Synthesis and Stereochemical Analysis of $[Ni_3(\eta^5\text{-}C_5H_4Me)_3]_2(C_2S_6)$ Containing the Previously Unknown Hexathioethane Ligand, $C_2S_6^{6-}$: Crystallographic Redetermination and Structural Reformulation of the Crystal-Disordered $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)$ as $[Ni_3(\eta^5\text{-}C_5H_5)_3]_2(C_2S_6)$

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In connection with an attempt to synthesize the methylcyclopentadienyl analogue of the 53-electron $Ni_3Cp_3(\mu_3\text{-}S)_2$ (where Cp denotes $\eta^5\text{-}C_5H_5$), an intriguing minor product, $[Ni_3Cp'_3]_2(C_2S_6)$ (**1**, where Cp′ denotes $\eta^5\text{-}C_5H_4Me$), was isolated in ca. 2% yield from the reaction between $Ni_2Cp'_2(\mu_2\text{-}CO)_2$ and CS_2. The stoichiometry and stereochemistry of this air- and moisture-sensitive brown solid, which is only slightly soluble in benzene and toluene but highly soluble in THF, were unambiguously determined from single-crystal X-ray crystallographic and mass spectral measurements. Anisotropic least-squares refinement of **1** under triclinic $P\bar{1}$ symmetry converged at $R(F) = 3.08\%$, $R_w(F) = 3.56\%$, GOF = 1.38 for 3891 independent reflections ($|F| > 3\sigma(F)$) with a data-to-parameter ratio of 14.81/1. The molecular configuration of the crystal-ordered **1** of crystallographic $C_i\text{-}\bar{1}$ site symmetry is composed of two identical chairlike Ni_3S_3 moieties connected by two central ethane carbon atoms, which are each bonded in a tetrahedral-like configuration to the other carbon and three sulfur atoms. The resulting $Ni_6(C_2S_6)$ architecture, which closely conforms to $C_{2h}\text{-}2/m$ symmetry, can be described as orginating from a bidentate linkage of six $[NiCp']^+$ ion fragments to a formal hexathioethane $C_2S_6^{6-}$ hexaanion, which is formed from an initial metal-promoted head-to-head reductive dimerization of CS_2. The observed configuration is a consequence of two different modes of metallo-dithio chelation to the trigonal-antiprismatic array of sulfur atoms in the C_2S_6 ligand, viz., two end-on 1,1′-dithio chelating NiS_2C ring linkages and four side-on 1,2-dithio chelating NiS_2C_2 ring linkages. The pseudo-$C_{2h}\text{-}2/m$ symmetry of the $Ni_6(C_2S_6)$ core, which is reduced to the observed crystallographic $C_i\text{-}\bar{1}$ site symmetry by the inclusion of the C_5H_4Me rings, accounts for the ^1H NMR spectrum of **1** exhibiting two different Cp′ signals in a 4:2 ratio. Each Ni(II) conforms to an 18-electron count (i.e., the EAN rule) without invoking any metal–metal bonds. The geometries of the hexathioethane fragment in **1** and in hexakis(phenylthio)ethane, $C_2(SPh)_6$, are compared. This identification of the previously unknown C_2S_6 ligand in **1** led to the realization that the "averaged structure" of the crystal-disordered $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ (**1a**) was incorrectly formulated. A structural redetermination of **1a**, which included a detailed modeling of the crystal-disordered electron density of **1a** in terms of two mirror-related orientations of the crystal-ordered $Ni_6(C_2S_6)$ core of **1**, substantiated our premise that **1a** should be reformulated as $[Ni_3Cp_3]_2(C_2S_6)$. Nevertheless, the original proposal that **1a** is formed by the cycloaddition of a $(CpNi)_2S$ fragment across each of the two pairs of sulfur-containing atoms of the planar tetrathiolene-like $Ni_2Cp_2(C_2S_4)$ precursor is still considered to be valid and also applicable to **1**. The revised connectivity in **1a** additionally requires concomitant bonding of the S atom in each of the $(CpNi)_2S$ fragments to one of the C atoms of the C_2S_4 ligand, thereby forming the hexathioethane C_2S_6 ligand.

Introduction

The synthesis and structural characterization of $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ (**1a**) (where Cp denotes $\eta^5\text{-}C_5H_5$) reported by Maj et al.[2] in 1982 was the impetus for a highly fruitful area of research in our laboratories involving metal-promoted head-to-head reductive coupling of CS_2. Refinement of this complex in the centrosymmetric *Pbcm* space group with crystallographic molecular site symmetry $C_s\text{-}m$ gave a crystal-disordered structure. This compound was deduced to be an insertion product formed by the cycloaddition of a CpNi–S–NiCp fragment across each of the pairs of nickel-chelated sulfur atoms of the planar $NiS_2C_2S_2Ni$ moiety in $Ni_2Cp_2(C_2S_4)$, which contains the previously unknown bis(1,2-dithiolene-like) metal-bridging C_2S_4 ligand. The fact that formulation of the C_2S_4-bridged ligand necessitated a reductive head-to-head dimerization of CS_2 led us to try the corresponding reaction of $Ni_2Cp^*_2(\mu_2\text{-}CO)_2$ (where Cp* denotes $\eta^5\text{-}C_5Me_5$) with neat CS_2; our hope that the analogous $Ni_2Cp^*_2(C_2S_4)$ would form but that the bulky pentamethylcyclopentadienyl ligands would prevent further cycloaddition was realized. The resulting formation of $Ni_2Cp^*_2(C_2S_4)$, a metal bis(1,2-dithiolene-like) complex, via a metal-promoted reductive coupling of CS_2 was unprecedented. Further work in this area in our laboratories has led to the synthesis and experimental–theoretical studies of $Co_2Cp^*_2(C_2S_4)$,[3,4] $Fe_2Cp^*_2(CO)_2(C_2S_4)$,[3,5] and $[TiCp_2]_2(C_2S_4)$,[6] which represent additional examples of C_2S_4-bridged dimetal com-

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plexes resulting from reductive head-to-head dimerizations of CS_2.

Presented herein are the synthesis and X-ray structural characterization of $[Ni_3Cp'_3]_2(C_2S_6)$ (1, where Cp′ denotes η^5-C_5H_4Me), which contains the first recognized example of the hexathioethane ligand, $C_2S_6^{6-}$, in a metal complex. This compound was an unexpected byproduct of our efforts to prepare the methylcyclopentadienyl analogue of $Ni_3Cp_3(\mu_3\text{-}S)_2$[7] by the reaction of $Ni_2Cp'_2(\mu_2\text{-}CO)_2$ with carbon disulfide. This same reaction produced (in 10–30% yields) three major products, viz., the Fischer–Palm analogue, $Ni_3Cp'_3(\mu_3\text{-}CO)_2$, and $Ni_3Cp'_3(\mu_3\text{-}CS)(\mu_3\text{-}CO)$ and $Ni_3Cp'_3(\mu_3\text{-}CS)_2$, which contain the rare triply bridging thiocarbonyl ligand; a comparative experimental/theoretical analysis of these Cp′-containing triangular metal clusters and their Cp-containing counterparts is presented in the preceding paper.[8]

The structural characterization of the crystal-ordered 1 led to the realization that the geometry of its $Ni_6(C_2S_6)$ core represented the geometry of the corresponding core in the crystal-disordered 1a. A structural redetermination of $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ (1a) was then undertaken. A modelling of its crystal-disordered electron density in terms of two mirror-related, half-weighted orientations of the crystal-ordered $Ni_6(C_2S_6)$ core of 1 substantiated the reformulation of 1a as $[Ni_3Cp_3]_2(C_2S_6)$. Details of this analysis including the least-squares re-refinement are also given here.

Experimental Section

General Techniques and Materials. Proton NMR data were obtained with a Bruker WP200 FT-NMR spectrometer. Chemical shifts were referenced indirectly to TMS via residual proton signals in the deuterated solvent. Mass spectra were obtained with an EXTREL FTMS-2000 laser desorption Fourier-transform (LD/FT) mass spectrometer; details of the instrumentation and procedure are given elsewhere.[9]

Preparation and General Properties of $[Ni_3(\eta^5\text{-}C_5H_4Me)_3]_2(C_2S_6)$ (1). $[Ni_3Cp_3]_2(C_2S_6)$ was isolated as a minor product (~2%) from the reaction between $Ni_2Cp'_2(\mu_2\text{-}CO)_2$ and CS_2. In a typical preparation, 1.00 g (3.01 mmol) of $Ni_2Cp'_2(\mu_2\text{-}CO)_2$ was slowly added to 75 mL of CS_2 under a N_2 purge. The reaction mixture was refluxed for 1 h, at which time an IR spectrum showed that all the nickel dimer had been consumed. During the course of the reaction, the solution turned from red to brown. The CS_2 was removed under vacuum; exhaustive extraction of the resulting products with toluene, followed by THF, gave a black NiS residue.

The toluene extract yielded the major products of the reaction: $Ni_3Cp'_3(\mu_3\text{-}CO)_2$ (~20%), $Ni_3Cp'_3(\mu_3\text{-}CS)(\mu_3\text{-}CO)$ (~30%), and $Ni_3Cp'_3(\mu_3\text{-}CS)_2$ (~10%). These compounds are discussed elsewhere.[8]

The THF extract of the reaction residue was reduced in volume and loaded directly onto a chromatographic column containing oxygen-free silica gel packed with THF. A faint green band was eluted quickly from the column with THF. A brown band followed more slowly, and after solvent removal yielded $[Ni_3Cp'_3]_2(C_2S_6)$ (1, ~2%).

$[Ni_3Cp'_3]_2(C_2S_6)$ forms an air- and moisture-sensitive brown solid that is soluble in polar organic solvents and slightly soluble in benzene and toluene. Although mass spectral measurements obtained via laser desorption with a pulsed infrared CO_2 laser did not exhibit a parent-ion peak, $[M]^+$, other fragment ion peaks substantiated the molecular formula. The heaviest mass peak that was assignable in the positive ion mass spectrum was at m/z 964 and corresponds to the $[M - Cp']^+$ ion (i.e., the loss of a Cp′ ligand from the parent ion). The base peak in every spectrum recorded was at m/z 426, corresponding to the $[Ni_2Cp'_2(C_2S_4)]^+$ ion. It is reasonable to assume that this ion is formed from the fragmentation of 1; however, the possibility that this ion may be due to $Ni_2Cp'_2(C_2S_4)$ as an impurity in the sample has not been conclusively ruled out. A ^1H NMR spectrum in C_6D_6 exhibited resonances corresponding to the six Cp′ ligands possessing two different molecular environments in a 4:2 ratio. Complicated AA′BB′ patterns were observed at [δ 5.18 (m, 2 H) δ 5.11 (m, 2 H)] and [δ 4.98 (m, 4 H), δ 4.89 (m, 4 H)] for the ring protons, and resonances corresponding to the methyl protons were observed at δ 1.57 (s, 3 H) and δ 1.53 (s, 6 H).

Table I. Crystal Data, Data Collection, and Refinement Parameters for $[Ni_3Cp'_3]_2(C_2S_6)$ (1)

formula wt, g/mol	1043.42
cryst syst	triclinic
a, b, c, Å	9.649 (1), 9.722 (1), 11.614 (1)
α, β, γ, deg	103.94 (1), 99.61 (1), 109.44 (1)
vol, Å^3	960.2 (2)
space group	$P\bar{1}$
Z	1
d_{calcd}, g/cm^3	1.80
temp, °C	−85
μ, cm^{-1}	32.4
scan mode	ω
2θ limits, deg	3.0–55.0
scan speed, deg/min.	variable; 3.0–29.3
backgrd anal.	profile
no. of check reflns/freq	3/47
no. of data collected	4671 in 4 octants
no. of indep data, $\|F\| > 3\sigma(F)$	3891
no. of params refined	263
data/parameter ratio	14.8/1
$R(F)$,[a] $R_w(F)$[b]	3.08%, 3.56%
GOF[c]	1.38

[a] $R(F) = R_1(F) = [\sum(||F_o| - |F_c||)/\sum|F_o|] \times 100$. [b] $R_w(F) = R_2(F) = [\sum w_i(||F_o| - |F_c||)^2/\sum w_i(|F_o|)^2]^{1/2} \times 100$.

X-ray Structural Analysis. Crystal Structure of $[Ni_3Cp'_3]_2(C_2S_6)$ (1). Black single crystals of 1 were grown from a slowly evaporating THF solution under N_2. An irregularly shaped block of dimensions 0.45 × 0.35 × 0.28 mm was immobilized with epoxy glue inside an argon-filled Lindemann glass capillary, which was then flame-sealed. Intensity data were collected on a Siemens P3/F diffractometer with graphite-monochromated Mo Kα radiation. Axial photographs were taken to confirm lattice lengths and cell symmetry. Refined triclinic lattice constants were then determined from 25 well-centered reflections that were obtained from a thin shell of high-angle data collected at maximum scan speed. Crystal data, data collection, and refinement parameters are summarized in Table I. The intensities of three standard reflections, which were monitored after every 47 reflections, showed less than 1% variations during the course of data collection. An empirical absorption correction based on 252 ψ-scan measurements was applied to the intensity data via the XEMP program in the SHELXTL package. The value for R_{merge} improved from 3.14% to 2.16% for the ψ scan data, while $R(F)$ for all data decreased by ca. 1%.

The crystal structure was found to conform to centrosymmetric triclinic symmetry $P\bar{1}$ with the single molecule in the unit cell situated on a crystallographic inversion center. The positions of the nickel atoms were located by direct methods and those of all other atoms except for the methyl hydrogens by successive Fourier difference maps. All non-hydrogen and ring hydrogen atoms were refined without constraints. Idealized positions for the methyl hydrogen atoms were initially calculated and then refined as rigid groups with their positional parameters moving with those of the attached carbon atom. All nonhydrogen atoms were refined anisotropically; isotropic temperature factors for all hydrogen atoms were fixed at $U = 0.08$ Å^2. A final electron-density difference map showed no residual peaks greater than 1.0 e/Å^3.

All calculations were performed on a DEC MicroVax II system with the SHELXTL-Plus program package. Neutral atomic scattering factors were used with anomalous dispersion corrections

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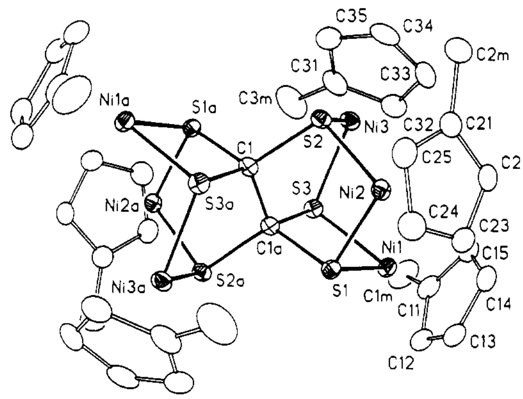

Figure 1. $[Ni_3Cp'_3]_2(C_2S_6)$ (1) which has crystallographic C_i-$\bar{1}$ site symmetry. All atomic thermal ellipsoids are drawn at the 50% probability level.

for all non-hydrogen atoms. Interatomic distances and selected bond angles are presented in Table II. Positional parameters, anisotropic thermal parameters, other bond angles for the non-hydrogen atoms, and coordinates and isotropic temperature factors for the hydrogen atoms are available as supplementary material (see paragraph at end of paper).

Re-refinement of the Crystal-Disordered $[Ni_3Cp_3]_2(C_2S_6)$ (1a) with Its $Ni_6(C_2S_6)$ Core Analogous to That in $[Ni_3(Cp'_3]_2(C_2S_6)$ (1). Best results were obtained by modeling the atomic coordinates of the $Ni_6(C_2S_6)$ core of **1a** to those obtained from the triclinic structure of 1.[10-14] The resulting positional parameters of **1a** were then refined under *Pbcm* symmetry with a second disordered molecular orientation generated by the mirror-plane symmetry. The $Ni_6(C_2S_6)$ core was initially refined as a rigid group, but the constraints were removed in the later stages of the refinement. On the basis of their normal atomic thermal ellipsoids the positions of the independent S(1), S(2), Ni(1), and Ni(2) atoms are superimposed in the two mirror-disordered orientations; these atoms were refined with anisotropic thermal parameters and with the positions of the Ni(1) and Ni(2) atoms fixed on the mirror plane. All other atoms in the $Ni_6(C_2S_6)$ core are disordered between two mirror-related positions and were thus refined isotropically with site-occupancy factors fixed at one-half. The solvated benzene molecule and each of the three independent crystal-disordered Cp rings were constrained to their well-known geometries and refined as rigid groups with anisotropic thermal parameters; this anisotropic thermal refinement of each crystal-disordered Cp ligand in an "averaged orientation" did not give rise to any carbon atom becoming nonpositive definite. This final refinement converged with $R(F) = 10.5\%$, $R_w(F) = 11.6\%$, and a data-to-parameter ratio of 6.1/1 for the 1259 independent data with $I > 2\sigma(I)$. A final difference Fourrier map revealed no unusual features with no peaks greater or less than 1.1 e/Å^3; the highest residual positive peaks were located near atomic positions. The relatively high discrepancy factors are readily attributed to the crystal-disorder problem. Tables of positional and thermal parameters for the non-hydrogen atoms, interatomic diatances, and bond angles are available as supplementary material.

Table II. Selected Interatomic Distances and Bond Angles for $[Ni_3Cp'_3]_2(C_2S_6)$ (1)

Distances, Å			
Ni(1)–S(1)	2.177 (1)	Ni(1)–S(3)	2.166 (1)
Ni(2)–S(1)	2.179 (1)	Ni(2)–S(2)	2.172 (1)
Ni(3)–S(2)	2.178 (1)	Ni(3)–S(3)	2.177 (1)
S(1)–C(1A)	1.841 (3)	S(2)–C(1)	1.822 (3)
S(3)–C(1A)	1.837 (3)	C(1)–S(1A)	1.841 (3)
C(1)–S(3A)	1.837 (3)	C(1)–C(1A)	1.502 (6)
Ni(1)–C(11)	2.109 (3)	Ni(1)–C(12)	2.139 (4)
Ni(1)–C(13)	2.093 (4)	Ni(1)–C(14)	2.166 (3)
Ni(1)–C(15)	2.147 (4)	Ni(2)–C(21)	2.110 (3)
Ni(2)–C(22)	2.146 (3)	Ni(2)–C(23)	2.087 (3)
Ni(2)–C(24)	2.136 (3)	Ni(2)–C(25)	2.159 (3)
Ni(3)–C(31)	2.171 (3)	Ni(3)–C(32)	2.095 (4)
Ni(3)–C(33)	2.128 (4)	Ni(3)–C(34)	2.083 (4)
Ni(3)–C(35)	2.184 (4)	C(11)–C(12)	1.419 (5)
C(11)–C(15)	1.431 (4)	C(11)–C(1M)	1.500 (4)
C(12)–C(13)	1.415 (3)	C(13)–C(14)	1.431 (5)
C(14)–C(15)	1.391 (4)	C(21)–C(22)	1.412 (5)
C(21)–C(25)	1.442 (5)	C(21)–C(2M)	1.503 (5)
C(22)–C(23)	1.408 (5)	C(23)–C(24)	1.441 (5)
C(24)–C(25)	1.385 (5)	C(31)–C(32)	1.444 (5)
C(31)–C(35)	1.387 (6)	C(31)–C(3M)	1.489 (4)
C(32)–C(33)	1.407 (4)	C(33)–C(34)	1.404 (6)
C(34)–C(35)	1.434 (4)		
Bond Angles, deg			
Ni(1)–S(1)–Ni(2)	100.7 (1)	S(1)–Ni(2)–S(2)	94.2 (1)
Ni(1)–S(3)–Ni(3)	103.7 (1)	S(2)–Ni(3)–S(3)	93.7 (1)
Ni(2)–S(2)–Ni(3)	109.2 (1)	S(1)–Ni(1)–S(3)	81.6 (1)
Ni(1)–S(1)–C(1A)	87.8 (1)	Ni(2)–S(2)–C(1)	97.0 (1)
Ni(1)–S(3)–C(1A)	88.2 (1)	Ni(3)–S(2)–C(1)	95.6 (1)
Ni(2)–S(1)–C(1A)	100.3 (1)	S(1A)–C(1)–C(1A)	111.7 (2)
Ni(3)–S(3)–C(1A)	100.6 (1)	S(3A)–C(1)–C(1A)	111.1 (3)
S(2)–C(1)–S(1A)	112.4 (2)	S(2)–C(1)–C(1A)	108.2 (3)
S(2)–C(1)–S(3A)	112.4 (1)	S(1A)–C(1)–S(3A)	100.9 (1)

Results and Discussion

Structural and Electronic Features of $[Ni_3Cp'_3]_2(C_2S_6)$ (1). This molecular compound contains one molecule with crystallographic C_i-$\bar{1}$ site symmetry in the triclinic unit cell. Figure 1 shows the $[Ni_3Cp'_3]_2(C_2S_6)$ molecule with the centrosymmetrically related atoms labelled with an "a". The center of symmetry is located at the midpoint of the C(1)–C(1a) bond. The two identical Ni_3S_3 units, which possess a chairlike conformation, are connected by the two central ethane carbon atoms, which are each bonded in a tetrahedral-like configuration to the other carbon and three sulfur atoms. Distances typical of single bonds are observed in the $Ni_6(C_2S_6)$ core for the C–C

(10) Crystals of $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) as a benzene solvate (FW, 1037.4 g/mol) were obtained by Maj et al.[2] from slow evaporation of a benzene solution. X-ray data were obtained via a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation for an orthorhombic crystal with unit cell dimensions a = 12.273 (3) Å, b = 17.366 (5) Å, and c = 18.077 (9) Å, V = 3853 (2) Å^3; d_{calc} = 1.79 g/cm^3 for Z = 4. Systematic absences of k odd for $0kl$ and l odd for $h0l$ indicate the probable space groups to be $Pbc2_1$ (C_{2v}^5, No. 29; nonstandard axial setting of $Pca2_1$) and $Pbcm$ (D_{2h}^{11}, No. 57). The atomic positional parameters from the original refinement[11] of the crystal-disordered $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ by Maj et al.[2] were used as a starting point for its rerefinement as $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) under the centrosymmetric space group *Pbcm*. The crystal structure of $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) also contains an ordered solvated benzene molecule of crystallographic C_2-2 site symmetry. Its positional parameters were included in our re-refinements without modification. Refinement of all non-hydrogen atoms with anisotropic thermal parameters gave results that were nearly identical to those reported by Maj et al.[2] However, some problems arose because the anisotropic thermal parameters for several carbon atoms in the three independent crystal-disordered Cp rings become nonpositive definite. The original refinement of **1a** by Maj et al.[2] employed the least-squares program RAELS[12] which allowed the application of librational thermal motion via a TLX model[13] for each Cp ring; this librational thermal motion cannot be reproduced with the SHELXTL program. Hydrogen atoms were not included in the re-refinement. However, the $R(F)$ and $R_w(F)$ values of 10.0 and 11.3%, respectively, obtained from our anisotropic refinement agreed well with those (viz., $R_1(F)$ = 10.2% and $R_2(F)$ = 10.5%) from the previously published results. A prior isotropic refinement of the Cp and solvated benzene carbon atoms gave $R(F)$ = 11.4% and $R_w(F)$ = 12.4%. Extensive attempts to solve the structure in the noncentrosymmetric space group $Pbc2_1$ as a crystal-ordered structure either by direct methods or Patterson maps were not successful. Attempted refinements under $Pbc2_1$ also gave unsatisfactory results. Hence, we concur with the original findings of Maj et al.[2] that their crystal data for **1a** conform to the centrosymmetric space group *Pbcm*, which is consistent with **1a** possessing an "averaged structure" with two half-weighted, crystal-disordered orientations related by the crystallographic mirror plane.

(11) Reference 2, supplementary material. The F_{obs} data from the F_{obs}/F_{calc} table of the original crystal-disordered $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) were used in our re-refinements.

(12) Rae, A. D. *RAELS, A Comprehensive Least-Squares Program*; University of New South Wales, Kensington, 1976.

(13) Rae, A. D. *Acta Crystallogr.* **1975**, *A31*, 570–574.

(14) Fractional atomic coordinates based upon the crystal-ordered $Ni_6(C_2S_6)$ core in the triclinic structure of 1 were first orthogonalized by the ORTH command in the XP graphics program of the SHELXTL-Plus package and then fit as a rigid group by use of the OFIT instruction to the crystal-disordered $Ni_6(C_2S_6)$ core in the orthorhombic structure of **1a**.

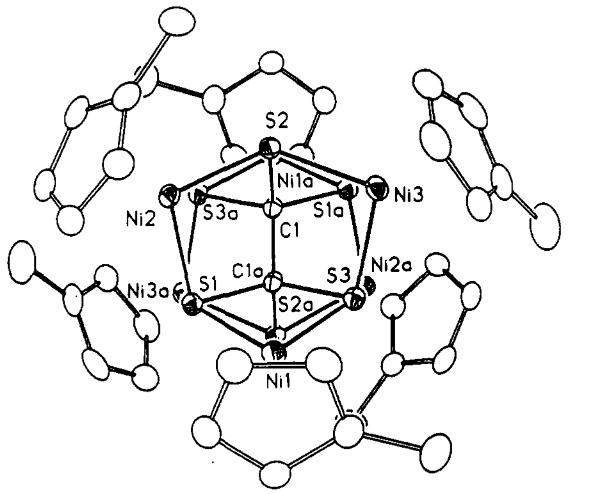

Figure 2. View of $[Ni_3Cp'_3]_2(C_2S_6)$ (1) down the pseudo mirror plane of the $Ni_6(C_2S_6)$ core which conforms to pseudo C_{2h}-$2/m$ symmetry. All atomic thermal ellipsoids are drawn at the 50% probability level.

distance (1.502 (6) Å) and six independent Ni–S distances, which vary from 2.166 (1) to 2.179 (1) Å (mean, 2.175 Å). The three independent C–S bond lengths of 1.822 (3)–1.841 (3) Å (mean, 1.833 Å) are slightly longer than the single-bond C–S distances of 1.79–1.81 Å predicted from covalent radii.[15] The average Ni–C bond length of 2.13 Å (range 2.083 (3)–2.184 (4) Å) for the three independent Cp′ rings and the average C–C distance of 1.50 Å (range 1.489 (4)–1.503 (5) Å for the methyl carbon to its Cp′ ring carbon atom are normal. The three independent Ni···Ni distances within one chairlike Ni_3S_3 ring are expectedly nonbonding with a mean value of 3.44 Å.

The structure of 1 is best envisioned as a bidentate linkage of six $[NiCp']^+$ ion fragments to a formal hexathioethane $C_2S_6^{6-}$ hexaanion. In fact, electron counting may be readily accomplished by the consideration of 1 as a composite of six d^8 Ni(II), six $[Cp']^-$ ligands, and a $C_2S_6^{6-}$ ligand. Under this formalism, all of the mercapto sulfur atoms function as electron-pair donors to the nickel atoms such that each Ni(II) conforms to an 18-electron count (i.e., the EAN rule) without invoking any metal–metal bonds.[16,17]

The six sulfur atoms are arranged in a trigonal antiprismatic array around the ethane C–C bond. Two modes of metallo-dithio chelation to the central C_2S_6 ligand are found among the nickel atoms. Ni(1) and Ni(1a) are each coordinated to the two sulfur atoms via an end-on 1,1′-dithio chelating NiS_2C ring linkage, while Ni(2), Ni(2a), Ni(3), and Ni(3a) are each coordinated to the two sulfur atoms via a side-on 1,2-dithio chelating NiS_2C_2 ring linkage.

These particular chelations result in the $Ni_6(C_2S_6)$ core of 1 possessing a C_{2h}–$2/m$ architecture within experimental error. Figure 2 clearly shows close conformity of the core atoms to the horizontal mirror plane passing through Ni(1), Ni(1a), S(2), S(2a), C(1), and C(1a); a least-squares calculation established that these atoms form a nearly perfect plane in that the perpendicular deviations of these atoms

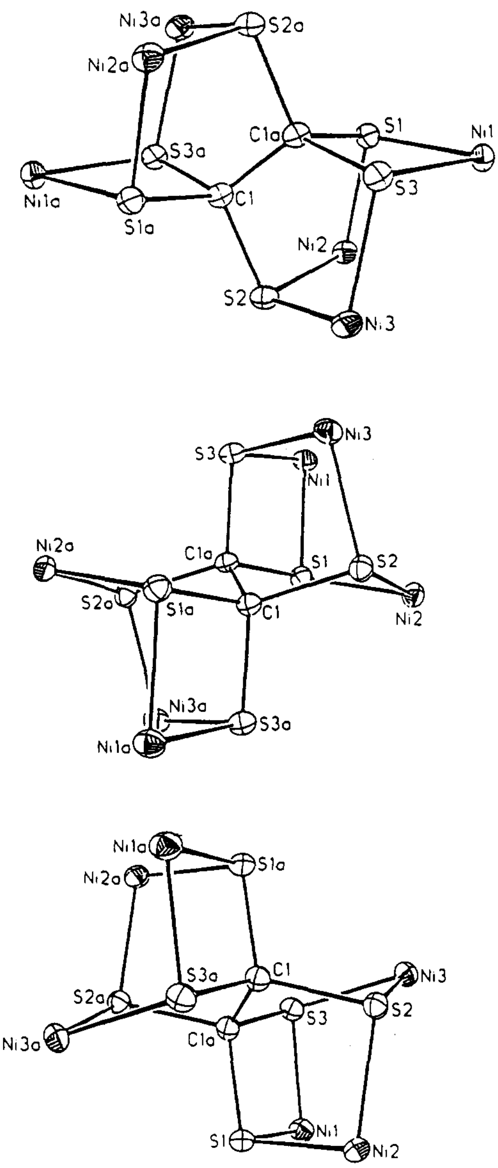

Figure 3. Three views of the crystal-ordered $Ni_6(C_2S_6)$ core of $[Ni_3Cp'_3]_2(C_2S_6)$ (1). All atomic thermal ellipsoids are drawn at the 50% probability level. (a) Projection nearly down the pseudo-2-fold axis giving an edge-on view of the two centrosymmetrically related NiS_2C rings formed by the end-on 1,1′- and 2,2′-(metallo–dithio) chelations of Ni(1) and Ni(1a) to the C_2S_6 ligand. (b) Edge-on view of the highly distorted $Ni_2S_2C_2S_2Ni_2$ plane resulting from the side-on 1,2- and 1′,2′-(metallo–dithio) chelations of Ni(2) and Ni(2a) to the C_2S_6 ligand. (c) Edge-on view of a (pseudo-mirror)-related $Ni_2S_2C_2S_2Ni_2$ plane resulting from the side-on 1,2- and 1′,2′-(metallo–dithio) chelations of Ni(3) and Ni(3a) to the C_2S_6 ligand.

from their mean plane are ≤0.006 Å. Figure 2 also reveals that the pseudo-C_{2h}-$2/m$ symmetry of the $Ni_6(C_2S_6)$ core is reduced to the observed crystallographic C_i-$\bar{1}$ symmetry upon inclusion of the C_5H_4Me rings. A projection of the $Ni_6(C_2S_6)$ core nearly parallel to the principal 2-fold axis is presented in Figure 3a, which gives an edge-on view of the two centrosymmetrically related pairs of sulfur atoms participating in end-on chelations to the Ni(1) and Ni(2) atoms. Parts b and c of Figure 3 provide similar edge-on views showing the analogous (pseudo-mirror)-related distorted $NiS_2C_2S_2Ni$ planes formed by the side-on chelations of the pairs of sulfur atoms to the Ni(2) and Ni(2a) atoms and to the Ni(3) and Ni(3a) atoms, respectively. In this connection, it is noteworthy that the C_{2h} symmetry of the $Ni_6(C_2S_6)$ core readily accounts for the ^1H NMR spectrum of 1 exhibiting two different Cp′ signals in a 4:2 ratio.

(15) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260. (b) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 258.

(16) A thiolato-bridged trinuclear nickel(II) $[Ni_3(C_5H_6NO_3S)_3]^{3-}$ complex of N-(2-mercaptopropionyl)glycine containing a chairlike Ni_3S_3 core was recently reported by Baidya et al.[17] Nonbonding Ni···Ni distances with an average value of 3.097 (1) Å were found together with two sets of Ni–S distances of 2.16 Å (av) and 2.20 Å (av) for the two kinds of Ni–S bonds.

(17) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* 1989, 28, 3426–3432.

Geometrical Comparison of the Hexathioethane Fragment in $[Ni_3Cp'_3]_2(C_2S_6)$ (1) with the Same Fragment in Hexakis(phenylthio)ethane and Resulting Implications. To our knowledge 1 is the first example of a complex containing a metal-coordinated C_2S_6 ligand. Although an ionic salt of the $C_2S_6^{6-}$ hexaanion is not known, a few hexakismercapto-substituted ethane molecules, $C_2(SR)_6$, have been prepared and characterized by Seebach et al.[18] Of these, only the prototype hexakis(phenylthio)ethane, $C_2(SPh)_6$, has been structurally characterized by an X-ray diffraction study.[19] The crystal structure of $C_2(SPh)_6$ is composed of two crystallographically independent molecules, each of site symmetry C_i-$\bar{1}$. The formal $C_2S_6^{6-}$ anion in each of the two molecules contains a virtually identical trigonal antiprismatic sulfur arrangement of pseudo trigonal D_{3d}-$\bar{3}2/m$ symmetry about the ethane C–C bond. Furthermore, the six sulfur atoms closely conform to a regular octahedral polyhedron with the independent nonbonding S···S contacts having narrow ranges of 3.09 (1)–3.12 (1) Å and 3.09 (1)–3.13 (1) Å in the two $C_2(SPh)_6$ molecules. Both the ethane C–C bond distances (1.56 (3), 1.59 (3) Å) and C–S bond lengths (1.85 Å (av); 1.83 (2)–1.88 (2) Å range) in the two $C_2(SPh)_6$ molecules are statistically equivalent to those of the C_2S_6 ligand in 1.

The observed reduction in symmetry of the formal $C_2S_6^{6-}$ anion from the idealized trigonal antiprismatic D_{3d}-$\bar{3}2/m$ polyhedron in $C_2(SPh)_6$ to the idealized C_{2h}-$2/m$ arrangement in the $Ni_6(C_2S_6)$ core of 1 is a consequence of the two types of metallo–dithio chelation previously described. An examination of the molecular parameters of 1 reveals large variations in the six independent nonbonding S···S distances from those in the regular polyhedron of sulfur atoms found in $C_2(SPh)_6$. The shortest S···S distance of 2.837 (2) Å is between the (pseudo-mirror)-related S(1) and S(3) atoms across the four-membered NiS_2C ring, while the longest S···S distance of 3.431 (2) Å involves the (pseudo-2-fold)-related S(1) and S(3a) atoms between the two four-membered rings within the two separate Ni_3S_3 fragments (Figure 3). The (pseudo-mirror)-related S(2)···S(1) and S(2)···S(3) distances of 3.188 (2) and 3.177 (2) Å, respectively, are within the same Ni_3S_2 fragment, while the (pseudo-mirror)-related S(2a)···S(1) and S(2a)···S(3) distances of 3.044 (2) and 3.041 (2) Å, respectively, are between the two Ni_3S_2 fragments. The mean S···S contact of 3.12 Å is virtually identical to the mean S···S contacts found in the nonchelating $C_2(SPh)_6$ molecules (vide supra). The acute S–Ni–S bond angle of 81.6 (1)° within the four-membered NiS_2C ring vs the obtuse S–Ni–S bond angles of 93.7 (1)° and 94.2 (1)° within the two mirror-related five-membered NiS_2C_2 rings are also natural consequences of the different ring sizes.

Seebach et al.[18] established that the pyrolysis of $C_2(SPh)_6$ above 100 °C and $C(SPh)_4$ above 165 °C with or without solvents produced decomposition products that are readily explained on the basis that the initial reaction step involved the homolysis of the C–C bond in the hexamercaptoethane molecule and of the C–SPh bond in the tetramercaptomethane molecule to give the tris(phenylthio)methyl radical. They also showed from ^{13}C-labeled scrambling experiments that formation of the ethylenic $(PhS)_2C{=}C(SPh)_2$ molecule from $C_2(SPh)_6$ must be preceded by C–C bond dissociation of the latter ethane molecule. They attributed the easy homolysis of the C–C and C–S bonds in $C_2(SPh)_6$ and $C(SPh)_4$, respectively, to give the $C(SPh)_3$ radical to steric hindrance in the dimeric and the tetramercaptomethane molecules.

(18) (a) Seebach, D.; Beck, A. K.; Stegmann, H. B. *Tetrahedron Lett.* **1970**, 1933–1936. (b) Seebach, D.; Beck, A. K.; Stegmann, H. B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 500–501. (c) Seebach, D.; Beck, A. K. *Chem. Ber.* **1972**, *105*, 3892–3904. (d) Seeback, D.; Stegmann, H. B.; Scheffler, K.; Beck, A. K.; Geiss, K.-H. *Chem. Ber.* **1972**, *105*, 3905–3914.

(19) Roelofsen, G.; Kanters, J. A.; Seebach, D. *Chem. Ber.* **1974**, *107*, 253–262.

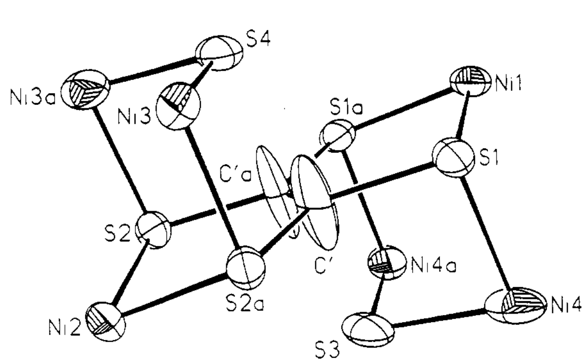

Figure 4. Atomic thermal ellipsoids at the 30% probability level obtained for the "averaged structure" of the $Ni_6(C_2S_6)$ core from the re-refinement of the originally presumed $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)$ (**1a**). This crystal-disordered structure is consistent with the crystallographically imposed C_s-m site symmetry resulting from refinement under the centrosymmetirc *Pbcm* space group.

In this connection, it is not surprising that $[Ni_3Cp'_3]_2(C_2S_6)$ (1) exhibits instability in solution. Proton NMR spectra showed that 1 is sensitive to chlorine-containing solvents such as $CDCl_3$. In this solvent additional Cp′ ^1H resonances were observed over a short time, presumably due to other Cp′-containing decomposition products of 1. The moisture sensitivity of 1 was also evidenced by its reaction with residual water (e.g., approximately several 100 ppm) in the $CDCl_3$ solvent used in one of the ^1H NMR measurements. Although a solvent blank of this "wet" $CDCl_3$ clearly displayed a resonance corresponding to the water protons at 1.53 ppm, this resonance was no longer present in the spectrum of 1 obtained in the same "wet" $CDCl_3$ solvent. Instead, other Cp′ resonances were detected in addition to a singlet at ca. 8.50 ppm, consistent with hydroxylation of a Cp′ ring.

Comparison of the Structural Features of $[Ni_3Cp'_3]_2(C_2S_6)$ (1) and $[Ni_3Cp_3]_2(C_2S_6)$ (1a). Upon the X-ray structural determination of $[Ni_3Cp'_3]_2(C_2S_6)$ (1), we immediately recognized its similarity to the unsubstituted Cp analogue, $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**), which was previously reported by Maj et al.[2] as $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$. Because they had been unable to refine an assumed crystal-ordered structure under $Pbc2_1$ symmetry, they chose the centrosymmetric space group *Pbcm*, which requires the molecular structure to possess crystallographic C_s-m site symmetry. This in turn leads to an averaged molecular structure involving two crystal-disordered mirror-related orientations. As shown in Figure 4, one-half of the $Ni_6(C_2S_6)$ core of **1a** is crystallographically independent and related to the other half by the crystallographic mirror plane that contains Ni(1), Ni(2), S(3), and S(4). This molecule (**1a**) is similar to 1 except these two nickel atoms are each chelated by a C_2S_4 ligand that was incorrectly presumed not to be connected by C–S bonds to either mirror-containing μ_2-S atom. Although an averaged structure involving at least two positions for each mirror-related carbon atom was evident from the unusually elongated thermal ellipsoids of the two carbon atoms (Figure 4) and from the artificially short C–C distance of only 1.13 Å, the centrosymmetrically related C–S bond linkage of each μ_2-S atom to one of the carbon atoms was not envisioned. With the characterization of the structure of the Cp′ analogue (1), it became apparent that the crystal disorder in **1a** involved the near-superposition of two $Ni_6(C_2S_6)$ cores that are related

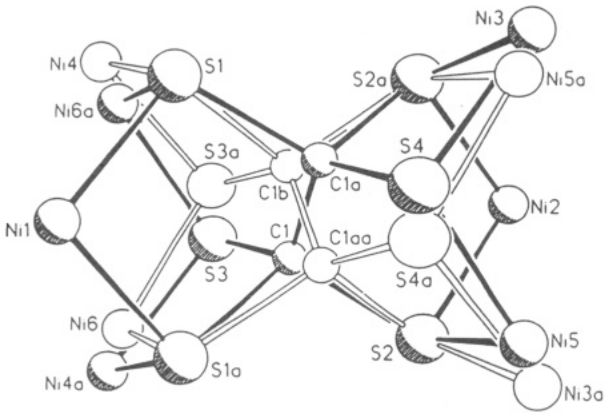

Figure 5. Ball–stick representation of the crystal-disordered $Ni_6(C_2S_6)$ core of $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) modeled as two half-weighted orientations related by a crystallographic mirror plane. The close conformity of the aggregate of these two orientations to the experimental atomic thermal ellipsoids of the "averaged structure" given in Figure 4 provides convincing evidence for the reconstitution of the crystal-disordered **1a** as a cyclopentadienyl analogue of the crystal-ordered 1.

by the crystallographic mirror plane under the orthorhombic space group *Pbcm*.

Maj et al.[2] recognized that the presence of a crystal disorder was consistent with the centrosymmetric structural solution of **1a** but attributed the crystal disorder in the "ethylene" carbon atoms to nonbonding instead of bonding interactions with the "bare" sulfur atoms. From a comparison of the $Ni_6(C_2S_6)$ core of 1 (Figure 3) with the corresponding core of **1a** (Figure 4), it is not difficult to see the relationship between the X-ray results of the Cp′ structure and its unsubstituted Cp analogue. To obtain the structure of 1 from **1a**, the two carbon atoms (C′ and C′a) in **1a** need only be moved in opposite directions parallel to the crystallographic mirror plane in accordance with their elongated thermal ellipsoids. The thermal parameters of the S(3) and S(4) atoms are elongated (due to the crystal disorder) perpendicular to the mirror plane. Moving these two sulfur atoms off their positions on the mirror plane in opposite directions to form bonds with the approaching carbon atoms gives the actual molecular structure of 1.

Nevertheless, we consider that the previous description[2] for the formation of **1a** is still valid and can be applied to 1 as well. The cycloaddition of a $(CpNi)_2S$ fragment across each of the two pairs of sulfur-chelating atoms of the planar tetrathiolene-like $Ni_2Cp_2(C_2S_4)$ precursor is accompanied by a marked distortion of the molecule that completely disrupts the delocalized π-system. The revised connectivity in **1a** additionally requires concomitant bonding of the sulfur atom in each of the $(CpNi)_2S$ fragments to one of the carbon atoms of the C_2S_4 ligand, thereby forming the hexathioethane C_2S_6 ligand.

The crystal-disordered structure of **1a** can be successfully described by modeling the average atomic positional parameters of the $Ni_6(C_2S_6)$ core to those obtained from the triclinic structure solution of 1. The resulting parameters of **1a** were then refined under *Pbcm*. By averaging the atomic positions for the two disordered orientations given in Figure 5, the abnormal shapes of the atomic thermal ellipsoids of **1a** (Figure 4) can be accounted for. Our ability to reproduce the discrepancy *R* values obtained in the original refinement of the "averaged structure" provides an equally plausible molecular configuration that permits the reformulation of $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ as $[Ni_3Cp_3]_2(C_2S_6)$, consistent with the molecular configuration of 1.

It is ironic that the incorrect molecular connectivity of the crystal-disordered **1a** provided the insight and hence the stimulus for the subsequent synthetic–stereochemical–bonding studies in our laboratories on the tetrathiolate-bridged dimetal complexes of nickel, cobalt, iron, and titanium formed via the reductive head-to-head dimerization of CS_2. Whether the actual molecular configuration of **1a** presented herein would have provided the impetus for further work remains unclear.

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Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, bond angles for the non-hydrogen atoms, and coordinates and isotropic temperature factors for the hydrogen atoms for $[Ni_3Cp'_3]_2(C_2S_6)$ (**1**) and positional and thermal parameters for the non-hydrogen atoms and interatomic distances for $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) (9 pages). Ordering information is given on any current masthead page.

OM9204604

Notes

Crystal and Molecular Structure of $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CCH_2OMe)][Na(15\text{-crown-}5)]$

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The transformations of hydrogen-poor hydrocarbyls (C_nH_x, $x \le n$) on multimetallic sites are of interest in connection with the study of surface "cokes" and "carbides" formed during catalytic reactions of hydrocarbons or CO on metal surfaces.[1–6] A facile route to multimetallic carbon-rich, hydrogen-poor complexes is through the reactions of alkynes or acetylides with metal–metal dimers

(1) Thompson, S. J.; Webb, G. *J. Chem. Soc., Chem. Commun.* **1976**, 526.

