration.

3.2.4. $Ni_2(CS)_4$ Structures. A total of seven structures were found for $Ni_2(CS)_4$. However, only the three structures within 20 kcal/mol of the lowest energy structure are discussed in this Article (Figure 10 and Table 8). The lowest energy $Ni_2(CS)_4$ structure **24-1** is a D_{2h} planar structure with two bridging η^2,η^2-μ-SCCS groups. The BP86 method predicts a very small imaginary frequency at 28i cm^{-1}, whereas the B3LYP method predicts all real vibrational frequencies. The Ni—Ni distance of ~2.8 Å is short enough to suggest a direct interaction. The C_{2h} structure **24-2**, lying 11.9 kcal/mol (B3LYP) or 19.0 kcal/mol (BP86) in energy above **24-1**, is related to **24-1** with the nickel atoms bridged by two η^2,η^2-μ-SCCS groups. However, **24-2** is a nonplanar structure with a clearly nonbonding Ni·· ·Ni distance of ~3.4 Å. Structure **24-2** can also be described as an NiC_2NiC_2 hexagonal ring with the four Ni—C edges each bridged by a sulfur atom.

Table 8. Total Energies (E, hartrees), Relative Energies (ΔE, kcal/mol), and Numbers of Imaginary Vibrational Frequencies (N_{imag}) for the $Ni_2(CS)_4$ Structures

		24-1	24-2	24-3
B3LYP	$-E$	4761.91440	4761.89541	4761.88759
	ΔE	0	11.9	16.8
	N_{imag}	0	0	0
BP86	$-E$	4762.52980	4762.49945	4762.50070
	ΔE	0	19.0	18.3
	N_{imag}	1 (28i)	0	0

The next $Ni_2(CS)_4$ structure **24-3**, lying 16.8 kcal/mol (B3LYP) or 18.3 kcal/mol (BP86) in energy above **24-1**, has four separate CS ligands and is analogous to the a previously optimized[38] lowest energy $Ni_2(CS)_2(CO)_2$ structure (Figure 10 and Table 8). Structure **24-3** can be generated from **25-3** by loss of a CS moiety from the SCCS group. In this structure, the upper bridging CS ligand in **24-3** (Figure 10) is a one-electron donor to each Ni atom. However, the lower bridging CS ligand in **24-3** is an η^2-μ-CS ligand donating two electrons to each nickel atom. The remaining two CS ligands in **24-3** are two-electron donors bonded to each Ni atom through only the C atom (**1a** in Figure 1). The Ni−Ni distance in **24-3** is predicted to be 2.430 Å (B3LYP) or 2.411 Å (BP86), which is slightly shorter than that in **25-3** and can be interpreted as a formal single bond. This gives each Ni atom in **24-3** a 16-electron configuration.

3.3. Vibrational Frequencies.

The harmonic vibrational frequencies and infrared intensities for all of the structures were evaluated using both the B3LYP and BP86 methods. These results were initially used to determine if a structure is a genuine minimum. The ν(CS) stretching frequencies predicted using the BP86 method are listed in Table 9 for the mononuclear derivatives $Ni(CS)_n$ and in Table 10 for the binuclear derivatives $Ni_2(CS)_n$. The BP86 method was chosen for the ν(CS) frequencies since it has been shown to predict values close to the experimental results without using any scaling factors.[39,40] The ν(CS) frequencies for the usual type of terminal CS groups (bonded to the Ni atom solely through their carbon atoms) range from 1282 to 1371 cm^{-1}. In the binuclear $Ni_2(CS)_n$ derivatives the ν(CS) frequencies for bridging CS groups are significantly lower than those for terminal CS groups, falling in the narrow range from 1207 to 1228 cm^{-1}. The ν(CS) frequencies for side-on bonded η^2-CS groups in **13-5**, **12-2**, **11-2**, **26-1**, and **24-3** are still lower than those for bridging CS groups, ranging from 950 to 1122 cm^{-1}. The experimental ν(CS) frequencies ranging from 1286 to 1364 cm^{-1} for $Ni(CS)_4$ trapped in an argon matrix at 10 K[11] are consistent with structure **14-6** rather than lower energy isomers with coupled CS ligands.

Table 9. ν(CS) Vibrational Frequencies (cm^{-1}) and Corresponding Infrared Intensities (km/mol, in Parentheses) Predicted by the BP86 Method for $Ni(CS)_n$ (n = 4, 3, 2, 1)[a]

	ν(CS)
14-1	**1072(0)**, **1076(113)**, *1770(1079)*, *1836(89)*
14-2	**1064(88)**, **1067(0)**, *1763(2451)*, *1796(0)*
14-3	**1028(79)**, 1326(764), 1372(386), *1818(545)*
14-4	**961(41)**, , **1076(196)**, *1651(231)*,, *1882(41)*
14-5	**1045(13)**, **1058(108)**, *1667(1099)*, *1694(114)*
14-6	1293(913), 1293(913), 1293(913), 1355(0)
13-1	**972(43)**, 1369(536), *1872(12)*
13-2	1282(1064), 1282(1064), 1348(0)
13-3	**1056(123)**, 1340(708), *1483(35)*
13-4	**1038(160)**, 1323(687), *1697(90)*
13-5	1011(61), 1306(880), 1353(296)
12-1	1282(1251), 1361(49)
12-2	1065(173), 1331(631)
12-3	**1064(258)**, *1544(206)*
11-1	1370(254)
11-2	950(59)

[a] For the coupled SCCS ligands, the ν(CS) frequencies for the symmetric CS stretching are in bold type, and those for the asymmetric CS stretching are in italics.

Table 10. ν(CS) Vibrational Frequencies and Corresponding Infrared Intensities (in Parentheses) Predicted by the BP86 Method for $Ni_2(CS)_n$ (n = 4, 5, 6, 7)[a]

	ν(CS)
27-1	1089(39), 1107(10), 1120(324), 1165(109), 1267(50), 1271(3), 1349(99), 1525(84)
27-2	1090(3), 1136(97), 1202(194), 1258(3), 1316(74), 1324(1155), 1409(186), 1524(20)
27-3	1042(1), 1131(45), 1193(519), 1280(23), 1283(71), 1372(0), 1499(21),, 1523(2)
27-4	1141(91),, 1195(26), 1294(252), 1299(75), 1321(1487), 1335(670), 1447(86)
26-1	1184(21), 1188(102),, 1264(183), 1294(6),, 1325(1163), 1364(37)
26-2	1082(6), 1183(20), 1202(60), 1272(165), 1310(2), 1386(36)
26-3	1083(11), 1137(85), 1175(286), 1254(0), 1310(40), 1408(171), 1525(16)
26-4	**974(65)**, **1066(2)**, **1076(65)**, *1526(392)*, *1727(686)*, *1754(237)*
26-5	**974(57)**, **1062(74)**, **1069(31)**, *1545(473)*, *1715(940)*, *1778(811)*
26-6	**992(2)**, **1001(80)**, **1071(99)**, *1629(563)*, *1654(366)*, *1719(396)*
25-1	1177(24), 1188(115), 1255(222), 1287(1), 1371(36)
25-2	**974(115)**, 1211(235), 1325(1045), 1355(504), *1660(278)*
25-3	**1016(48)**, 1210(237), 1327(1365), 1359(371), *1798(1045)*
24-1	**1012(126)**, **1018(0)**, *1685(1645)*, *1840(0)*
24-2	**958(0)**, **961(182)**, *1422(706)*, *1486(0)*
24-3	1122(403), 1207(185), 1319(1437), 1345(178)

[a] The ν(CS) frequencies for the symmetric CS stretching in SCCS coupling are in bold type, and those for asymmetric CS stretching are in italics. The ν(CS) frequencies for the pentathiocroconate and hexathiorhodizonate ligands are underlined.

The coupled SCCS groups are characterized by a pair of ν(CS) frequencies, namely, a low asymmetric CS stretching frequency and a much higher symmetric CS stretching frequency. The latter frequencies involve some stretching of the CC bond as well as the CS bond. The values of these ν(CS) frequencies depend somewhat on the mode of bonding of the SCCS group to the nickel atom. Thus, for terminal η^2-SCCS groups bonded to a nickel atom through a CS bond, the asymmetric ν(CS) frequencies range from 1002 to 1076 cm^{-1} and the symmetric ν(CS) frequencies from 1700 to 1818 cm^{-1}. For terminal η^2-SCCS groups bonded to a nickel atom through the CC bond, the asymmetric ν(CS) frequencies are similar, ranging from 984 to 1076 cm^{-1}, but the symmetric ν(CS) frequencies are significantly lower ranging from 1614 to 1697 cm^{-1}. For the tetrahapto η^4-SCCS groups in **14-4** and **13-1**, the spread between the asymmetric and symmetric ν(CS) frequencies is wider with asymmetric ν(CS) frequencies of 961 and 972 cm^{-1} and symmetric ν(CS) frequencies of 1882 and 1872 cm^{-1}, respectively. The pentathiocroconate η^2-C_5S_5 ligand in **27-4**, **26-1**, **26-2**, and **25-1** exhibits five ν(CS) frequencies in the narrow ranges 1162 ± 21, 1195 ± 7, 1279 ± 15, 1298 ± 12, and 1405 ± 21 cm^{-1}. Similar ν(CS) frequencies are found for the hexathiorhodizonate η^2-C_6S_6 ligand in **27-1**, **27-2**, **27-3**, and **26-3**. These results suggest that the values of the ν(CS) frequencies can be used to deduce the nature of the bonding of a SCCS ligand to a metal atom.

3.4. Dissociation Energies.

Table 11 reports the bond dissociation energies (BDEs) in terms of the single thiocarbonyl dissociation steps

$$Ni(CS)_n \rightarrow Ni(CS)_{n-1} + CS \quad (n = 4, 3, 2) \tag{1}$$

$$Ni_2(CS)_m \rightarrow Ni_2(CS)_{m-1} + CS \quad (m = 7, 6, 5) \tag{2}$$

The BDE for the loss of CS from the mononuclear $Ni(CS)_4$ (**14-1**) is 40.6 kcal/mol (B3LYP). The BDEs for CS losses from the mononuclear $Ni(CS)_n$ (n = 3, 2) are even larger, e.g., 74.5 kcal/mol (B3LYP) for $Ni(CS)_2$. The BDEs for loss of CS

Table 11. Bond Dissociation Energies (BDE, kcal/mol) for Successive Removal of Carbonyl Groups from the Lowest Energy $Ni(CS)_n$ (n = 4, 3, 2) and $Ni_2(CS)_m$ (m = 7, 6, 5) Structures[a]

	B3LYP	BP86
$Ni(CS)_4 \rightarrow Ni(CS)_3 + CS$	40.6	53.6
$Ni(CS)_3 \rightarrow Ni(CS)_2 + CS$	47.6	49.0
$Ni(CS)_2 \rightarrow Ni(CS) + CS$	74.5	85.2
$Ni_2(CS)_7 \rightarrow Ni_2(CS)_6 + CS$	52.5	68.0
$Ni_2(CS)_6 \rightarrow Ni_2(CS)_5 + CS$	54.5	63.7
$Ni_2(CS)_5 \rightarrow Ni_2(CS)_4 + CS$	34.9	23.1

[a] All dissociation energies refer to global minima.

from the binuclear $Ni_2(CS)_m$ (m = 7, 6, 5) are somewhat lower but still substantial. Thus, the BDE for loss of CS from $Ni_2(CS)_5$ is 34.9 kcal/mol (B3LYP).

Table 12 shows the dissociation energies for binuclear derivatives into mononuclear fragments. The lowest dissociation energy for processes of this type is 43.7 kcal/mol (B3LYP) from $Ni_2(CS)_5$ to $Ni(CS)_3$ + $Ni(CS)_2$. This is much higher than the previously reported[16] dissociation energies for the $Ni_2(CO)_n$ (n = 7, 6) analogues into $Ni(CO)_4$ + $Ni(CO)_{n-4}$. This may relate to the presence of pentathiocroconate η^2-C_5S_5 ligands in the lowest energy $Ni_2(CS)_n$ (n = 7, 6, 5) structures. Dissociation of such structures into mononuclear $Ni(CS)_n$ fragments necessarily requires rupture of carbon−carbon bonds in the pentathiocroconate ligand.

Table 12. Dissociation Energies (kcal/mol) for the Binuclear Complexes $Ni_2(CS)_n$ (n = 7, 6, 5, 4) into Two Mononuclear Fragments

	B3LYP	BP86
$Ni_2(CS)_7 \rightarrow Ni(CS)_4 + Ni(CS)_3$	62.5	70.7
$Ni_2(CS)_6 \rightarrow Ni(CS)_4 + Ni(CS)_2$	57.6	51.8
$Ni_2(CS)_6 \rightarrow Ni(CS)_3 + Ni(CS)_3$	50.6	56.4
$Ni_2(CS)_5 \rightarrow Ni(CS)_3 + Ni(CS)_2$	43.7	41.8
$Ni_2(CS)_5 \rightarrow Ni(CS)_4 + Ni(CS)$	77.7	73.3
$Ni_2(CS)_4 \rightarrow Ni(CS)_3 + Ni(CS)$	83.3	103.8
$Ni_2(CS)_4 \rightarrow Ni(CS)_2 + Ni(CS)_2$	56.4	67.7

The dissociation energy of $Ni_2(CS)_5$ into $Ni(CS)_3$ and $Ni(CS)_2$ is substantial at 43.7 kcal/mol (B3LYP) and that into $Ni(CS)_4$ + $Ni(CS)$ is even larger at 77.7 kcal/mol (B3LYP). The much higher dissociation energy for $Ni_2(CS)_4$ into mononuclear fragments $Ni(CS)_3$ and $Ni(CS)$ is even higher at 83.3 kcal/mol (B3LYP). This may be relate to two "handrail" SCCS groups in **24-1**, which strengthen the interaction between the two mononuclear fragments.

4. SUMMARY

The conventional mononuclear $Ni(CS)_4$ with tetrahedrally coordinated nickel analogous to the well-known stable $Ni(CO)_4$ is predicted to be disfavored by ∼17 kcal/mol relative to isomeric $Ni(C_2S_2)_2$ structures in which the CS ligands couple pairwise through C−C bond formation to give dimeric S═C═C═S ligands. The novel lowest energy $Ni(C_2S_2)_2$ structures have their C_2S_2 ligands bonded to the nickel atom through their C═S double bonds rather than their C═C double bond. Coupling of CS ligands is also found in isomers of the coordinately unsaturated $Ni(CS)_n$ (n = 3, 2). However, such coupled products are less energetically favorable than those with $Ni(CS)_4$.

Coupling of CS ligands in the lowest energy binuclear $Ni_2(CS)_n$ (n = 7, 6, 5) structures occurs to a greater extent to give unprecedented C_nS_n (n = 5, 6) ligands containing five- and six-membered carbocyclic rings. Such ligands, which are the sulfur analogues of the well-known croconate (n = 5) and rhodizonate (n = 6) oxocarbon ligands, function as bidentate ligands to the central Ni_2 unit. Higher energy $Ni_2(CS)_n$ (n = 7, 6, 5) structures contain dimeric C_2S_2 ligands, which can bridge the central Ni_2 unit. Dimeric C_2S_2 ligands rather than tetrathiosquare C_4S_4 ligands are found in the lowest energy $Ni_2(CS)_4$ structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables S1−S8 listing the total energies (E, hartrees), relative energies (ΔE, kcal/mol), relative energies corrected by ZPE (ΔE_{ZPE}, kcal/mol), numbers of imaginary frequencies (N_{imag}) for the optimized structures of $Ni(CS)_n$ (n = 4, 3, 2, 1) and $Ni_2(CS)_n$ (n = 7, 6, 5, 4) by B3LYP and BP86 methods, Figure S1−S8 showing the optimized structures of $Ni(CS)_n$ (n = 4, 3, 2, 1) and $Ni_2(CS)_n$ (n = 7, 6, 5, 4), Tables S9−S16 listing harmonic vibrational frequencies (cm^{-1}) and corresponding infrared intensities (in parentheses) predicted by the BP86 method for the optimized structures $Ni(CS)_n$ (n = 4, 3, 2, 1) and $Ni_2(CS)_n$ (n = 7, 6, 5, 4), Table S17 listing ν(CS) stretching frequencies predicted for mononuclear $Ni(CS)_n$ (n = 4, 3, 2, 1) by the BP86 method, Table S18 listing ν(CS) stretching frequencies predicted for binuclear $Ni_2(CS)_n$ (n = 7, 6, 5, 4) by BP86 method, Tables S19−S26 listing Cartesian coordinates for the optimized structures $Ni(CS)_n$ (n = 4, 3, 2, 1) and $Ni_2(CS)_n$ (n = 7, 6, 5, 4) by B3LYP and BP86 methods, and text providing the complete Gaussian 09 reference (ref 32). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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