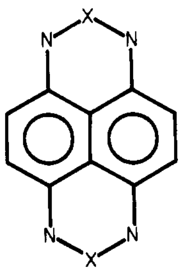

III

X= S, Se

results in the deviation of the P1–Ir–P2 angle from linearity as well as larger P1–Ir–S angles than P2–Ir–S angles (vide supra; cf. Table IV).

Other molecular planes and the dihedral angles are tabulated in Table V (see also Table IX, supplementary material).

Solvent Molecules. The solvent molecules are refined with unity weight as indicated by the density measurements. For **1**, the isotropic thermal parameter for benzene ranges from 8.6 to 9.8 Å^2 and for acetonitrile from 9.0 to 10.1 Å^2. For **2**, the coresponding values are 14.1–22.7 and 7.7–11.0 Å^2. These values are to be compared with the average value of ca. 4 Å^2 for the phenyl carbon atoms in both structures. It is apparent that both solvent molecules undergo larger thermal motions and/or they are partially lost in the data collection process. In particular, the latter is a likely cause of the high thermal parameters for the benzene molecule in **2**.

The solvent molecules are hydrogen bonded to the iridium complexes, thereby contributing to the stability of the crystal. In **1**, the methyl group of the acetonitrile (C53) makes hydrogen-bonding contacts of 3.77, 3.86, and 3.75 Å with S1, Cl1, and Cl4 while the nitrogen atom (N) makes contacts of 4.15 and 5.32 Å with Cl1 and Cl4, respectively. In **2**, the orientation of the acetonitrile molecule is rotated by 180° with respect to that in **1** (viz., interchange of C53 and N positions) such that N now makes contacts of 4.93 and 3.88 Å with S1 and Cl1 while C53 makes hydrogen-bonding contacts of 3.66, 4.19, and 4.38 Å with Cl4, S1, and Cl1, respectively. Despite the opposite orientations exhibited by the acetonitrile molecules in these crystals, the C–C and C–N bonds are determined to be 1.48 (3) and 1.11 (2) Å in **1** and 1.42 (3) and 1.16 (2) Å in **2**, respectively, in accord with the single- and triple-bond characters of these bonds.

The C–C bond lengths in the benzene molecules show a larger range of scattering than the phenyl rings in the complexes: 1.21 (4)–1.50 (5) Å vs. 1.35 (2)–1.46(2) Å in **2** but not in **1** (1.37 (3)–1.45 (3) Å vs. 1.38 (2)–1.45 (2) Å). The average values of 1.39 Å in **1** and 1.35 Å in **2** appear to be normal.

Registry No. **1**, 87763-87-9; **2**, 87763-88-0.

Supplementary Material Available: Table VI (anisotropic thermal parameters), Table VII (distances involving phenyl groups and solvent molecules), Table VIII (angles involving phenyl groups and solvent molecules), Table IX (least-squares planes and the atomic displacements), and Table X (structure factor amplitudes) (101 pages). Ordering information is given on any current masthead page.

Contribution from the Departament de Química Inorgànica and the Departament de Cristal.lografia i Mineralogia,
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Synthesis and Crystal and Molecular Structure of *cyclo*-Tetrakis[bis(μ-*N*-methylpiperidine-4-thiolato)nickel(II)]

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The reaction of nickel chloride with 4-mercapto-*N*-methylpiperidine in a basic solution gives the title complex. Crystals of the compound are monoclinic, space group $P2/n$, with a = 24.345 (3) Å, b = 10.638 (2) Å, c = 12.323 (2) Å, and β = 92.34 (2)°. With $Z = 2$ the calculated density is 1.32 g cm^{-3} (measured density 1.33 g cm^{-3}). Solution of the structure by direct methods led to a final weighted R factor of 0.077 for 2433 independent reflections. The crystal structure of the complex consists of a cyclic tetranuclear array of nickel atoms, bridged by eight sulfur atoms. The approximate square-planar NiS_4 units form the faces of a skew parallelogram with the sulfur atoms located at the corners. Axial and equatorial ligands alternate around the ring. The Ni–Ni distances average 2.665 (5) Å, and the closest S–S distances average 2.868 (6) Å. The Ni–S–Ni angles are 74.3 (1)°. The steric bulk of the piperidine rings provides a reasonable rationalization for the tetrameric structure.

Introduction

As a part of our work on the coordination of γ-mercapto amines to metal ions we have recently reported some solid complexes formed by *N*-methyl-4-mercaptopiperidine.[2-5] The reaction of this ligand with $NiCl_2$ in a basic solution yields a brown precipitate whose properties suggested a cyclic polynuclear structure, similar to the cyclic hexameric mercaptides of nickel previously reported.[6-8] The molecular weight determination, however, was consistent with a tetrameric structure. To our knowledge no cyclic tetrameric mer-

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Table I. Data for the X-ray Diffraction Study of $[(SC_5H_9N(CH_3))_2Ni]_4$

(A) Crystal Parameters at Room Temperature

cryst syst: monoclinic
space group: $P2/n$
$a = 24.345$ (3) Å
$b = 10.638$ (2) Å
$c = 12.323$ (2) Å
$\beta = 92.34$ (2)°
$V = 3189$ (2) Å^3

$Z = 2$
mol wt = 1276.7
$F(000) = 1360$
μ(Mo Kα) = 14.1 cm^{-1}
$D_{calcd} = 1.32$ g cm^{-3}
$D_{obsd}{}^a = 1.33$ g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: Philips PW-1100
radiation: Mo Kα ($\lambda = 0.71069$ Å)
monochromator: graphite crystal
scan technique: ω
scan width: 1°
scan speed: 0.03° s^{-1}
θ scan range: 25°
measd intens: 2757
obsd intens: 2433 ($I > 2.5\sigma(I)$)

[a] Measured by flotation in $ZnCl_2$ aqueous solution.

captides of nickel(II) have been reported so far. Therefore, a structural investigation of this compound was undertaken by X-ray diffraction methods. The results of this study are reported herein.

Experimental Section

N-Methyl-4-mercaptopiperidine was synthesized by following a previously reported method.[9]

Preparation of $[(SC_5H_9N(CH_3))_2Ni]_4$. $NiCl_2 \cdot 6H_2O$ (0.9 g) was dissolved in 50 mL of H_2O. About 2 mL of a concentrated ammonium hydroxide solution was added, and the solution was added slowly to another solution containing *N*-methyl-4-mercaptopiperidine (1 g) and 3 or 4 drops of methanol in H_2O (50 mL). After being stirred for some minutes, the mixture was cooled for some hours at 4 °C. The brown product was filtered off, washed with cold water and diethyl ether, and dried in vacuo over silica gel. The dry product was recrystallized from dry cyclohexane.

Anal. Calcd for $[(SC_5H_9(CH_3))_2Ni]_4$: C, 45.16; H, 7.58; N, 8.78; S, 20.09; Ni, 18.39. Found: C, 45.0; H, 7.58; N, 8.59; S, 20.1; Ni, 18.2. The molecular weight was determined cryoscopically in benzene: calculated for the tetramer, 1276.7; measured, 1320. The density calculated on the basis of two molecules per unit cell is 1.33 g cm^{-3}, while the observed value 1.32 g cm^{-3} is obtained by flotation in a $ZnCl_2$ aqueous solution.

Crystal Data and Intensity Measurements. A small crystal was selected for crystal data and intensity measurements on a Philips PW-1100 four-circle diffractometer. The unit cell was measured by automatic centering of 25 independent reflections and refining of the orientation matrix and unit-cell parameters by the least-squares method. Intensities were collected with use of monochromatized Mo Kα radiation and the ω-scan mode. A summary of the main crystal data is shown in Table I. Lorentz–polarization corrections, but no absorption corrections, were made.

Crystal Structure Determination and Refinement. The density calculation suggests eight $(C_6H_{12}NS)_2Ni$ units in the unit cell. The structure was solved by direct methods, with the MULTAN system of computer programs.[10] An E map computed with the phases of the set with the highest combined figure of merit revealed the position of Ni and S atoms. A subsequent Fourier synthesis revealed the remaining non-hydrogen atoms.

The structure was refined by the full-matrix least-squares method, with first isotropic and then anisotropic thermal parameters, to a final $R = 0.073$ ($R_w = 0.077$) for all observed reflections. The refinement was carried out with the program SHELX76.[11] Scattering factors were corrected for anomalous dispersion. A difference synthesis only revealed the position of 20 hydrogen atoms.

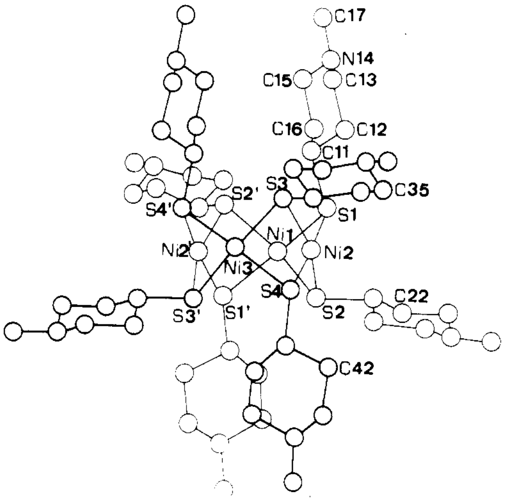

Figure 1. Perspective view of $[(SC_5H_9N(CH_3))_2Ni]_4$ showing the numbering scheme. Each atom on the piperidine rings has been assigned a number that first consists of the number of the sulfur atom to which it is bonded, followed by a sequential number starting at the carbon atom bonded to the sulfur and increasing around the ring. Primed atoms are related to those without primes by the binary axis passing through Ni(1) and Ni(3).

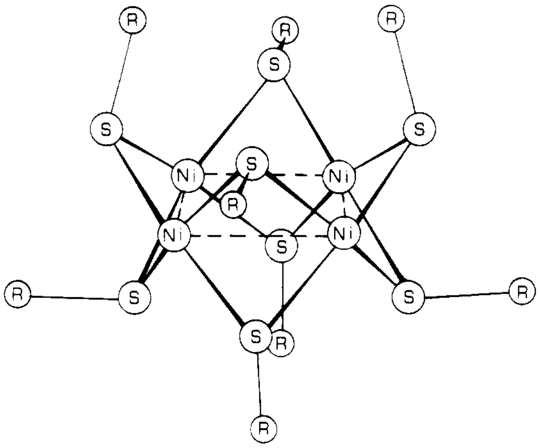

Figure 2. Perspective view of the nickel–sulfur skeleton.

Electronic spectra have been obtained with a Beckman Acta III spectrophotometer.

Results and Discussion

A tabulation of selected intramolecular distances and angles is presented in Table III. A perspective view of the molecule, showing the atom-numbering scheme, is given in Figure 1. For the sake of clarity, the nickel–sulfur skeleton has been represented in Figure 2. Figure 3 provides a stereoscopic view of the molecule.

The structure contains discrete molecules having a crystallographically imposed C_i symmetry, and there are two molecules in the unit cell, related by an inversion center. The packing of the molecules is due to van der Waals forces.

The structure consists of a cyclic tetranuclear array of nickel atoms, all lying rigorously in a plane due to the presence of a crystallographic twofold symmetry axis passing through the Ni(1) and Ni(3) atoms, bridged by eight sulfur atoms. The approximate square-planar NiS_4 units form the faces of a skew parallelogram with the eight sulfur atoms located at the corners. The distortions of the parallelogram are those of the point group D_{2d}-$\bar{4}2m$, where the virtual S_4 axis passes through the top and bottom faces of the polyhedron. The sulfur atoms lie in least-squares planes 1.423 (3) Å above and below the plane of the nickel atoms. The eight sulfurs belong approx-

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Table II. Atomic Coordinates (×10^4) in Crystalline $[(SC_5H_9N(CH_3))_2Ni]_4$[a]

atom	*x*	*y*	*z*
Ni(1)	2500 (0)	1516 (3)	7500 (0)
Ni(2)	1958 (1)	3307 (2)	6380 (2)
Ni(3)	2500 (0)	5088 (3)	7500 (0)
S(1)	1605 (1)	1630 (4)	7150 (3)
S(2)	2502 (1)	1849 (4)	5730 (3)
S(3)	1603 (1)	4755 (4)	7428 (3)
S(4)	2368 (1)	4981 (4)	5726 (3)
C(11)	1192 (5)	1941 (14)	8314 (11)
C(12)	612 (6)	2320 (19)	7913 (14)
C(13)	283 (8)	2624 (19)	8928 (19)
N(14)	232 (5)	1534 (13)	9616 (12)
C(15)	778 (7)	1078 (21)	9975 (16)
C(16)	1132 (7)	809 (17)	9041 (15)
C(17)	−102 (9)	1852 (20)	10558 (18)
C(21)	2072 (6)	724 (16)	4911 (17)
C(22)	1774 (7)	1358 (17)	3994 (18)
C(23)	1433 (8)	364 (19)	3375 (16)
N(24)	1748 (8)	−601 (19)	3007 (16)
C(25)	2032 (11)	−1214 (23)	3839 (25)
C(26)	2424 (7)	−368 (17)	4610 (17)
C(27)	1417 (9)	−1621 (21)	2406 (16)
C(31)	1242 (5)	5957 (14)	6599 (12)
C(32)	1132 (9)	7047 (18)	7322 (17)
C(33)	694 (19)	7969 (35)	6558 (27)
N(34)	270 (9)	7340 (26)	6118 (24)
C(35)	419 (9)	6431 (20)	5418 (22)
C(36)	726 (9)	5406 (20)	6154 (23)
C(37)	−57 (9)	8418 (22)	5578 (21)
C(41)	2991 (5)	4694 (14)	4958 (13)
C(42)	2815 (6)	4247 (17)	3803 (14)
C(43)	3326 (7)	4009 (18)	3145 (15)
N(44)	3629 (5)	5156 (14)	3077 (13)
C(45)	3801 (6)	5592 (20)	4149 (16)
C(46)	3309 (6)	5868 (15)	4863 (14)
C(47)	4128 (8)	4998 (25)	2402 (18)
H(11)	1414 (44)	2792 (103)	8754 (92)
H(12)	660 (44)	3049 (113)	7444 (99)
H(13A)	380 (59)	3478 (125)	9008 (127)
H(13B)	−110 (49)	2859 (106)	8661 (92)
H(15A)	1023 (48)	1803 (108)	10289 (106)
H(15B)	654 (41)	361 (111)	10326 (98)
H(16A)	931 (48)	140 (115)	8597 (97)
H(16B)	1448 (50)	356 (116)	8886 (97)
H(21)	1815 (49)	181 (103)	5618 (99)
H(23A)	2144 (52)	−1837 (118)	3815 (104)
H(23B)	1799 (57)	−1410 (127)	4303 (125)
H(33A)	985 (63)	8294 (142)	6307 (134)
H(33B)	779 (74)	8451 (172)	7119 (173)
H(36)	489 (47)	4847 (114)	6595 (99)
H(41)	2638 (44)	4262 (116)	5201 (92)
H(42)	2658 (48)	3666 (120)	3799 (97)
H(43)	3631 (48)	3295 (109)	3550 (101)
H(45)	4005 (49)	6120 (115)	4040 (96)
H(46A)	3091 (47)	6642 (106)	4614 (93)
H(46B)	3360 (43)	6315 (103)	5769 (101)

[a] Here and in subsequent tables, the numbers in parentheses are the estimated standard deviations for the last significant figures. Lists of anisotropic thermal parameters and observed structure factors are presented in the supplementary material.

imately to two sets of four chemically equivalent atoms related by the virtual S_4 axis. The diagonal planes defined by S(1), S(2), S(3′), S(4′), and S(3), S(4), S(1′), S(2′) are perfect within experimental error. The D_{2d} core polyhedron is compressed along the S_4 axis.

The nickel atoms have an approximately square-planar configuration with Ni–S distances (2.208 (4) Å) equal, within experimental error. The nickel atoms are displaced by 0.22 (1) Å from the best plane defined by the four sulfur atoms surrounding them, toward the outside of the Ni_4S_8 core. The Ni–Ni distances average 2.665 (5) Å and have been considered to provide a weak metal–metal bonding stabilization of the structure.[12]

Table III. Principal Intramolecular Distances (Å) and Angles (deg) for the Nickel–Sulfur Skeleton

(a) Distances

Ni(1)· · ·Ni(2)	2.669 (2)	Ni(3)–S(4)	2.200 (3)
Ni(2)· · ·Ni(3)	2.662 (2)	S(1)· · ·S(2)	2.863 (4)
Ni(1)–S(1)	2.206 (3)	S(3)· · ·S(4)	2.872 (4)
Ni(1)–S(2)	2.210 (4)	S(1)· · ·S(3)	3.342 (4)
Ni(2)–S(1)	2.211 (4)	S(2)· · ·S(4)	3.348 (4)
Ni(2)–S(2)	2.211 (3)	S(1)· · ·S(2′)	3.338 (4)
Ni(2)–S(3)	2.209 (3)	S(3)· · ·S(4′)	3.323 (4)
Ni(2)–S(4)	2.209 (4)	Ni(1)· · ·Ni(3)	3.800 (3)
Ni(3)–S(3)	2.211 (3)	Ni(2)· · ·Ni(2′)	3.740 (3)

(b) Angles

S(2)–Ni(1)–S(1)	80.8 (1)	Ni(2)–S(3)–Ni(3)	74.1 (1)
S(2)–Ni(2)–S(1)	80.7 (1)	Ni(2)–S(4)–Ni(3)	74.3 (1)
S(4)–Ni(2)–S(3)	81.8 (1)	Ni(2)–S(1)–Ni(1)	74.4 (1)
S(4)–Ni(3)–S(3)	81.3 (1)	Ni(2)–S(2)–Ni(1)	74.3 (1)
S(3)–Ni(2)–S(1)	98.3 (1)	Ni(1)–Ni(2)–Ni(3)	90.9 (1)
S(4)–Ni(2)–S(2)	98.4 (1)	Ni(2)–Ni(1)–Ni(2′)	89.0 (1)
S(1)–Ni(1)–S(2′)	98.2 (1)	Ni(2)–Ni(3)–Ni(2′)	89.2 (1)
S(3)–Ni(3)–S(4′)	97.8 (1)		

Ligand Geometry

	n			
	1	2	3	4
	(a) Bond Lengths			
S(*n*)–C(*n*1)	1.82 (1)	1.86 (1)	1.84 (1)	1.85 (1)
C(*n*1)–C(*n*2)	1.53 (2)	1.48 (2)	1.49 (2)	1.54 (2)
C(*n*2)–C(*n*3)	1.55 (2)	1.53 (2)	1.70 (4)	1.53 (2)
C(*n*3)–N(*n*4)	1.45 (2)	1.37 (2)	1.33 (4)	1.43 (2)
N(*n*4)–C(*n*5)	1.47 (2)	1.38 (3)	1.36 (3)	1.45 (2)
C(*n*5)–C(*n*6)	1.49 (2)	1.60 (3)	1.59 (2)	1.54 (2)
C(*n*1)–C(*n*6)	1.51 (2)	1.50 (2)	1.47 (2)	1.48 (2)
N(*n*4)–C(*n*7)	1.48 (2)	1.53 (2)	1.53 (2)	1.51 (2)
	(b) Bond Angles			
S(*n*)–C(*n*1)–C(*n*2)	109 (1)	112 (1)	108 (1)	109 (1)
S(*n*)–C(*n*1)–C(*n*6)	113 (1)	109 (1)	108 (1)	110 (1)
C(*n*6)–C(*n*1)–C(*n*2)	107 (1)	116 (2)	111 (1)	108 (1)
C(*n*1)–C(*n*2)–C(*n*3)	107 (1)	108 (1)	104 (1)	110 (1)
C(*n*2)–C(*n*3)–N(*n*4)	112 (1)	113 (1)	113 (3)	109 (1)
C(*n*3)–N(*n*4)–C(*n*7)	110 (1)	114 (2)	101 (2)	112 (1)
C(*n*7)–N(*n*4)–C(*n*5)	111 (1)	105 (2)	114 (2)	109 (1)
	(c) Puckering Parameters			
q_2	0.066	0.045	0.102	0.021
q_3	0.596	0.532	−0.692	0.607
Q	0.599	0.534	0.610	0.607
Φ	307.8	274.4	269.6	320.1
θ	6.3	4.9	−9.6	2.0

The S–Ni–S angles for which both sulfur atoms lie on the same side of the plane of nickel atoms average 98.2 (3)° and are 17° greater than those for which the sulfur atoms lie on opposite sides of the plane (81.2 (5)°). The Ni–S–Ni angles average 74.3 (1)°.

The S···S distances for the sulfur atoms lying all above or all below the nickel plane average 3.338 (10) Å, while for the sulfur atoms lying on opposite sides of the plane the distances average 2.868 (6) Å, 0.83 Å shorter than the van der waals radius for sulfur. These latter interactions are considered strong enough to be bonding interactions.[12] A displacement of the nickel atoms toward the center of the planes defined by the four nearest sulfur atoms would result not only in a shorter Ni–Ni distance, thus increasing the metal–metal interactions, but also in an increase of the S(1)···S(2) and S(3)···S(4) distances (sulfur atoms lying on opposite sides of the nickel planes), thus weakening the S···S interactions. Attractive S···S interactions may well be more important than attractive M–M forces in describing the bond.

Half of the thiolate ligands are attached to nickel atoms in such a way that the S–C bond is approximately parallel to the

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[12] Fackler, J., Jr. *Prog. Inorg. Chem.* **1976**, *21*, 55.

Table IV. Selected Least-Squares Planes and Deviations (Å) of Individual Atoms from These Planes[a]

plane 1		plane 2		plane 3		plane 4		plane 5	
Ni(1)	0	S(1)	−0.114	S(1)	−0.115	S(3)	−0.118	S(1)	0.120
Ni(2)	0	S(2)	−0.114	S(2)	0.115	S(4)	0.118	S(3)	−0.120
Ni(3)	0	S(1')	0.114	S(3)	0.115	S(3')	−0.118	S(2')	−0.120
Ni(2')	0	S(2')	0.114	S(4)	−0.115	S(4')	0.118	S(4')	0.120
		Ni(1)[b]	−0.231	Ni(2)[b]	−0.214	Ni(3)[b]	0.233		
A	0.710	*A*	0	*A*	0.705	*A*	0	*A*	0.709
B	0	*B*	1	*B*	0	*B*	1	*B*	0
C	−0.705	*C*	0	*C*	0.710	*C*	0	*C*	−0.705
D	−2.022	*D*	1.846	*D*	9.006	*D*	5.179	*D*	−3.456

Angles between Planes (deg): 1-2, 90.0; 1-3, 90.0; 1-4, 90.0; 1-5, 0.1

[a] *A*, *B*, *C*, and *D* are the variables for the normal form of the equation of a plane, $AX + BY + CZ = D$, in orthogonal axes *a*, *b*, c^*. [b] These atoms are not included in mean-plane calculations.

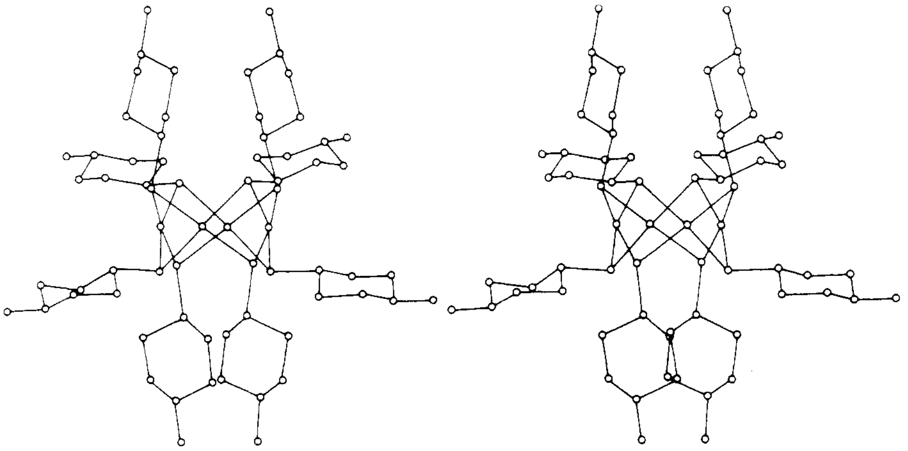

Figure 3. Stereoview of the molecule. Atoms are represented as circles of arbitrary size.

plane of nickel atoms (axial), while in the others the bond is approximately normal to the plane (equatorial). The S···S–C angles (the angles at sulfur atoms between a S–C bond and a line connecting the sulfur atom to the nearest sulfur atom on the other side of the plane of nickel atoms) for equatorial ligands are 81.1 and 81.3° while for the axial ligands they are 158.3 and 158.7°. Axial and equatorial ligands alternate around the ring.

The "puckering parameters"[13] of the piperidine rings describe slightly distorted "chair" conformations. The distorted geometry of the piperidine rings is probably forced by steric interactions between adjacent rings. Although not all the hydrogen atoms were located experimentally, some of them were deduced from the positions of the carbon atoms, with the assumption of a C–H bond length of 1.08 Å. The H(46)···H(32) distance, for example, is 2.1 Å, smaller than twice the van der Waals radius for hydrogen (2.4 Å).

Such a repulsive interaction would cause the C(33)–C(32)–C(31) angle to decrease from the idealized tetrahedral value, to 104°, and the C(33)–C(32) bond distance to increase from the idealized value of 1.54 to 1.70 Å (see Table III). Moreover, puckering of the rings would help relieve close contacts between the proton of the carbon bonded to a sulfur atom in the equatorial ligands and the nearest sulfur atom on the other side of the plane of nickel atoms. Thus the S(1)···H(21) distance is 2.51 Å, smaller than the van der Waals contact distance 3.05 Å, causing the C(22)–C(21)–C(26) angle to increase to 116° and the C(21)–C(22) bond distance to decrease to 1.48 Å. This steric hindrance probably prevents the formation of the stable six-membered ring found in other nickel thiolates. If the NiS units were to form a six-membered ring, impossible short nonbonded H···H contact distances would result. If the dihedral angle between adjacent NiS_4 units were able to open further to 120°, the H(46)···H(32) distance would be only 1.6 Å.

Table V. Comparison of Some Distances (Å) and Angles (deg) in Cyclic Mercaptide Complexes of Nickel, $[NiL_2]_n$

L[a]	*n*	Ni-Ni	Ni-S	Ni-S-Ni	S-Ni-S	S-S
A	6	2.92	2.21 (1)	82.9 (5)	82.6 (3), 97.5 (6)	3.32
B	6	2.92	2.20			2.9[b]
C	6	2.93 (1)	2.20 (1)	83.5 (6)	81.7 (6), 98.0 (5)	3.31 (1), 2.88 (2)
D	4	2.665 (5)	2.208 (4)	74.3 (1)	81.0 (3), 98.2 (3)	3.34 (1), 2.867 (6)

[a] Key: A = SC_2H_4OH;[8] B = SC_2H_5;[6] C = $SC_3H_6NH(CH_3)_2$;[14] D = $SC_5H_9N(CH_3)$ (this work). [b] Distance approximate from limited data presented.

The steric bulk of the piperidine rings provides a reasonable rationalization for the tetrameric structure. Further studies of the steric effect of the ligands on the resulting geometry are in progress.

A comparison between the structural parameters in $[(SC_5H_9N(CH_3))_2Ni]_4$ with those reported for six-membered-ring-bridged mercaptide complexes of nickel is shown in Table V. The principal effects caused by the smaller ring in the tetrameric molecule are decreases in the Ni–Ni distance and in the Ni–S–Ni angle.

Molecular weight determinations for this compound in benzene give a good agreement with the weight expected for the tetrameric formulation, indicating that the tetrameric structure is maintained in solution.

The magnetic moment was determined by the Faraday method. With use of the diamagnetic correction $\chi_{dia} = -168 \times 10^{-6}$, estimated from Pascal's constants,[15] the room-tem-

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Table VI. Electronic Spectra[a] of $Ni(Et_2dtc)_2$ and $[Ni(SC_5H_9N(CH_3))_2]_4$

transitions	$Ni(Et_2$-$dtc)_2$	calcd	$[Ni(SC_5H_9N$-$(CH_3))_2]_4$	assignt
$^1A_g \rightarrow {}^1B_{1g}$	15.9	15.62	15.7	$^1A_1 \rightarrow {}^1A_2$
$\rightarrow {}^1B_{2g}$	17.0	17.10	16.9	$\rightarrow {}^1B_1$
$\rightarrow {}^1B_{3g}$	19.0	19.10	18.7	$\rightarrow {}^1B_2$
$\rightarrow {}^1B_{1g}$	21.0	21.03	20.2	$\rightarrow {}^1A_2$
CT	23.0	23.59	23.2	CT
solvent (?)	25.0		26.6	CT
CT	31.0	30.30, 31.65		
r_{Ni-S}, Å	2.201		2.208	
α (bite angle), deg	79.2		81.3	

[a] In 10^3 cm^{-1}.

perature magnetic moment was 0.79 μ_B/Ni atom. We are currently investigating the magnetic behavior at lower temperatures.

Electronic Spectra. The solid-state spectrum at room temperature is very similar to the soluution spectrum obtained in methanol and ethanol, thus showing that the symmetry is not altered in solution. The spectra show strong absorptions at 23 200 and 26 600 cm^{-1} ($\epsilon \approx 5000$ L mol^{-1} cm^{-1}) and a strong and broad unresolved absorption at ~20 000 cm^{-1} ($\epsilon \approx 4300$ L mol^{-1} cm^{-1}) rapidly decreasing until ~14 000 cm^{-1}. The fourth-derivative curves with the spectrum manually digitized from chart paper[16] (with use of the integer set 20, 19, 18, 16) reveal that four maxima are clearly resolved at 15 700, 16 900, 18 700, and 20 200 cm^{-1} (Table VI). The lowest lying band is much weaker than the other transitions. The energies of these resolved maxima agree well with those reported for complexes with NiS_4 chromophores.[17]

The crystal structure of bis(diethyldithiocarbamato)nickel(II) ($Ni(Et_2dtc)_2$) is known.[18,19] The molecualr symmetry is D_{2h} with Ni–S bond distances of 2.201 (2) Å and S–Ni–S angles of 79.2°, values very similar to those reported here. The electronic absorptions and their assignment are shown in Table VI.[20] The absorptions at 17 000 cm^{-1} ($d_{yz} \rightarrow d_{xy}$) and 19 000 cm^{-1} ($d_{xz} \rightarrow d_{xy}$) are very weak and are only observed in the polarized single-crystal spectra.

In our case the extinction coefficients for these bands are substantially higher. This may be explained because in our case the nickel atoms are lifted out of the planes of the sulfur atoms by 0.22 (1) Å. Upon this C_{2v} distortion, the transitions $d_{xz} \rightarrow d_{xy}$ and $d_{yz} \rightarrow d_{xy}$ become group theoretically allowed, whereas the transitions $d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ remain forbidden. The small distortion does not significantly change the energy level positions[21] (the angle the Ni–S bonds make with the z axis is 95°).

Recently, Atanassov and Nikolov[17] have made a study of the electronic spectra of planar $Ni(L-L)_2$ complexes using the crystal field and angular overlap methods. The effect of the chelate angle on the s–d mixing as well as that of the configurational and spin–orbit interaction on the transition energy have been traced. The parameters derived from the d–d spectral analysis have been used to interpret the charge-transfer spectra. The calculated transition energies are shown in Table VI and show a good agreement with the experimental values.

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Supplementary Material Available: Packing diagram and listings of thermal parameters, bond distances and angles, least-squares planes and deviations therefrom, and observed and calculated structure factors for $[(SC_5H_9N(CH_3))_2Ni]_4$ (25 pages). Ordering information is given on any current masthead page.

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