

Transition-Metal Complexes with Sulfur Ligands. 55.¹ Nickel Complexes with Thiolato-Thioether Ligands Including Nitrogen and Oxygen Donors in S₆, S₅, OS₄, NS₄, and S₄ Donor Sets. Syntheses, Properties, and X-ray Structure Determinations of [Ni('S₆')], [Ni('S₅')], [Ni('OS₄')]₂, [Ni('S₄-C₅')]₂, and [Ni('S₄-C₃')][†]

Dieter Sellmann,* Stefan Fünfgelder, Georg Pöhlmann, Falk Knoch, and Matthias Moll

Received February 27, 1990

In order to investigate specific properties of nickel-sulfur complexes, a series of novel compounds with multidentate thioether-thiolate ligands were synthesized and characterized by spectroscopic methods and X-ray structure analyses. The ligands derive from two benzenedithiol units linked by bridges of different length and nature. The reactions of [Ni(acac)₂] (acac = acetylacetonate) with 'S₆'²⁻ (= 1,2-bis((2-(2-mercaptophenyl)thio)ethyl)thio)ethanato(2-)) and 'OS₄'²⁻ (= bis(2-((2-mercaptophenyl)thio)ethyl)etherato(2-)) yield [Ni('S₆')] (1) and [Ni('OS₄')]₂·3THF (2). In [Ni('S₆')] (monoclinic space group P2₁/n, Z = 4, a = 693.6 (2) pm, b = 2001.2 (5) pm, c = 1459.3 (2) pm, β = 100.33 (1)°, R/R_w = 0.037/0.029), the C₂H₄SC₂H₄SC₂H₄ linkage spans like a handle diagonally over a square-planar [Ni(S₂C₆H₄)₂] unit. The two thioether atoms in the linkage do not coordinate. The binuclear [Ni('OS₄')]₂·3THF (triclinic space group P1, Z = 2, a = 1146.5 (3) pm, b = 1360.2 (4) pm, c = 1613.6 (6) pm, α = 92.79 (2)°, β = 107.04 (3)°, γ = 93.86 (2)°, R/R_w = 0.094/0.082) contains two cofacial square-planar [NiS₄] centers connected by the O(C₂H₄)₂ linkages of both ligands, the thiolate sulfurs being trans to each other. The Ni-Ni distance is 770 pm, producing a cage-like cavity between the [NiS₄] entities. [Ni('S₅')] (3), [Ni('S₄-C_x')] (x = 1 (4), 3 (5), 5 (6), 7 (7)), and [Ni('N_HS₄')] (8) ('S₅'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)sulfidato(2-)), 'S₄-C₁'²⁻ = bis((2-mercaptophenyl)thio)methanato(2-)), 'S₄-C₃'²⁻ = 1,3-bis((2-mercaptophenyl)thio)propanato(2-)), 'S₄-C₅'²⁻ = 1,5-bis((2-mercaptophenyl)thio)pentanato(2-)), 'S₄-C₇'²⁻ = 1,7-bis((2-mercaptophenyl)thio)heptanato(2-)), 'N_HS₄'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)aminato(2-)) were synthesized by template alkylation of Na₂[Ni(S₂C₆H₄)₂] with bis(2-bromoethyl) sulfide, CH₂I₂, 1,3-dibromopropane, 1,5-dibromopentane, 1,7-dibromoheptane, and bis(2-bromoethyl)amine, respectively. In the mononuclear [Ni('S₅')] (monoclinic space group P2₁/c, Z = 4, a = 1071.2 (5) pm, b = 1119.7 (5) pm, c = 1416.5 (5) pm, β = 91.11 (3)°, R/R_w = 0.085/0.071), the Ni center is five-coordinate and has a square-pyramidal geometry. This is the first five-coordinate Ni complex that is surrounded by sulfur donors only. The thiolate sulfur atoms lie cis to each other in the basal plane, and the linkage thioether atom occupies the apical position. [Ni('S₄-C₃')] (monoclinic space group P2₁/c, Z = 4, a = 1065.2 (4) pm, b = 813.5 (3) pm, c = 1758.2 (6) pm, β = 98.85 (3)°, R/R_w = 0.054/0.048) is mononuclear and has a slightly distorted square-planar structure with cis thiolate atoms. [Ni('S₄-C₅')]₂·2THF (monoclinic space group P2₁/c, Z = 2, a = 938.7 (4) pm, b = 1230.9 (5) pm, c = 1872.5 (5) pm, β = 97.11 (2)°, R/R_w = 0.075/0.061) adopts the same binuclear bridged structure as [Ni('OS₄')]₂·3THF. The structural differences of the complexes are discussed in terms of the nature of the linkage between the C₆H₄S₂ units. Important factors are the preferred conformation of the uncoordinated ligand, the "hard" or "soft" character of the donor atom within the linkage, and the formation of five- and six-membered chelate rings.

Introduction

The discovery of nickel-sulfur interactions in CO-dehydrogenases and hydrogenases has stimulated the interest in nickel complexes with sulfur ligands.² These enzymes catalyze CO₂ reduction to methane and H₂/H⁺ exchange under ambient conditions, i.e. reactions that are difficult to be performed chemically. The active centers of the enzymes must be highly efficient catalysts whose structures and function are of interest not only for understanding the enzymes on a molecular basis but also for developing industrial catalysts.

The detailed structure of the nickel centers in the enzymes remains as yet uncertain, but EXAFS results indicate the predominance of sulfur in the nickel coordination sphere and the additional presence of nitrogen and/or oxygen donors in some enzymes. The geometry of the nickel centers may be distorted octahedral, but distorted five-coordinate or planar structures cannot be ruled out.³ Thus, novel nickel complexes with sulfur ligands are of interest as standards of comparison.

As important as the synthesis of structural model compounds is the elucidation of characteristic reactivity patterns of nickel-sulfur centers. Specific properties imposed on metal centers by sulfur donors were previously demonstrated in several cases. The stabilization of five-coordinate 16-valence-electron Cr⁰ centers of [Cr(CO)₃(S₂C₆H₄)₂]²⁻⁴ or the stabilization of unstable molecules like diazene, HN=NH, in [(μ-N₂H₂) {Fe('N_HS₄')}]⁵ ('N_HS₄'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)aminato(2-)) may serve as examples.

* To whom correspondence should be addressed.

[†] Ligand abbreviations: 'S₄-C₃'²⁻ = 1,3-bis((2-mercaptophenyl)thio)propanato(2-); 'S₄-C₅'²⁻ = 1,5-bis((2-mercaptophenyl)thio)pentanato(2-); 'S₅'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)sulfidato(2-); 'OS₄'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)etherato(2-); 'S₆'²⁻ = 1,2-bis(2-((2-mercaptophenyl)thio)ethyl)thio)ethanato(2-).

In enzymes, distortions of coordination spheres from regular geometries are certainly due to the protein environment whose peptide chains containing thiolate and thioether donors in cysteine and methionine entities act as multidentate chelating ligands. As a first step in the search for structural and functional model compounds of nickel centers in CO-dehydrogenase and hydrogenases, we investigated the coordination of multidentate ligands with thiolate, thioether, and additional ether and amine donor functions to nickel(II). Ligands and abbreviations are shown in Figure 1. Ligand abbreviations are as follows: 'S₄-C₁'²⁻ = bis((2-mercaptophenyl)thio)methanato(2-); 'S₄-C₃'²⁻ = 1,3-bis((2-mercaptophenyl)thio)propanato(2-); 'S₄-C₅'²⁻ = 1,5-bis((2-mercaptophenyl)thio)pentanato(2-); 'S₄-C₇'²⁻ = 1,7-bis((2-mercaptophenyl)thio)heptanato(2-); 'S₅'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)sulfidato(2-); 'S₆'²⁻ = 1,2-bis(2-((2-mercaptophenyl)thio)ethyl)thio)ethanato(2-); 'OS₄'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)etherato(2-); 'N_HS₄'²⁻ = bis(2-((2-mercaptophenyl)thio)ethyl)aminato(2-).

Experimental Section

General Methods. Unless noted otherwise all reactions were carried out under nitrogen at room temperature by using the Schlenk technique. Solvents were dried and distilled under nitrogen before use. Spectra were

- (1) Part 54: Sellmann, D.; Weiss, R.; Knoch, F.; Moll, M. *J. Organomet. Chem.*, submitted for publication.
- (2) Lancaster, J. R., Jr. *The Bioinorganic Chemistry of Nickel*; VCH Verlagsgesellschaft: Weinheim, West Germany, 1988.
- (3) (a) Bastian, N. R.; Wink, D. A.; Wackett, L. P.; Livingston, D. J.; Jordan, L. M.; Fox, J.; Orme-Johnson, W. H.; Walsh, C. T. In ref 2, p 240. (b) Eidsness, M. K.; Sullivan, R. J.; Scott, R. A. In ref 2, p 85.
- (4) Sellmann, D.; Ludwig, W.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *294*, 199.
- (5) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271.

Table I. Summary of Crystallographic Data

compd	[Ni('S ₆ ')]	[Ni('S ₅ ')]	[Ni('OS ₄ ')] ₂ ·3THF	[Ni('S ₄ -C ₃ ')] ₂ ·2THF	[Ni('S ₄ -C ₃ ')]
formula	C ₁₈ H ₂₀ NiS ₆	C ₁₆ H ₁₆ NiS ₅	C ₄₄ H ₅₆ Ni ₂ O ₅ S ₈	C ₄₂ H ₅₂ Ni ₂ O ₂ S ₈	C ₁₅ H ₁₄ NiS ₄
M _r	487.45	427.34	1038.87	962.81	381.24
cryst size, mm ³	0.4 × 0.25 × 0.25	0.4 × 0.3 × 0.03	0.5 × 0.4 × 0.2	0.4 × 0.3 × 0.2	0.5 × 0.3 × 0.3
space group	P2 ₁ /n	P2 ₁ /c	P $\bar{1}$	P2 ₁ /c	P2 ₁ /c
cryst system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
cell dimens					
a, Å	6.936 (2)	10.712 (5)	11.465 (3)	9.387 (4)	10.652 (4)
b, Å	20.012 (5)	11.197 (5)	13.602 (4)	12.309 (5)	8.135 (3)
c, Å	14.593 (2)	14.165 (5)	16.136 (6)	18.725 (5)	17.582 (6)
α, deg			92.79 (2)		
β, deg	100.33 (1)	91.11 (3)	107.04	97.11 (2)	98.85 (3)
γ, deg			93.86 (2)		
Z	4	4	2	2	4
V, Å ³	1992 (1)	1698 (1)	2394 (1)	2146 (1)	1505 (1)
ρ _{calc} , g/cm ³	1.63	1.67	1.44	1.49	1.68
μ, cm ⁻¹	15.8	17.3	11.3	12.9	18.2
2θ range, deg	3–50	3–50	3–52	3–54	3–56
no. of reflns measd	3474	3132	8168	5226	6147
no. of unique reflns	2791	2760	7897	4370	3621
no. of obsd reflns	2379	1802	5606	2908	3314
σ criterion	F > 4σ(F)	F > 6σ(F)	F > 6σ(F)	F > 6σ(F)	F > 4σ(F)
R, %	3.7	8.5	9.4	7.5	5.4
R _w , %	2.9	7.1	8.2	6.1	4.8
weight	1/σ ²	1/σ ²	1/σ ²	1/σ ²	1/σ ²
no. of refined params	227	200	458	245	182
ΔF map max, e/Å ³	0.52	0.79	1.37	0.85	1.04

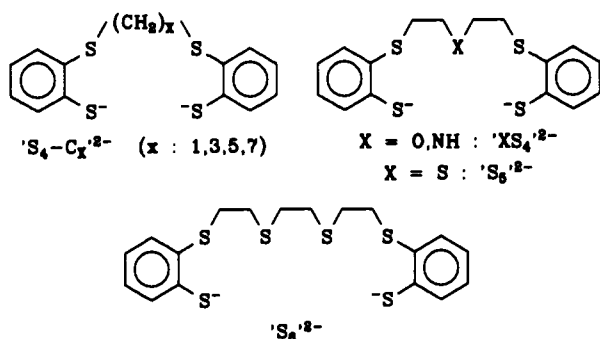


Figure 1. Ligands and abbreviations.

recorded on the following instruments: Zeiss IMR 25 infrared spectrometer (solutions in CaF₂ cuvettes with compensation of solvent bands, solids in KBr pellets), Jeol JNM-GX 270 FT-NMR spectrometer, and Varian Mat 212 mass spectrometer. Magnetic moments were measured with a Johnson Matthey magnetic susceptibility balance at 295 K and molecular weights determined with a Knauer vapor-pressure osmometer.

o-Benzenedithiol,⁶ bis(2-bromoethyl) ether,⁷ 'OS₄'-H₂,⁸ bis(2-bromoethyl)amine hydrobromide,⁹ 'N_HS₄'-H₂,⁸ Na₂[Ni('S₂')₂],¹⁰ bis(2-bromoethyl) sulfide,¹¹ 'S₆'-H₂,¹² and [Ni(acac)₂]¹³ were prepared by literature methods. CH₂I₂ was purchased from Aldrich, and 1,3-dibromopropane, 1,5-dibromopentane, and 1,7-dibromoheptane were purchased from EGA.

Caution! Bis(2-bromoethyl) sulfide, bis(2-bromoethyl)amine, and bis(2-bromoethyl) ether are mustard gas analogues and must be handled with care!

X-ray Data Collection, Structure Determination, and Refinement of [Ni('S₆')], [Ni('S₅')], [Ni('OS₄')]₂·3THF, [Ni('S₄-C₃')], and [Ni('S₄-C₃')]₂·2THF. Single crystals of [Ni('S₆')] and [Ni('S₅')] were grown by slowly cooling a saturated DMF solution from 100 °C to room temper-

Table II. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (pm² × 10⁻¹) of the Non-Hydrogen Atoms of [Ni('S₆')]

	x	y	z	U(eq) ^a
Ni(1)	-82 (1)	5069 (1)	1606 (1)	21 (1)
S(1)	-1559 (2)	5846 (1)	2277 (2)	28 (1)
S(2)	2778 (2)	5403 (2)	2319 (1)	24 (1)
S(3)	2328 (2)	4307 (1)	4934 (1)	40 (1)
S(4)	-2692 (2)	3206 (1)	3320 (1)	36 (1)
S(5)	-2950 (2)	4685 (1)	1010 (1)	22 (1)
S(6)	1348 (2)	4324 (1)	863 (1)	26 (1)
C(15)	2307 (6)	6161 (2)	2872 (3)	23 (2)
C(14)	3847 (7)	6559 (2)	3291 (3)	32 (2)
C(13)	3457 (7)	7149 (2)	3697 (3)	38 (2)
C(12)	1543 (7)	7342 (2)	3693 (3)	39 (2)
C(11)	9 (7)	6939 (2)	3277 (3)	32 (2)
C(10)	364 (7)	6341 (2)	2855 (3)	24 (2)
C(25)	-2526 (6)	4036 (2)	234 (3)	21 (2)
C(24)	-4099 (6)	3710 (2)	-301 (3)	26 (2)
C(23)	-3732 (7)	3193 (2)	-876 (3)	30 (2)
C(22)	-1830 (7)	3024 (2)	-919 (3)	29 (2)
C(21)	-262 (6)	3360 (2)	-401 (3)	24 (2)
C(20)	-589 (6)	3879 (2)	200 (3)	20 (2)
C(16)	3339 (6)	4847 (2)	3330 (3)	27 (2)
C(17)	2016 (6)	4947 (2)	4042 (3)	32 (2)
C(18)	927 (7)	3633 (2)	4313 (3)	36 (2)
C(26)	-3540 (6)	4185 (2)	1975 (3)	25 (2)
C(27)	-2193 (6)	3600 (2)	2259 (3)	28 (2)
C(28)	-1293 (7)	3752 (2)	4179 (3)	37 (2)

^a Equivalent isotropic U(eq) defined as one-third of the orthogonalized U_{ij} tensor.

ature. Single crystals of [Ni('OS₄')]₂·3THF and [Ni('S₄-C₃')]₂·2THF grew from a saturated THF solution that was slowly cooled from 60 °C to room temperature. Single crystals of [Ni('S₄-C₃')] were obtained by covering a saturated CH₂Cl₂ solution with MeOH. The single crystals were sealed in glass capillaries and mounted on a Nicolet-3m/V diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 200 K with the ω-scan technique (scan speed 3–15°/min). A correction for absorption was not applied. The structures were solved by direct methods (SHELXTL-PLUS). The non-hydrogen atoms were refined with anisotropic thermal parameters, and the phenyl H atoms were placed at calculated positions and refined as rigid groups. The hydrogen atoms of the methylene groups were placed in ideal tetrahedral positions and rotated around their central carbon atom during refinement. The hydrogen atoms were refined with common isotropic thermal parameters. The asymmetric units of [Ni('OS₄')]₂·3THF and [Ni('S₄-C₃')]₂·2THF contain THF. These molecules were refined by using iso-

- Degani, J.; Fochi, R. *Synthesis* **1976**, 7, 471.
- Müller, E., Ed. *Methoden der Organischen Chemie (Houben-Weyl)*, 4th ed.; G. Thieme Verlag: Stuttgart, West Germany, 1960; Vol. V/4 Halogenverbindungen, p 389.
- Sellmann, D.; Kunstmann, H.; Knoch, F.; Moll, M. *Inorg. Chem.* **1988**, 27, 4183.
- Peacock, D. H.; Dutta, C. U. *J. Chem. Soc.* **1934**, 1305.
- Baker-Hawkes, M. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, 88, 4870.
- Steinkopf, W.; Herold, J.; Stöhr, J. *Ber. Dtsch. Chem. Ges.* **1920**, 53, 1007.
- Sellmann, D.; Kleine-Kleffmann, U. *J. Organomet. Chem.* **1983**, 258, 315.
- Watson, H. W., Jr.; Lin, C.-T. *Inorg. Chem.* **1966**, 5, 1074.

Table III. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{pm}^2 \times 10^{-1}$) of the Non-Hydrogen Atoms of $[\text{Ni}(\text{S}_6)]$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Ni(1)	1291 (1)	1769 (1)	7802 (1)	20 (1)
S(1)	214 (3)	778 (3)	8827 (2)	23 (1)
S(2)	-307 (3)	2964	7515 (2)	22 (1)
S(3)	658 (3)	625 (3)	6150 (2)	26 (1)
S(4)	2597 (3)	2744 (3)	6876 (2)	25 (1)
S(5)	2900 (3)	788 (3)	8396 (2)	29 (1)
C(15)	-1532 (12)	2422 (9)	8230 (7)	19 (3)
C(14)	-2674 (14)	2961 (11)	8208 (9)	34 (4)
C(13)	-3626 (13)	2494 (14)	8762 (8)	39 (5)
C(12)	-3389 (12)	1547 (12)	9362 (8)	30 (4)
C(11)	-2224 (12)	1031 (11)	9375 (7)	23 (4)
C(10)	-1259 (10)	1447 (9)	8821 (7)	17 (3)
C(25)	3887 (11)	1747 (11)	6801 (7)	27 (4)
C(24)	4775 (12)	1835 (14)	6093 (8)	38 (4)
C(23)	5730 (15)	1038 (13)	6057 (10)	44 (5)
C(22)	5899 (12)	227 (12)	6769 (10)	40 (4)
C(21)	5060 (13)	133 (13)	7491 (9)	35 (4)
C(20)	4021 (11)	910 (10)	7508 (7)	21 (3)
C(16)	-984 (12)	2604 (11)	6362 (7)	26 (4)
C(17)	-854 (12)	1302 (12)	6076 (8)	30 (4)
C(26)	1983 (12)	2707 (12)	5669 (8)	32 (4)
C(27)	1532 (12)	1505 (11)	5338 (8)	27 (4)

^aEquivalent isotropic *U*(eq) defined as one-third of the orthogonalized U_{ij} tensor.

tropic thermal parameters, and their disorder is the reason for the relatively high *R* factors.

Table I summarizes crystallographic data. The fractional atomic coordinates are given in Tables II–VI.

Preparation of Compounds. $[\text{Ni}(\text{S}_6)]$ (1). A 1.38-mL (2.2-mmol) volume of a 1.6 M solution of BuLi in hexane is added to 0.47 g (1.1 mmol) of $\text{S}_6\text{-H}_2$ in 15 mL of THF at -78°C . The resulting mixture is warmed to room temperature and added dropwise to the suspension of 0.28 g of Ni(acac)₂ in 40 mL of THF within 15 min. The resulting brown suspension is refluxed for 1 h and filtered hot. When the solution is cooled to -25°C , orange crystals of $[\text{Ni}(\text{S}_6)]$ separate, which are collected, washed with 50 mL of pentane, and dried under high vacuum for 5 h. When the filtered solution is covered with a layer of pentane, additional crystalline $[\text{Ni}(\text{S}_6)]$ can be isolated. Yield: 0.35 g (66%). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{NiS}_6$ ($M_r = 487.42$): C, 44.36; H, 4.14. Found: C, 44.26; H, 4.22. FD MS (*m/e*): 486 [M^+].

$[\text{Ni}(\text{OS}_4)_2]$ (2). A 0.11-g (2-mmol) amount of NaOMe and 0.35 g (1 mmol) of $\text{OS}_4\text{-H}_2$ are dissolved in 30 mL of MeOH. Addition of 0.25 g (1 mmol) of Ni(acac)₂ yields a light brown suspension, which is stirred for 12 h. The precipitate is collected and washed with 20 mL of MeOH and 10 mL of ether. Recrystallization from THF ($65/-25^\circ\text{C}$) yields an orange brown, microcrystalline powder, which is dried under high vacuum. Yield: 0.35 g (85%). Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{Ni}_2\text{O}_2\text{S}_8$ ($M_r = 822.54$): C, 46.73; H, 3.92; S, 31.19. Found: C, 46.47; H, 3.88; S, 30.25. FD MS (*m/e*): 410 [$\text{M}^+/2$], 820 [M^+]. ¹H NMR (δ , ppm, DMF-*d*₇): 7.2 (m, 8 H); 3.8, 3.2 (s, 4 H).

$[\text{Ni}(\text{S}_2)]$ (3). A 0.12-g (0.5-mmol) amount of bis(2-bromoethyl) sulfide is added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. When the solution is stirred for 3 h, a brown precipitate forms, which is collected, washed with 20 mL of MeOH and 10 mL of ether, and dried under high vacuum. Recrystallization from DMF (100/20 °C) yields brown crystals. Yield: 0.17 g (80%). Anal. Calcd for $\text{C}_6\text{H}_{16}\text{NiS}_2$ ($M_r = 427.34$): C, 44.97; H, 3.77; S, 37.52. Found: C, 45.13; H, 3.79; S, 36.89. FD MS (*m/e*): 426 [M^+], 852 [2M^+]. ¹H NMR (δ , ppm, DMF-*d*₇): 7.2 (m, 8 H); 4.0, 3.4 (s, 4 H).

$[\text{Ni}(\text{S}_4\text{-C}_1)]$ (4). A 0.14-g (0.5-mmol) sample of diiodomethane is added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. After 10 min of stirring, the solution is allowed to stand for 20 h. Brown microcrystals form, which are collected, washed with 40 mL of MeOH and 10 mL of ether, and dried under high vacuum. Yield: 0.08 g (21%). Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{NiS}_4$ ($M_r = 353.19$): C, 44.21; H, 2.85; S, 36.31. Found: C, 44.29; H, 2.86; S, 35.80. FD MS (*m/e*): 704 [2M^+].

$[\text{Ni}(\text{S}_4\text{-C}_3)]$ (5). A 0.10-g (0.5-mmol) amount of 1,3-dibromopropane is added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. When the solution is stirred for 20 min, orange-brown microcrystals form, which are collected, washed with 20 mL of MeOH, and dried under high vacuum. Redissolution in 20 mL of CH_2Cl_2 and addition of 30 mL of MeOH yields brown needles of $[\text{Ni}(\text{S}_4\text{-C}_3)]$ within

Table IV. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{pm}^2 \times 10^{-1}$) of the Non-Hydrogen Atoms of $[\text{Ni}(\text{OS}_4)_2]\cdot 3\text{THF}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Ni(1)	1818 (1)	365 (1)	279 (1)	26 (1)
S(1)	2838 (3)	1569 (2)	1200 (2)	38 (1)
S(2)	1455 (2)	1341 (2)	-782 (2)	29 (1)
S(3)	975 (3)	-869 (2)	-666 (2)	40 (1)
S(4)	2023 (2)	-594 (2)	1347 (1)	26 (1)
C(15)	2108 (9)	2525 (7)	-282 (6)	31 (3)
C(14)	1993 (11)	3345 (8)	-796 (8)	47 (4)
C(13)	2462 (14)	4262 (9)	-396 (9)	63 (6)
C(12)	3034 (13)	4352 (10)	483 (10)	64 (6)
C(11)	3149 (13)	3559 (9)	986 (8)	54 (5)
C(10)	2702 (9)	2621 (7)	598 (6)	32 (4)
C(25)	1523 (8)	-1800 (7)	851 (6)	30 (3)
C(24)	1547 (10)	-2610 (8)	1344 (7)	41 (4)
C(23)	1114 (12)	-3530 (9)	943 (9)	57 (5)
C(22)	678 (13)	-3637 (9)	45 (10)	60 (5)
C(21)	649 (10)	-2855 (8)	-427 (8)	44 (4)
C(20)	1051 (9)	-1907 (7)	-48 (6)	31 (3)
C(16)	2452 (8)	1070 (8)	-1457 (6)	31 (3)
C(17)	3771 (7)	1055 (7)	-925 (6)	30 (3)
C(26)	3676 (8)	-693 (7)	1812 (5)	27 (3)
C(27)	4275 (8)	-899 (8)	1099 (6)	34 (3)
O(1)	5549 (5)	-927 (4)	1522 (4)	28 (2)
Ni(2)	3145 (1)	337 (1)	4619 (1)	27 (1)
S(5)	3353 (3)	1822 (2)	5243 (2)	41 (1)
S(6)	2370 (2)	880 (2)	3346 (2)	28 (1)
S(7)	2777 (2)	-1172 (2)	4020 (2)	35 (1)
S(8)	4117 (2)	-176 (2)	5875 (2)	31 (1)
C(35)	2240 (9)	2161 (8)	3538 (7)	40 (4)
C(34)	1768 (10)	2751 (9)	2850 (7)	42 (4)
C(33)	1719 (11)	3748 (9)	3026 (9)	53 (5)
C(32)	2172 (12)	4152 (9)	3865 (10)	56 (5)
C(31)	2697 (12)	3589 (8)	4539 (9)	53 (5)
C(30)	2734 (9)	2561 (7)	4385 (7)	34 (4)
C(45)	4015 (9)	-1480 (8)	5700 (7)	35 (4)
C(44)	4593 (10)	-2052 (10)	6385 (7)	45 (4)
C(43)	4526 (11)	-3050 (9)	6224 (9)	54 (5)
C(42)	3970 (12)	-3478 (9)	5409 (9)	53 (5)
C(41)	3428 (11)	-2927 (8)	4739 (8)	44 (4)
C(40)	3452 (9)	-1914 (8)	4880 (7)	35 (4)
C(36)	759 (8)	422 (8)	2976 (6)	33 (3)
C(37)	113 (9)	597 (8)	3655 (6)	38 (4)
C(46)	3117 (8)	-11 (7)	6557 (6)	30 (3)
C(47)	1786 (8)	-356 (9)	6103 (6)	40 (4)
O(2)	-1135 (5)	259 (5)	3286 (4)	28 (2)
O(3)	-717 (15)	7098 (11)	3007 (10)	120 (4)
C(51)	-616 (22)	7647 (18)	3734 (15)	118 (7)
C(52)	-95 (18)	7155 (14)	4481 (12)	95 (5)
C(53)	-171 (19)	6069 (15)	4132 (13)	102 (6)
C(54)	-133 (19)	6236 (15)	3218 (13)	102 (6)
O(4)	7690 (17)	3802 (12)	1744 (11)	134 (5)
C(61)	7663 (20)	2399 (16)	2368 (13)	107 (6)
C(62)	6557 (28)	2249 (21)	1569 (18)	144 (9)
C(63)	8039 (25)	3482 (19)	2512 (17)	128 (7)
C(64)	6657 (26)	3237 (20)	1156 (17)	134 (8)
O(5)	5747 (31)	5456 (22)	3047 (19)	215 (9)
C(71)	6174 (30)	5791 (23)	2430 (20)	152 (9)
C(72)	5594 (28)	6642 (22)	2269 (18)	140 (8)
C(73)	4570 (20)	6606 (16)	2641 (13)	109 (6)
C(74)	4714 (23)	5753 (17)	3122 (14)	115 (6)

^aEquivalent isotropic *U*(eq) defined as one-third of the orthogonalized U_{ij} tensor.

10 h. Yield: 0.125 g (66%). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{NiS}_4$ ($M_r = 381.24$): C, 47.26; H, 3.70; S, 33.64. Found: C, 47.59; H, 3.62; S, 33.07. FD MS (*m/e*): 380 [M^+], 720 [2M^+]. ¹H NMR (δ , ppm, CD_2Cl_2): 7.2 (m, 8 H); 3.43, 3.41 (s, 2 H); 1.18, 1.15 (s, 1 H).

$[\text{Ni}(\text{S}_4\text{-C}_5)]_2$ (6). A 0.12-g (0.5-mmol) amount of 1,5-dibromopentane is added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. When the solution is stirred for 10 h, an orange-brown precipitate forms, which is collected, washed with 20 mL of MeOH and 10 mL of ether, and dried under high vacuum. Recrystallization from THF yields orange-brown needles. Yield: 0.14 g (66%). Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{Ni}_2\text{S}_8$ ($M_r = 818.60$): C, 49.89; H, 4.43; S, 31.34. Found: C, 49.96; H, 4.52; S, 30.77. FD MS (*m/e*): 408 [$\text{M}^+/2$], 816 [M^+]. ¹H

Table V. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{pm}^2 \times 10^{-1}$) of the Non-Hydrogen Atoms of $[\text{Ni}(\text{S}_4\text{-C}_x)]_2 \cdot 2\text{THF}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U(eq)^a</i>
Ni(1)	4096 (1)	2432 (1)	3707 (1)	23 (1)
S(1)	3662 (2)	7891 (2)	6419 (1)	32 (1)
S(2)	6114 (2)	6486 (1)	7220 (1)	24 (1)
S(3)	1861 (2)	2715 (2)	3853 (1)	32 (1)
S(4)	4340 (2)	1289 (1)	4592 (1)	24 (1)
C(15)	4329 (7)	6271 (5)	7391 (4)	26 (2)
C(14)	4002 (9)	5483 (6)	7913 (4)	34 (2)
C(13)	2615 (10)	5387 (6)	8050 (4)	41 (3)
C(12)	1541 (9)	6066 (6)	7728 (4)	35 (2)
C(11)	1860 (9)	6840 (6)	7244 (4)	33 (2)
C(10)	3264 (8)	6946 (5)	7071 (3)	24 (2)
C(25)	2678 (8)	1304 (5)	4951 (4)	28 (2)
C(24)	2487 (9)	662 (6)	5561 (4)	32 (2)
C(23)	1154 (10)	669 (7)	5807 (4)	40 (3)
C(22)	47 (9)	1272 (7)	5454 (4)	38 (3)
C(21)	231 (9)	1886 (7)	4860 (4)	37 (3)
C(20)	1576 (8)	1914 (5)	4603 (3)	23 (2)
C(16)	6652 (8)	5138 (5)	6951 (3)	27 (2)
C(17)	5848 (8)	4729 (5)	6252 (4)	26 (2)
C(26)	5554 (8)	1911 (6)	5311 (4)	29 (2)
C(27)	5264 (8)	3106 (5)	5434 (3)	27 (2)
C(28)	6117 (8)	3528 (5)	6125 (3)	27 (2)
O(1)	-196 (8)	713 (7)	1611 (4)	73 (3)
C(1)	62 (11)	435 (9)	902 (6)	60 (4)
C(2)	1659 (11)	542 (7)	904 (5)	52 (3)
C(3)	2097 (10)	1413 (7)	1465 (5)	46 (3)
C(4)	774 (12)	1574 (8)	1841 (5)	54 (3)

^a Equivalent isotropic *U*(eq) defined as one-third of the orthogonalized U_{ij} tensor.

Table VI. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{pm}^2 \times 10^{-1}$) of the Non-Hydrogen Atoms of $[\text{Ni}(\text{S}_4\text{-C}_x)]_2$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U(eq)^a</i>
Ni(1)	3675 (1)	1808 (1)	7803 (1)	21 (1)
S(1)	1998 (2)	579 (2)	8079 (1)	27 (1)
S(2)	2744 (2)	2430 (2)	6659 (1)	24 (1)
S(3)	5469 (2)	2775 (2)	7550 (1)	23 (1)
S(4)	4482 (2)	1628 (2)	9015 (1)	28 (1)
C(15)	1259 (6)	1421 (7)	6546 (3)	27 (2)
C(14)	408 (7)	1489 (7)	5860 (3)	35 (2)
C(13)	-747 (7)	707 (8)	5806 (4)	38 (2)
C(12)	-1077 (6)	-121 (7)	6442 (4)	37 (2)
C(11)	-265 (6)	-159 (7)	7134 (4)	32 (2)
C(10)	932 (6)	623 (7)	7208 (3)	27 (2)
C(25)	6631 (6)	2016 (6)	8326 (3)	25 (2)
C(24)	7900 (6)	1995 (7)	8292 (3)	29 (2)
C(23)	8745 (6)	1470 (7)	8926 (3)	32 (2)
C(22)	8275 (6)	1008 (7)	9593 (3)	31 (2)
C(21)	6992 (6)	1059 (7)	9632 (3)	29 (2)
C(20)	6125 (6)	1560 (6)	8994 (3)	23 (2)
C(16)	3584 (6)	1337 (7)	5969 (3)	28 (2)
C(17)	4931 (6)	2018 (7)	5992 (3)	28 (2)
C(26)	5882 (6)	1667 (7)	6717 (3)	28 (2)

^a Equivalent isotropic *U*(eq) defined as one-third of the orthogonalized U_{ij} tensor.

NMR (δ , ppm, DMF-*d*₇): 7.2 (m, 8 H); 3.8, 3.4 (m, 4 H); 1.3 (m, 6 H).

$[\text{Ni}(\text{S}_4\text{-C}_7)]_2$ (7). A 0.13-g (0.5-mmol) amount of 1,7-dibromoheptane is added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. When the solution is stirred for 10 h, an orange-brown precipitate forms, which is collected, washed with 10 mL of MeOH, and dried under high vacuum. Redissolution in 25 mL of CH_2Cl_2 and addition of 30 mL of MeOH to the filtered solution yields a light brown powder, which is collected, washed with 20 mL of MeOH and 10 mL of ether, and dried under high vacuum. Yield: 0.17 g (78%). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{NiS}_4$ ($M_r = 437.35$): C, 52.18; H, 5.07; S, 29.33. Found: C, 52.32; H, 5.27; S, 28.89. FD MS (*m/e*): 436 [M^+], 872 [$2M^+$].

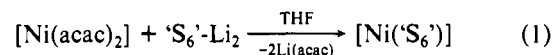
$[\text{Ni}(\text{N}_\text{H}\text{S}_4)]_2$ (8). A 0.15-g (0.5-mmol) amount of bis(2-bromoethyl)amine hydrobromide and 0.03 g (0.5 mmol) of NaOMe are added to a solution of 0.19 g (0.5 mmol) of $\text{Na}_2[\text{Ni}(\text{S}_2)_2]$ in 25 mL of MeOH. After 10 min, a brown precipitate forms, which is collected after 2 h of stirring, washed with 40 mL of MeOH and 10 mL of ether, and dried

under high vacuum. Yield: 0.15 g (73%). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}\text{-NiS}_4$ ($M_r = 410.29$): C, 46.84; H, 4.18; N, 3.41. Found: C, 46.59; H, 4.05; N, 3.14. FD MS (*m/e*): 409 [M^+].

H⁺/D⁺ Exchange of 8. About 50 mg of 8 is suspended in 5 mL of CH_3OD . One drop of concentrated D_2SO_4 is added and the resulting mixture stirred for 2 h. The precipitate is collected, washed with 5 mL of CH_3OD , and dried under high vacuum. The resulting brown powder was identified by IR spectroscopy to be unreacted 8.

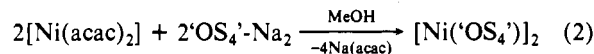
Results

Synthesis and General Properties of the New Complexes. Addition of a THF solution of 'S₆'-Li₂ to a suspension of $[\text{Ni}(\text{acac})_2]$ yields brown $[\text{Ni}(\text{S}_6)]_2$ (1). Boiling for 1 h completes the reaction (eq 1).



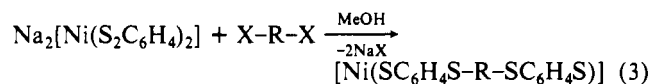
$[\text{Ni}(\text{S}_6)]_2$ is sparingly soluble only in THF, CH_2Cl_2 , and hot DMF. The measurement of the magnetic moment proved $[\text{Ni}(\text{S}_6)]_2$ diamagnetic. Octahedrally surrounded Ni(II) has two unpaired electrons and a magnetic moment of 2.9–3.3 μ_B .¹⁴ Thus, despite of the possibility of higher coordination, in $[\text{Ni}(\text{S}_6)]_2$ the Ni atom can be surrounded by only four or five of the ligand's donor atoms.

$[\text{Ni}(\text{OS}_4)]_2$ (2) is obtained according to



2 forms immediately as a brown powder when $[\text{Ni}(\text{acac})_2]$ is added to the ligand solution. The reaction is complete after stirring overnight or boiling the reaction solution for 0.5 h. 2 is also diamagnetic and sparingly soluble only in CH_2Cl_2 , THF, DMF, and DMSO.

Attempts to synthesize $[\text{Ni}(\text{OS}_4)]_2$ by template reaction of $[\text{Ni}(\text{S}_2\text{C}_6\text{H}_4)_2]^{2-}$ with $\text{O}(\text{C}_2\text{H}_4\text{Br})_2$ led to very low yields. Major products were insoluble, probably polynuclear species. The attempted template synthesis of $[\text{Ni}(\text{S}_6)]_2$ failed totally. According to the mass spectra of the product only complexes with variable degrees of alkylation formed. In contrast to these observations $[\text{Ni}(\text{S}_5)]_2$ (3), $[\text{Ni}(\text{S}_4\text{-C}_x)]_2$ ($x = 1$ (4) 3 (5) 5 (6) 7 (7)), and $[\text{Ni}(\text{N}_\text{H}\text{S}_4)]_2$ (8) can be obtained in good yields by template alkylation (eq 3).



X = Br, I

R = $\text{C}_2\text{H}_4\text{SC}_2\text{H}_4$, $(\text{CH}_2)_n$ ($n = 1, 3, 5, 7$), $\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4$

3 forms as a dark brown powder within 12 h. It is diamagnetic and slightly soluble only in DMF. In solution a molecular weight of 425 was found, indicating mononuclearity of 3.

The reaction times for alkylation of the deep brown solution of $[\text{Ni}(\text{S}_2\text{C}_6\text{H}_4)_2]^{2-}$ with $(\text{CH}_2)_n\text{X}_2$ markedly depend on *n*. Addition of CH_2I_2 yields $[\text{Ni}(\text{S}_4\text{-C}_1)]_2$ (4) as dark brown crystals within 20 h. 4 is only sparingly soluble in DMF. $[\text{Ni}(\text{S}_4\text{-C}_3)]_2$ (5) forms analogously as orange-brown crystals, but within 20 min. The reactions with 1,5-dibromopentane and 1,7-dibromoheptane need several hours for completion and yield $[\text{Ni}(\text{S}_4\text{-C}_5)]_2$ (6) and $[\text{Ni}(\text{S}_4\text{-C}_7)]_2$ (7) as orange-brown powders. 5–7 are soluble in THF, CH_2Cl_2 , and DMSO, $[\text{Ni}(\text{S}_4\text{-C}_3)]_2$ having the best and $[\text{Ni}(\text{S}_4\text{-C}_5)]_2$ having the least solubility. All four $[\text{Ni}(\text{S}_4\text{-C}_x)]_2$ complexes are diamagnetic. $[\text{Ni}(\text{N}_\text{H}\text{S}_4)]_2$ (8) forms according to eq 3 as a brown powder within 15 min. An identical product can be obtained from $\text{Ni}(\text{OOCCH}_3)_2$ and $\text{N}_\text{H}\text{S}_4\text{-H}_2$ in DMF. Like $[\text{Ni}(\text{S}_5)]_2$ it is only soluble in DMF or DMSO. The molecular weight determination in DMF yielded a relative mass of 406. In contrast to the other Ni complexes, 8 is paramagnetic with a magnetic moment of 1.9 μ_B , indicating the coordination of the NH donor. The NH coordination was further confirmed by H⁺/D⁺ exchange experiments. Amines undergo easy H⁺/D⁺

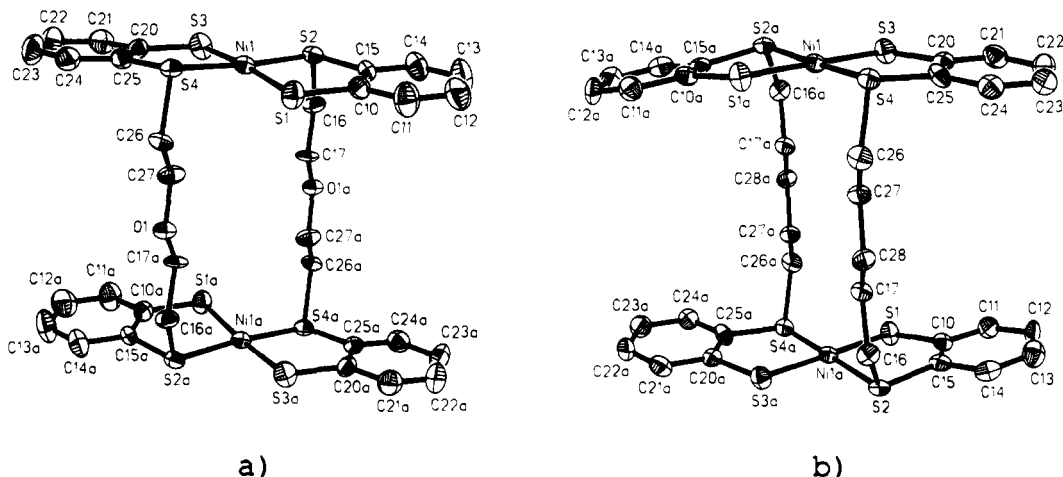


Figure 2. Molecular structures of (a) [Ni(OS₄)₂] (2) and (b) [Ni(S₄-C₅)₂] (6) (H atoms omitted).

Table VII. Selected Bond Distances (pm) and Bond Angles (deg)^a of [Ni(OS₄)₂]

Distances			
molecule 1		molecule 2	
Ni(1)-S(1)	217.8 (3)	Ni(2)-S(5)	218.0 (3)
Ni(1)-S(2)	217.8 (3)	Ni(2)-S(6)	217.2 (3)
Ni(1)-S(3)	218.0 (3)	Ni(2)-S(7)	218.5 (3)
Ni(1)-S(4)	217.8 (3)	Ni(2)-S(8)	218.0 (3)
S(1)-C(10)	175.9 (10)	S(5)-C(30)	175.6 (11)
S(2)-C(15)	177.9 (10)	S(6)-C(35)	177.8 (11)
S(2)-C(16)	183.7 (9)	S(6)-C(36)	182.2 (9)
C(15)-C(10)	137.8 (13)	C(35)-C(30)	138.5 (15)

Angles			
molecule 1		molecule 2	
S(2)-Ni(1)-S(1)	91.3 (1)	S(6)-Ni(2)-S(5)	91.3 (1)
S(3)-Ni(1)-S(2)	88.6 (1)	S(7)-Ni(2)-S(6)	89.2 (1)
S(4)-Ni(1)-S(1)	89.5 (1)	S(8)-Ni(2)-S(5)	88.6 (1)
S(4)-Ni(1)-S(3)	91.0 (1)	S(8)-Ni(2)-S(7)	91.5 (1)
C(20)-S(3)-Ni(1)	104.8 (3)	C(40)-S(7)-Ni(2)	104.4 (4)
C(25)-S(4)-Ni(1)	105.6 (3)	C(45)-S(8)-Ni(2)	104.9 (3)
C(26)-S(4)-Ni(1)	106.4 (3)	C(46)-S(8)-Ni(2)	105.5 (3)
C(20)-C(25)-S(4)	117.9 (7)	C(40)-C(45)-S(8)	119.3 (8)

^a Estimated standard deviations are given in parentheses.

exchange in acidic media via ammonium ions, but when **8** was treated with D₂SO₄ in MeOD, the IR spectra of the isolated products proved that no H⁺/D⁺ exchange had occurred. Thus, it is concluded that in solution [Ni(N_HS₄)], like [Ni(S₅)], is mononuclear and that the N atom of the 'N_HS₄' ligand is coordinated to the Ni center such that it cannot be protonated. No single crystals of **8** have been obtained so far.

Description and Discussion of the X-ray Structure Analyses of [Ni(S₆)] (1), [Ni(OS₄)₂·3THF (2), [Ni(S₅)] (3), [Ni(S₄-C₃)] (5), and [Ni(S₄-C₅)₂·2THF (6). Unambiguous structural characterization by X-ray structure determination was possible for **1**, **2**, **3**, **5**, and **6**.

[Ni(OS₄)₂] and [Ni(S₄-C₅)₂] have very similar molecular structures and represent a novel type of binuclear Ni complexes. The unit cell of [Ni(OS₄)₂] contains two independent molecules, which do not differ significantly. Figure 2a only shows a view of one of the molecules.

The Ni atoms of both complexes are approximately square-planar coordinated by four sulfur atoms. The cofacial NiS₄ entities are linked by either O(C₂H₄)₂ or (CH₂)₅ bridges, such that OS₄²⁻ and S₄-C₅²⁻ act as binucleating ligands. Ni, S, C, and, in the case of [Ni(OS₄)₂], O atoms form 16-membered macrocycles in which the Ni-Ni distances are 770 pm (**2**) and 802 pm (**6**). These distances are distinctly larger than Ni-Ni bond distances (250 pm in metallic Ni) and show that no direct interaction exists between the Ni centers. The Ni-S bond distances and angles, which are listed in Tables VII and VIII, cover the same range

Table VIII. Selected Bond Distances (pm) and Bond Angles (deg)^a of [Ni(S₄-C₅)₂]

Ni(1)-S(3)	217.7 (2)	Ni(1)-S(4)	216.5 (2)
Ni(1)-S(1A)	218.2 (2)	Ni(1)-S(2A)	217.7 (2)
S(3)-C(20)	176.4 (7)	S(4)-C(25)	177.3 (8)
S(4)-C(26)	182.1 (7)	C(15)-C(10)	137.9 (9)
S(3)-Ni(1)-S(4)	91.1 (1)	S(4)-Ni(1)-S(1A)	87.3 (1)
S(1A)-Ni(1)-S(2A)	91.1 (1)	S(3)-Ni(1)-S(2A)	90.5 (1)
Ni(1)-S(3)-C(20)	104.7 (2)	Ni(1)-S(4)-C(25)	105.6 (2)
Ni(1)-S(4)-C(26)	106.9 (2)	S(4)-C(25)-C(20)	118.1 (6)

^a Estimated standard deviations are given in parentheses.

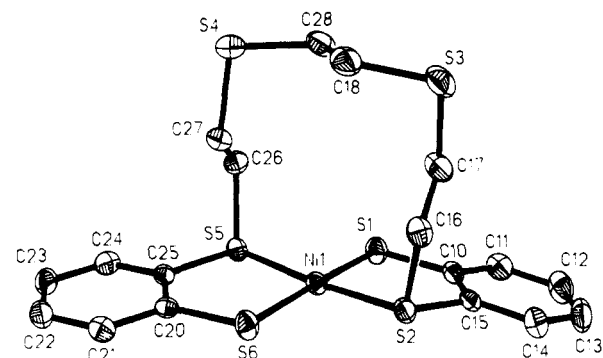


Figure 3. Molecular structure of [Ni(S₆)] (1) (H atoms omitted).

as found for other nickel(II) thiolato or thioether complexes.¹⁵ [Ni(OS₄)₂] has an average Ni-S distance of 217.8 pm, and [Ni(S₄-C₅)₂] one of 217.3 pm. These are almost the same as found for [Ni(14-ane-S₄)₂]²⁺ (217.6 pm)¹⁶ or [Ni₂(SC₂H₄SC₂-H₄S)₂] (217.6 pm)¹⁷ and very similar to the distances found in [Ni₃(dtb)₆] (221.9 pm)¹⁸ (dtb = dithiobenzoate), [Ni₆(SET)₁₂] (220 pm),¹⁹ or other sulfur-coordinated Ni complexes.

Several types of binuclear Ni complexes are known. Most of them have structures in which two square-planar-coordinated Ni atoms are connected via two bridging atoms.²⁰ Multidentate ligands can form two square-planar environments for two Ni atoms without such donor bridges, e.g. in the crown thioether complex

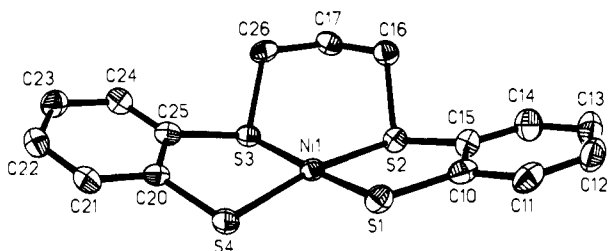
- (15) (a) Khare, G. P.; Shultz, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1971**, *93*, 3597. (b) Martin, J. M.; Newman, P. W. G.; Robinson, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, *20*, 2233. (c) Newman, P. W. G.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, *20*, 2239.
- (16) Davis, P. H.; White, L. K.; Belford, R. L. *Inorg. Chem.* **1975**, *14*, 1753.
- (17) Baker, D. J.; Goodall, D. C.; Moss, D. S. *J. Chem. Soc., Chem. Commun.* **1969**, 325.
- (18) Bonamico, M.; Dessy, G.; Fares, V. *J. Chem. Soc., Chem. Commun.* **1969**, 324.
- (19) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251.
- (20) Thewalt, U.; Hemmer, R.; Brune, H. A. *Z. Naturforsch.* **1979**, *34B*, 859.

Table IX. Selected Bond Distances (pm) and Bond Angles (deg)^a of [Ni('S₆')]]

Ni(1)–S(1)	218.7 (1)	Ni(1)–S(2)	217.3 (1)
Ni(1)–S(5)	216.4 (1)	Ni(1)–S(6)	218.4 (1)
S(1)–C(10)	175.3 (4)	S(2)–C(15)	177.6 (4)
S(2)–C(16)	183.3 (4)	C(15)–C(10)	139.1 (6)
S(1)–Ni(1)–S(2)	91.6 (1)	S(1)–Ni(1)–S(5)	87.8 (1)
S(2)–Ni(1)–S(6)	89.5 (1)	S(5)–Ni(1)–S(6)	91.4 (1)
Ni(1)–S(1)–C(10)	103.9 (2)	Ni(1)–S(2)–C(15)	104.7 (1)
Ni(1)–S(2)–C(16)	104.1 (1)	S(2)–C(15)–C(10)	118.0 (3)

^a Estimated standard deviations are given in parentheses.**Table X.** Selected Bond Distances (pm) and Bond Angles (deg)^a of [Ni('S₄-C₃')]]

Ni(1)–S(1)	216.6 (2)	Ni(1)–S(2)	216.2 (2)
Ni(1)–S(3)	217.5 (2)	Ni(1)–S(4)	217.5 (2)
S(1)–C(10)	176.1 (6)	S(2)–C(15)	176.6 (6)
S(2)–C(16)	184.3 (6)	C(15)–C(10)	142.2 (9)
S(1)–Ni(1)–S(2)	92.3 (1)	S(3)–Ni(1)–S(4)	89.9 (1)
S(2)–Ni(1)–S(3)	90.9 (1)	S(1)–Ni(1)–S(4)	88.0 (1)
Ni(1)–S(1)–C(10)	103.9 (2)	Ni(1)–S(2)–C(15)	105.7 (2)
Ni(1)–S(2)–C(16)	107.5 (2)	S(2)–C(15)–C(10)	116.6 (4)

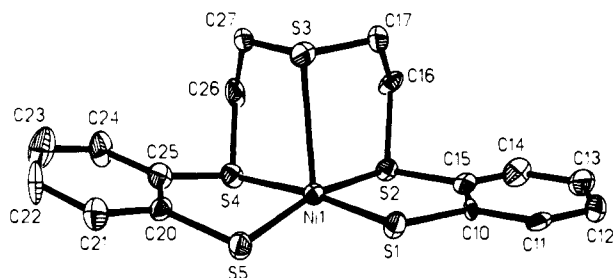
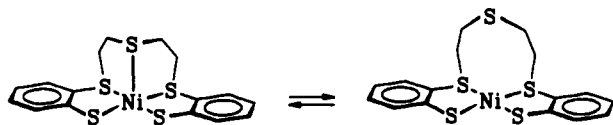
^a Estimated standard deviations are given in parentheses.**Figure 4.** Molecular structure of [Ni('S₄-C₃')] (5) (H atoms omitted).

[Ni₂(28-ane-S₈)]²¹ [Ni(C₆H₅CH₂CS₂)₂]²² and [Ni{(CH₂)₂PMe₂}]₂²³ have square-planar cofacial Ni centers, but in contrast to **2** and **6** they have additional Ni–Ni bonds. The closest structural similarity to **2** and **6** is shown by complexes like [Ni₂(BBI)]₂²⁴ (BBI = 5-*tert*-butyl-*m*-xylylenebis(acetylacetonate imine)) or [Ni₂(CN)₄(DMB)₂]²⁵ (DMB = 1,8-diisocyanomenthane). They, too, contain cofacial Ni centers but without Ni–Ni bonds.

The diamagnetism of [Ni('S₆')] indicated a square-planar coordination of the Ni center. This could be proved by the X-ray structure analysis. But in contrast to [Ni('OS₄')]₂ or [Ni('S₄-C₃')]₂, [Ni('S₆')] is mononuclear. Figure 3 shows that the bridge between the C₆H₄S₂ units diagonally spans over the NiS₄ plane like a handle. The "handle" thioether S atoms do not coordinate. They are turned away from the Ni center and their distances to the metal are 500.6 and 507.9 pm. Like in [Ni('OS₄')]₂ and [Ni('S₄-C₃')]₂, the thiolate S atoms occupy trans positions. The nickel–thioether distances (216.9 pm) are slightly shorter than the nickel–thiolate distances (218.5 pm) (Table IX), but the average Ni–S distance (217.7 pm) is again in the same range as found in [Ni('OS₄')]₂ (217.8 pm) or the Ni complexes cited above.

A mononuclear structure is also found in [Ni('S₄-C₃')] (5). Figure 4 shows that the Ni center again has an approximately square-planar coordination, but unlike in the complexes described before, here the thiolate sulfur atoms occupy cis positions. This may cause the tetrahedral distortion of the square, because in an ideal square the distance between the thiolate sulfur atoms would become shorter than van der Waals contacts (370 pm),²⁶ leading

- (21) Travis, K.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1970**, 1041.
 (22) Bonamico, M.; Dessy, G.; Fares, V. *J. Chem. Soc., Chem. Commun.* **1969**, 1106.
 (23) Karsch, H. H.; Schmidbaur, H. *Angew. Chem.* **1973**, *85*, 910.
 (24) Bradbury, J. R.; Hampton, J. L.; Martone, D. P.; Maverick, A. W. *Inorg. Chem.* **1989**, *28*, 2392.
 (25) Gladfelter, W. L.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 5909.
 (26) Pauling, L. *Die Natur der Chemischen Bindung*, 3rd ed.; Verlag Chemie: Weinheim, 1964; p 241.

**Figure 5.** Molecular structure of [Ni('S₅')] (3) (H atoms omitted).**Figure 6.** Thioether decoordination in [Ni('S₅')] (3).**Table XI.** Selected Bond Distances (pm) and Bond Angles (deg)^a of [Ni('S₅')]]

Ni(1)–S(1)	217.6 (3)	Ni(1)–S(2)	220.4 (3)
Ni(1)–S(3)	274.1 (3)	Ni(1)–S(4)	222.3 (3)
Ni(1)–S(5)	219.7 (4)	S(1)–C(10)	174.7 (11)
S(2)–C(15)	178.0 (12)	S(2)–C(16)	182.0 (11)
S(3)–C(17)	179.0 (13)	C(15)–C(10)	140.3 (15)
S(1)–Ni(1)–S(2)	90.8 (1)	S(1)–Ni(1)–S(3)	101.9 (1)
S(2)–Ni(1)–S(3)	87.0 (1)	S(1)–Ni(1)–S(5)	84.9 (1)
S(2)–Ni(1)–S(4)	95.0 (1)	S(3)–Ni(1)–S(4)	82.7 (1)
S(3)–Ni(1)–S(5)	105.8 (1)	S(4)–Ni(1)–S(5)	88.5 (1)
Ni(1)–S(1)–C(10)	105.6 (4)	Ni(1)–S(2)–C(15)	105.4 (4)
Ni(1)–S(2)–C(16)	109.0 (4)	Ni(1)–S(3)–C(17)	93.5 (4)
C(17)–S(3)–C(27)	102.3 (6)	S(2)–C(15)–C(10)	117.2 (9)

^a Estimated standard deviations are given in parentheses.

to repulsion. Consequently, the diagonal S–Ni–S angles deviate from 180°, showing angles of 169.2 (1) and 173.5 (1)°. The average Ni–S distance (217.0 pm) (Table X) compares with the distances in [Ni('OS₄')]₂ (217.8 pm) or [Ni('S₄-C₃')]₂ (217.3 pm).

[Ni('S₅')] (3), too, adopts a mononuclear structure but, in contrast to **1**, **2**, **5**, and **6**, has a five-coordinate Ni atom. Figure 5 shows that the coordination polyhedron is a slightly distorted square pyramid in which the sulfur atoms of the C₆H₄S₂ units form the basal plane and the linkage thioether S atom the apex.

Like in **5**, the thiolate atoms occupy cis positions. The nickel–thioether distances (221.3 pm) in the basal plane are slightly longer than the nickel–thiolate distances (218.6 pm) (Table XI), but the average basal Ni–S distance (220.0 pm) again compares well with the distances in **1**, **2**, **5**, and **6**. Contrasting the basal Ni–S distances, the apical Ni–S distance (274.1 (3) pm) is remarkably long. It is about 45 pm longer than the sum of the covalent radii of Ni(II) (125 pm) and thioether sulfur (104 pm) but more than 100 pm shorter than the van der Waals contact (380 pm).²⁶ This indicates a bonding interaction between the Ni center and the apical thioether S atom, which leads to a magnetically anomalous low-spin Ni center. Similar situations are also found in other square-pyramidal low-spin Ni(II) complexes,²⁷ e.g., in [Ni(DSP)I₂] (DSP = bis(2-(methylthio)phenyl)phenylphosphine) the basal Ni–S distance is 219 pm and the apical 279 pm.²⁸

Spectra. IR spectra in the range 4000–400 cm⁻¹ usually show only the ligand bands, allowing no conclusions with respect to the structure of the complexes. Only **2** and **8** have characteristic bands in their IR spectra at 1110 and 3220 cm⁻¹, which are assigned to the ν_{COC} and ν_{NH} absorptions of the ether and amine linkages, respectively.

In the FD mass spectra, peaks of mononuclear species can be observed for all complexes. The spectra of **2**, **3**, **5**, **6**, and **7** also display peaks of binuclear ions, although **3** and **5** were unam-

(27) Orioli, P. L. *Coord. Chem. Rev.* **1971**, *6*, 285.(28) Meek, D. W.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1915.

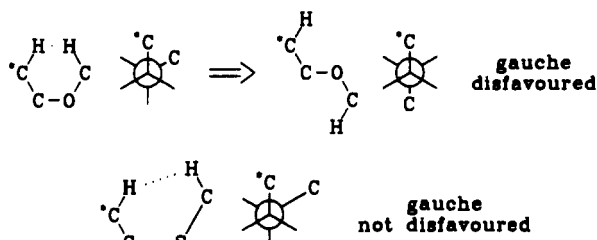


Figure 7. 1,4-Interactions in gauche $\text{CH}_2\text{-CH}_2\text{-O-CH}_2$ and $\text{CH}_2\text{-C-H}_2\text{-S-CH}_2$ linkages.

biguously proved mononuclear in solution as well as in the solid state. Accordingly, the mass spectra did not allow an unambiguous determination of the nuclearity of the complexes.

The compounds usually possess very low solubilities in organic solvents, and thus, NMR spectra could only be obtained from **2**, **3**, **5**, and **6**. The paramagnetism of **8** prevented the recording of a well-resolved NMR spectrum. The ^1H NMR spectra of **2**, **3**, **5**, and **6** each show four well-resolved multiplets for the aromatic hydrogen atoms. **5** shows four sharp singlets for its linkage H atoms. The others, however, especially **3**, show signals whose resolution is highly temperature dependent. This indicates that the bridges of the binuclear complexes are not rigid and that in $[\text{Ni}(\text{S}_5)]$ the linkage S atom may even decoordinate at higher temperatures (Figure 6).

The ^{13}C NMR spectra of **2**, **3**, and **6** each show six signals for the aromatic C atoms. The linkage carbon atoms of **2** and **3** give rise to two, and those of **6** to three signals. These results indicate highly symmetric structures of all complexes but do not allow a decision about their nuclearity. They do prove, however, that the bulk products do not contain mixtures of mono- and binuclear species and that the molecular structures found in the single-crystal X-ray structure determinations must be representative for the whole yield of the respective complexes.

Discussion and Conclusion

The results show that multidentate thiolate-thioether ligands with or without additional ether or amine donors yield either mononuclear or binuclear complexes with Ni(II). The resulting nuclearity can be explained in terms of preferred conformation of the free ligands, the presence of "hard" or "soft" donors in the bridge, and kinetically or sterically favored chelate ring closures. In an attempt to rationalize the structures of crown thioether complexes, it was suggested that ether and alkyl linkages form stretched chains because the gauche conformations in C-C-C-C or C-C-O-C but not in C-C-S-C units are disfavored in comparison to the anti conformation (Figure 7).²⁹

When these considerations are applied to the ligands and complexes described here, it can be expected that the bridges in the S_6 and S_5 ligands prefer bent conformations and those in the OS_4 and $\text{S}_4\text{-C}_5$ ligands, however, prefer stretched conformations. Accordingly, S_6 and S_5 will more easily wrap around one Ni center and form mononuclear complexes than the $\text{S}_4\text{-C}_5$ or OS_4 ligands, which should favor coordination to two Ni atoms and formation of binuclear species.

When the S_6 and S_5 ligands coordinate, these conformational effects may be supplemented by the softness of the bridge thioether S atoms. A Ni atom coordinated by four (soft) sulfur donors

certainly represents a soft center in terms of Pearson's theory and should bind more strongly to an additional thioether S donor of S_5 than to the hard oxygen donor of OS_4 . For the formation of $[\text{Ni}(\text{S}_5)]$ a similar course can be discussed until five donors are coordinated. Then, however, octahedral coordination of all six sulfur donors would force the Ni center into a high-spin state. This is apparently energetically disfavored. Thus, thioether donors decoordinate and the square-planar low-spin species forms.

In $[\text{Ni}(\text{S}_4\text{-C}_3)]$ a kinetic effect may become the decisive factor for structure selection. Intramolecular closure of a six-membered ring might be much faster than formation of a binuclear unit, which must include an intermolecular reaction step. This may also explain the difference in reaction times of the syntheses of $[\text{Ni}(\text{S}_4\text{-C}_3)]$ (20 min) in comparison to $[\text{Ni}(\text{S}_4\text{-C}_5)]$ (6 h).

In all complexes described here the nickel atom is essentially square-planar-coordinated by four sulfur donors. In the case of $[\text{Ni}(\text{S}_5)]$ the coordination sphere is supplemented by a fifth apical sulfur atom. This is the first example of a mononuclear 5-fold sulfur-coordinated nickel complex. Bond distances and ^1H NMR spectra at different temperatures indicate that this sulfur atom is rather loosely bound in comparison to the basal sulfur donors. A fifth donor is probably also present in $[\text{Ni}(\text{N}_4\text{S}_4)]$, where the apical position might be occupied by the amine donor.

It is not yet possible to decide how much these compounds resemble the nickel-sulfur centers in Ni enzymes. EXAFS data are partially contradictory. For example, the number of sulfur donors in Ni centers of hydrogenases range from 2.9 to 4 or more, and the nickel-sulfur distances range from 212 to 228 pm.³⁰ The distances can depend also on the redox state of the enzyme. In some cases, however, five-coordinate Ni centers are suggested; e.g., data from hydrogenases of *Methanobacterium thermoautotrophicum* can be correlated with a square-pyramidal coordination geometry around the Ni atom with a loosely bound axial ligand,³¹ and $[\text{Ni}(\text{S}_5)]$ and $[\text{Ni}(\text{N}_4\text{S}_4)]$ could serve as model compounds for such centers.

Acknowledgment. We gratefully acknowledge the support of this research from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. **1**, 129732-63-4; **2**, 129756-65-6; **3**, 129732-64-5; **4**, 129732-65-6; **5**, 129732-66-7; **6**, 129756-67-8; **7**, 129756-68-9; **8**, 129732-67-8; Ni(acac)₂, 3264-82-2; Na₂[Ni(S₂)₂], 129732-68-9; S₂-C₆H₄, 29869-28-1; bis(2-bromoethyl) sulfide, 7617-64-3; diiodomethane, 75-11-6; 1,3-dibromopropane, 109-64-8; 1,5-dibromopentane, 111-24-0; 1,7-dibromoheptane, 4549-31-9; bis(2-bromoethyl)amine, 3890-99-1.

Supplementary Material Available: Listings of crystallographic data and data collection parameters, anisotropic thermal parameters, all bond lengths and bond angles, and fractional coordinates of hydrogen atoms (23 pages); listings of F_o and F_c values (69 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, FRG, by citing the deposition nos. CSD 320057 ($[\text{Ni}(\text{S}_6)]$), CSD 320026 ($[\text{Ni}(\text{S}_5)]$), CSD 320059 ($[\text{Ni}(\text{OS}_4)]_2$), CSD 320017 ($[\text{Ni}(\text{S}_4\text{-C}_5)]_2$), and CSD 320039 ($[\text{Ni}(\text{S}_4\text{-C}_3)]$), the authors, and the reference.

(29) Wolf, R. E., Jr.; Hartmann, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(30) (a) Scott, R. A.; Wallin, S. A.; Czechowski, W.; DerVartanian, D. V.; Le Gall, J.; Peck, H. D., Jr.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864. (b) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062. (c) Cramer, S. P.; Pan, W.-H.; Eidsness, M. K.; Morton, T.; Ragsdale, S. W.; DerVartanian, D. V.; Ljungdahl, L. G.; Scott, R. A. *Inorg. Chem.* **1987**, *26*, 2477.

(31) Jordan, L. M. Ph.D. Dissertation, MIT, Cambridge, MA, 1985.