function, have not been observed to show sign inversion upon pH alteration. Second, the widespread tendency to correlate ligand chirality with optical behavior must be seriously questioned. The spatial arrangements of chelate rings may, in fact, be only a small factor in determining the signs of CD transitions, and, instead, the positions of the ligating atoms and their distortions from octahedral positions may be the determining factors.

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Some Nickel(II) Complexes with Sulfur-Containing Schiff Base Ligands[1a]

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The diverse stereochemistry and varied stereochemical equilibria of nickel(II) complexes with multidentate β-keto amine and salicylaldimine ligands has been discussed in detail.[2] Busch and his coworkers[3-7] have carefully studied some complexes of nickel(II) with various 2-aminoethanethiol derivatives, including some α-diimine ligands derived from α-diketones and 2-aminoethanethiol. In contrast with the chemistry of β-keto imine complexes, for example, the chemistry of the latter compounds is relatively simple. Nickel(II) complexes with mercapto amines and mercapto imines invariably exist in the low-spin planar configuration. The only substantial deviation from this simple stereochemistry is found in the marked tendency for the formation of polynuclear species involving bridging sulfur atoms, though such complexes have not been reported for α-diketobis(2-mercaptoethylimine) ligands. We report the synthesis of some nickel(II) complexes with sulfur-containing β-keto amine ligands and the details of the structure elucidation.

Experimental Section

Physical Measurements.—The visible and ultraviolet spectra were obtained in 1,2-dichloroethane using either a Cary Model 14 or a Beckman Model DB-G recording spectrophotometer; matched 10-mm cells were used for all measurements. Infrared spectra were obtained using either a Beckman Model IR-12 or a Perkin-Elmer Model 257 spectrophotometer. Both potassium bromide disk and Nujol mull techniques were employed. The nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer in saturated carbon disulfide solution. Tetramethylsilane was used as the standard. Molecular weights were determined with the Perkin-Elmer Hitachi Model 115 vapor pressure osmometer in *N,N*-dimethylacetamide. Analyses were performed by either Alfred Bernhardt Mikroanaltisches Laboratorium, Elbach, West Germany, or Micro-Tech Laboratories, Inc., Skokie, Ill.

Materials.—The metal salts employed were of reagent grade or the equivalent. β-Aminoethanethiol hydrochloride (96%) was obtained from Evans Chemetics, New York, N. Y. Acetylacetone, *o*-aminobenzenethiol, and salicylaldehyde (practical) were obtained from Eastman. All materials were used as obtained, without further purification.

Preparations. Bis(2-(2-mercaptoethyl)imino-4-pentanato)dinickel(II), $Ni_2(AME)_2$.—Two and a half grams (0.022 mol) of 2-mercaptoethylamine hydrochloride and 5.89 g (0.06 mol) of potassium acetate were dissolved in 50 ml of methanol and the potassium chloride removed by filtration. To the filtrate was added 2.47 ml (0.024 mol) of acetylacetone and the solution was heated on a steam bath for 10–15 min. This was added to a solution of 4.98 g (0.02 mol) of nickel acetate tetrahydrate in 50–100 ml of hot methanol. The product was filtered and purified by continuous extraction into benzene and recovered by evaporating to dryness. The burgundy red complex is soluble in common organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 432; found, 505. *Anal.* Calcd for $NiC_9H_{11}NSO$: C, 38.93; H, 5.13; N, 6.49; S, 14.85. Found: C, 39.12; H, 5.11; N, 6.59; S, 14.70.

Bis(2-(2-mercaptoethyl)salicylaldiminato)dinickel(II), $Ni_2(SME)_2$.—This compound was prepared in the same manner using 2.50 g of 2-mercaptoethylamine hydrochloride, 5.89 g of potassium acetate, 2.51 ml (0.024 mol) of salicylaldehyde, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is soluble in polar organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 476; found, 632. *Anal.* Calcd for NiC_9H_9NSO: C, 45.43; H, 3.81; N, 5.89; S, 13.48. Found: C, 46.14; H, 3.93; N, 5.95; S, 12.70.

Bis(2-(2-mercaptophenyl)imino-4-pentanato)dinickel(II), $Ni_2(AMA)_2$.—The nickel(II) complex of 2-(2-mercaptophenyl)-imino-4-pentanone was prepared similarly using 2.36 ml (0.022 mol) of 2-mercaptoaniline, 2.47 ml of acetylacetone, 5.89 g of potassium acetate, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is soluble in polar organic solvents. Molecular weight in *N,N*-dimethylacetamide: calcd for dimer, 572; found, 676. *Anal.* Calcd for $NiC_{11}H_{11}NSO$: C, 50.05; H, 4.20; N, 5.31; S, 12.15. Found: C, 52.34; H, 4.49; N, 5.46; S, 11.60.

Bis(2-(2-mercaptophenyl)salicylaldiminato)dinickel(II), $Ni_2(SMA)_2$.—The same method was employed using 2.36 ml of 2-mercaptoaniline, 2.51 ml of salicylaldehyde, 5.89 g of potassium acetate, and 4.98 g of nickel acetate tetrahydrate. The red-brown complex is sparingly soluble in organic solvents. *Anal.* Calcd for $NiC_{13}H_9NSO$: C, 54.65; H, 3.17; N, 4.90; S, 11.21. Found: C, 54.65; H, 3.30; N, 5.11; S, 11.08.

Results and Discussion

Magnetic susceptibilities were measured by the Gouy method. The data are summarized in Table I. The small residual paramagnetism may be attributed to

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR SOME NICKEL(II) COMPLEXES WITH SULFUR-CONTAINING SCHIFF BASE LIGANDS

Compound	T, °K	$10^6\chi_m$/Ni	μ/Ni[a]
$Ni_2(AME)_2$	296	12.1	0.17
$Ni_2(SME)_2$	296	22.0	0.22
$Ni_2(AMA)_2$	296	21.6	0.23
$Ni_2(SMA)_2$	296	66.5	0.40

[a] $\mu = 2.84 (\chi_m T)^{1/2}$.

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errors in the diamagnetic corrections for the ligands which were calculated from Pascal's constants;[8] the diamagnetism of these complexes is consistent with the proposal that each nickel ion is in a planar environment.[2]

The molecular weights of the compounds were determined by vapor pressure osmometry in *N*,*N*-dimethylacetamide. In each case, the experimentally determined molecular weight is greater than the calculated value. Though the precision of the measurements is limited by the low vapor pressure of the solvent, the data show that these molecules are at least dimers.

The electronic spectra are summarized in Table II.

TABLE II

ELECTRONIC SPECTRA OF SOME NICKEL(II) COMPLEXES WITH SULFUR-CONTAINING SCHIFF BASE LIGANDS

	Spectra, kK (ϵ)			
Complex	"d–d"		Symmetry allowed	
$Ni_2(AME)_2$	19.2 (1320)	28.0 (5750)	32.2 (10,900)	34.5 (154,000)
$Ni_2(SME)_2$	18.2 (1720)	26.2 (12,700)	...	38.4 (42,200)
$Ni_2(AMA)_2$	19.2 (1950)	...	32.2 (14,000)	34.5 (109,000)
$Ni_2(SMA)_2$	...	25.6 (16,600)	...	38.8 (44,600) 39.6 (41,900)

The spectra are complex, exhibiting the profusion of transitions expected of the singlet nickel(II) ion in an environment of C_s symmetry. No assignments of electronic states were attempted. It is useful to note, however, that the intensities of the spectral transitions are comparable with those observed in other planar, sulfur-containing nickel(II) complexes.[3-7]

TABLE III

NUCLEAR MAGNETIC RESONANCE DATA

$Ni_2(AME)_2$		$Ni_2(SME)_2$		$Ni_2(AMA)_2$	
δ, ppm	Assignment[a]	δ, ppm	Assignment	δ, ppm	Assignment
1.28		1.56		1.46	
1.54		1.66		1.83	Methyl (3)
1.78	Methyl (3)	1.78		2.22	Methyl (1)
1.90	Methyl (1)	3.38		5.25	Proton (2)
2.02		3.64	Proton (1)	6.63	
2.13		3.83		6.76	
2.23		3.92		6.93	
2.35		4.20		7.10	
2.45		6.30		7.24	
2.55		6.42		7.31	Benzene
2.87		6.55			
2.94		6.68			
3.07		6.93			
3.15		7.08			
3.28		7.23			
3.38		7.59			
3.52					
3.62					
3.73					
3.18					
4.85	Proton (2)				

[a] See Figure 1 for proton positions.

Infrared spectra have been assigned according to Martell and Ueno.[9] The two compounds which were derived from acetylacetone, $Ni_2(AME)_2$ and $Ni_2(AMA)_2$, show lower composite C=C and C=N stretching frequencies (1508 and 1512 cm^{-1}, respectively) than those of the compounds derived from salicylaldehyde, $Ni_2(SME)_2$ and $Ni_2(SMA)_2$ (1532 and 1522 cm^{-1}, respectively), suggesting that the C=N bonds are more extensively delocalized throughout the six-membered chelate ring in the former complexes than in the latter.

The proton magnetic resonance spectra of $Ni_2(AME)_2$, $Ni_2(SME)_2$, and $Ni_2(AMA)_2$ are summarized in Table III. The spectrum of $Ni_2(SMA)_2$ could not be obtained because of the low solubility in suitable solvents. The principal features of these spectra conform to the proposed structure. The pmr spectrum of $Ni_2(SME)_2$ shows a strong peak assignable to proton (1), structure III. (See Figure 1.) The signals arising from the aromatic nucleus have not been individually assigned; the signals arising from the ethylene linkage are discussed below.

In the complexes $Ni_2(AME)_2$ and $Ni_2(AMA)_2$, the

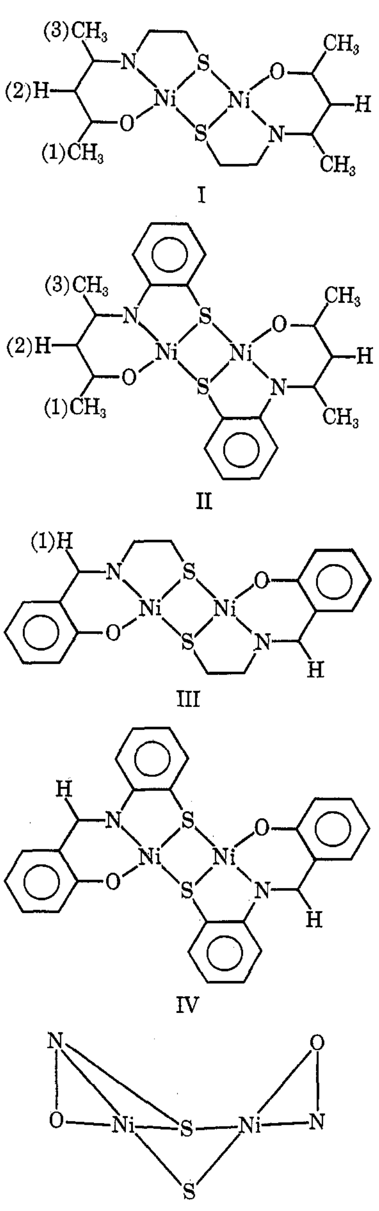

Figure 1.—Structures discussed in this paper: I, $Ni_2(AME)_2$; II, $Ni_2(AMA)_2$; III, $Ni_2(SME)_2$; IV, $Ni_2(SMA)_2$; V, perspective view showing the dihedral angle between planar nickel sites.

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methyl signals from the 2,4-pentanedione residues occur at 1.78 and 1.90 ppm downfield from TMS as an internal standard and at 1.83 and 2.22 ppm downfield, respectively. From a comparison of these spectra with the pmr spectrum of Ni(sacsac)(sacac)[10] and a consideration of the bond anisotropies of the C=N and C=O linkages, we have tentatively assigned the methyl signal at lower field to the group adjacent to the C=O bond. The proton (2), structures I and II, occurs at about 5 ppm downfield from TMS as a consequence of the deshielding effect of the pseudoaromatic chelate ring.

The spectra of the two compounds containing the 2-mercaptoethylamine residue show only very diffuse signals (if any) for the ABCD protons of the ethylene moiety. The proposed structure, like that of di-μ-(bis-(2-mercaptoethyl) sulfide)-dinickel(II),[11] possesses a C_2 axis as its only element of symmetry. The molecule is therefore optically active, with the enantiomers related by inversion of the dihedral angle about an axis joining the bridging sulfur atoms. For a stable optical isomer, a complex ABCD pattern should appear in the vicinity of the observed methyl signals of the 2,4-pentanedione residue. We have made no attempt to assign the signals observed in this region, but we note significant and reversible enhancement of the intensities (relative to the methyl signals) as temperature is lowered from 30 to −60°. This observation is consistent with a decreased rate of intramolecular racemization at lower temperatures.

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The Pyrolysis of Pentaborane(9)

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Although the pyrolysis of diborane has been studied extensively, very few data are available on the pyrolysis of other boron hydrides. Pentaborane(9) is known to be thermally stable up to 200° but to undergo considerable decomposition at 250° to give hydrogen and nonvolatile solids.[1] A short study by Houser and Greenough[2] of the pyrolysis of pentaborane(9) in a flow system at 590–645°K concluded that the decomposition was first order. A study was made by Cheney, *et al.*,[3] at 100–300 mm pressure and a temperature range of 194–243° by measuring initial rates of pressure increase. They also found the reaction to be first order. Hydrogen and nonvolatile solids were the only products found in both of these studies. The work reported here is a study of the pyrolysis of pentaborane(9) at 40–80 mm pressure and 202–228° in which pentaborane(9) was heated in sealed glass bulbs and gaseous products were analyzed in a vacuum line.

Experimental Section

Pentaborane(9) was prepared by introducing 440 mm of diborane and 100 mm of dimethyl ether into a reaction vessel to which a water condenser had been sealed at the top. The vessel was heated to 150° for 20 min.[4] The products were fractionated and pure pentaborane(9) was isolated. The 0° vapor pressure was 66 mm (lit.[5] 66 mm) and a fractionation–codistillation chromatograph[6] showed only one peak.

Using standard high-vacuum techniques, samples of pentaborane(9) were measured and condensed into 40-ml Pyrex glass bulbs which had been previously exposed to diborane at 0.5 atm pressure for at least 24 hr at room temperature to season the walls. The bulbs were then sealed off under vacuum and placed in a temperature bath of glycerin covered with General Electric SF-1017 silicone fluid to reduce evaporation. The bath was heated by a thermostated, stirring hot plate, which held the temperature of the bath constant to within ±1.0° during the time that the data were taken. A bulb was removed from the bath every 10 or 15 hr, cooled to room temperature, and then opened into vacuum with a tube breaker.[7] The hydrogen was transferred by a Toepler pump into a standard volume and measured. The gas which condensed at −196°, which was shown to be pure pentaborane(9) by fractionation–codistillation chromatography, was then measured.

Results and Discussion

Kinetics.—The pyrolysis of pentaborane(9) was studied at 202, 213.5, and 228° at a pressure of about 40 mm and at 204° at a pressure of about 80 mm. The reaction was found to be first order and rate constants are $1.68 \pm 0.03 \times 10^{-6}$, $1.79 \pm 0.05 \times 10^{-6}$, $2.62 \pm 0.2 \times 10^{-6}$, and $8.23 \pm 0.1 \times 10^{-6}$ sec^{-1} at 202, 204, 213.5, and 228°, respectively. The activation energy is 31.1 ± 1.5 kcal/mol. These results agree relatively well with the values reported by Cheney, *et al.*[3] They obtained first-order rate constants of 0.376×10^{-2}, 1.73×10^{-2}, 4.18×10^{-2}, and 11.6×10^{-2} hr^{-1} at 194.5, 216, 228.5, and 243°, respectively, and an activation energy of 33.9 ± 1 kcal/mol. Converting the rate constants to common units gives rate constants of 4.8×10^{-6} and 1.16×10^{-5} sec^{-1} at 216 and 228.5°, respectively, which are approximately 20% larger than the rate constants reported in this paper. The rate expression $k = 10^{8.1} \exp((-25{,}000 \pm 2000)/RT)$ sec^{-1} obtained by Houser and Greenough[2] is inconsistent with both this study and the study by Cheney, *et al.*, and

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