TABLE I

DIFFUSION DATA OF BOVINE PLASMA ALBUMIN AT 25°

ΔC, g./100 ml.	C_1, g./100 ml.	$\bar{C}$, g./100 ml.	Δt, sec.	$D(\bar{C})$, 10^{-7} cm.^{2}/sec.	Average deviation, %
0.198	0.198	0.099	2	6.686	0.096
0.204	0.222	0.102	130	6.675	0.16
0.200	0.305	0.205	2	6.688	0.08
0.170	0.375	0.290	55	6.660	0.064
0.350	0.505	0.330	90	6.680	0.13
0.250	0.530	0.405	64	6.669	0.13
0.202	0.602	0.501	42	6.638	0.08

A theoretical support to the possibility of such a reversal of slope with the change in temperature may probably be obtained from the work of Mandelkern and Flory.[12] According to these authors the concention dependence of the diffusion coefficient can be expressed by the equation

$$D/D_0 = [1 + 2\Gamma\bar{C} + (15/8)\Gamma^2\bar{C}^2]/(1 + k\bar{C}) \ldots \quad (1)$$

where both Γ and k are dependent, apart from other factors, on temperature. For a sufficiently dilute protein solution the slope of the D *vs.* $\bar{C}$ curve can be assumed equal to $(2\Gamma - k)$. Thus with the change in temperature, there arises a possibility that the expression $(2\Gamma - k)$ can change from a positive to a negative value or *vice versa*. In fact, an approximate calculation of the expression $(2\Gamma - k)$ at 25° and at a pH near about 4.6 has been made from the experimental data of different authors (Γ from the osmotic pressure data of Scatchard, *et al.*,[13] and k deduced from the S_0 value of Harrington, *et al.*,[14] after conversion to 25° and the value of the slope of the S *vs.* $\bar{C}$ curve taken as 0.2×10^{-13}, $\bar{C}$ being in g./100 ml.) and a negative value (−1.0) was obtained. No quantitative agreement with the present experimental value of the slope can, however, be expected as the calculations were not based upon the experimental data obtained under exactly the same conditions.

From the diffusion experiments performed thus far with the help of the Jamin interference optics and a microdiffusion cell it can be concluded that the straight line describing the concentration dependence of the diffusion coefficient of BPA at 25° has a small negative slope. This is, at least, in qualitative agreement with the theoretical deduction of Creeth referred to above.

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Reactions of Coordinated Ligands. VIII. The Reactions of Alkyl Halides with Mercapto Groups in Transition Metal Complexes of Mercaptoamines

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The reactions of mercaptoamine complexes of nickel(II) and palladium(II) with typical alkylating agents have been investigated. The complexes utilized contain the ligands: 2-aminoethanethiol, N-methyl-2,2'-dimercaptoethyldiethylamine, 2-(2-mercaptoethyl)pyridine, and α-diketobismercaptoethylimines. Pure products have been isolated in all cases and characterized insofar as possible, by determination and interpretation of elemental analyses, infrared spectra, molar conductances, magnetic moments, molecular weights, and electronic spectra. Reaction occurs at the coordinated mercaptide group, producing a thioether *in situ*. The relatively lesser coordinating ability of the newly formed thioether group is evident in the nature of the products. The planar nickel(II) reactant $[Ni(NH_2CH_2CH_2S)_2]$ yields the octahedral products $[Ni(NH_2CH_2CH_2SR)_2X_2]$; α-diketobis(mercaptoimine)nickel(II) complexes give similar results. Under the conditions employed bis[2-(2-mercaptoethyl)pyridine]nickel(II) yields no isolable thioether products. The altered ligand is displaced by the coordinated mercaptide groups of unreacted starting material yielding bridged complexes. Thus $C_6H_5CH_2Br$ produces $[Ni_2(C_5H_4NCH_2CH_2S)_2Br_2]$ and $(CH_3)_2SO_4$ yields $[Ni\{Ni(C_5H_4NCH_2CH_2S)_2\}_2](CH_3SO_4)_2$; bis(N-methyl-2-2'-dimercaptodiethylamine)dinickel(II) reacts with alkyl halides only at the terminal sulfur atoms, not at the bridged sulfurs.

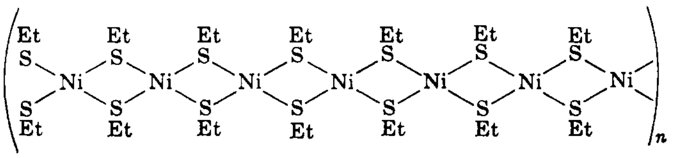
Introduction

In view of the ability of coordinated metal ions to influence the course of many complex reactions, particularly those which occur in living organisms,[1] an investigation of the reactivity toward nucleophiles of the coordinated sulfur atom might be expected to yield results of broad significance. Further, extensive investigation into the specific influence of metal ions on the reactions of organic species should reveal much new fundamental chemistry.[2,3] Among the principal limitations on the understanding of the functions of metal ions in influencing the course of complicated organic and biochemical reactions is the fact that the systems of interest are often labile. Although unusual effects may be observed, the actual nature of the sub-

(1) G. L. Eichhorn, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 37.

(2) D. H. Busch, ref. 1, p. 1.

(3) H. L. Bender, ref. 1, p. 19.



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strate–metal ion–reagent interaction is obscured by post- and pre-equilibration. The general tendency of mercaptide donors to produce relatively *inert* complexes makes these substances well suited for studies designed to show the effect of the metal ion on the course of reactions.

The reactions of coordinated mercaptide groups with alkyl halides were first investigated by Blomstrand (1888) as a consequence of his interest in the thioether complexes of platinum(II).[4,5] Blomstrand reasoned that since reactions 1 and 2 occur, processes corresponding to the reverse of eq. 1 should be feasible (eq. 3).

$$PtCl_2 + 2CH_3SCH_3 \longrightarrow Pt(SCH_3)_2 + 2CH_3Cl \quad (1)$$

$$MSR + HCl \longrightarrow M(HSR)Cl \quad (2)$$

$$Pt(SR)_2 + 2R'I \longrightarrow Pt(SRR')_2I_2 \quad (3)$$

Shortly after publication of Blomstrand's conclusions, Loir[6] (1889) showed that powdered mercuric sulfide reacts with ethyl iodide in a sealed tube at 100°, in ethanol solution, producing $HgS(C_2H_5)_2I_2$.

These studies were extended by other investigators,[7,8] who observed that $Pt(SEt)_2$ reacts with ethyl iodide and methyl iodide in sealed tubes at 70–80°, forming the thioether complexes. The reaction of $Hg(SEt)_2$ with ethyl iodide was also carried out. It was found to give two products, $HgI_2 \cdot IS(Et)_3$ and $HgI_4Et_4S_2$. These were said to be complexes of sulfonium salts. Later studies involving reactions of disulfide complexes of mercury produced somewhat similar results.[9]

A number of papers have been authored by Ray and co-workers[10–13] on the alkylation of the mercaptides and thioethers of mercury with ethyl iodide and methyl iodide. A great deal of the value of these experiments is lost because the reagents were not free of iodine, which resulted in competing oxidation reactions. All the reaction products were not characterized and the concepts applied to the discussion of the structures of the products do not reflect an awareness of Werner's development of modern inorganic stereochemistry.

The last of Ray's papers appeared in 1919 and no further work has been found on the subject prior to 1949, when Ewens and Gibson[14] reported the alkylation of the sulfur atom in diethyl-β-mercaptoethylaminegold(III). Preliminary reports[15,16] from these laboratories have revealed the fact that metal complexes of a variety of mercaptoamines react similarly.

Other recent investigations[17,18] have shown that the copper(I) derivatives of alkyl and aryl mercaptans will react with alkyl halides to form thioethers. The mode of separation, however, was intended only to recover the thioethers.

Spinelli and Salvemini[19] have studied the reaction shown in eq. 4.

$$C_6H_5HgSC_6H_5 + C_6H_5CH_2Cl \xrightarrow{C_6H_6} C_6H_5HgCl + C_6H_5SCH_2C_6H_5 \quad (4)$$

Under similar conditions diphenylmercury(II) does not react with $C_6H_5CH_2Cl$. Other electrophiles including $p\text{-}CH_3C_6H_4SO_2I$ and XC_6H_4SCl react similarly.

The early studies on the reactions of coordinated mercaptide functions suffered from one or more disadvantages. Often either or both the reactants and products were highly polymeric, insoluble solids, thus leading to heterogeneous reactions and preventing thorough characterization of the metal derivatives. Commonly, isolation procedures were such that only the organic material was obtained. Among the more severe limitations has been the fact that metal derivatives of mercaptans are commonly highly polymeric, sulfur bridged substances (I). Relatively detailed studies have recently become feasible as a result of the synthesis of a variety of complexes of mercaptoamines and related ligands,[16,20–25] for the presence of the amino groups prevents polymerization through sulfur bridges or results in complexes of limited and readily determined extent of polymerization. The results of studies on the reactions of a number of these compounds with alkyl halides are reported here.

Experimental

Reaction of $[Ni(NH_2CH_2CH_2S)_2]$ with Methyl Iodide. The Preparation of $[Ni(NH_2CH_2CH_2SCH_3)_2I_2]$.—$[Ni(NH_2CH_2CH_2S)_2]$ (3.16 g., 0.015 mole) was suspended in 300 ml. of dimethylformamide (technical grade) and 2.03 ml. of methyl iodide (0.20 ml. in excess of 0.030 mole) was added slowly by means of a syringe. The flask was stoppered and the suspension was stirred at room temperature for a period of approximately 2 hr. During this time the solid dissolved forming a deep red solution which upon continued stirring changed to an emerald-green color. The high vapor pressure of methyl iodide at room temperature (25°) frequently necessitated the further addition of a few drops of this reactant in order to achieve a green solution. The small amount

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(4) C. W. Blomstrand, *Z. prakt. chem.*, **38**, 529 (1888).

(5) C. W. Blomstrand, *ibid.*, **27**, 196 (1883).

(6) A. Loir, *Ann.*, **107**, 234 (1889).

(7) K. A. Hofman and W. O. Rabe, *Z. anorg. chem.*, **14**, 293 (1897).

(8) S. Smiles, *J. Chem. Soc.*, **77**, 106 (1900).

(9) T. P. Hilditch and S. Smiles, *ibid.*, **91**, 1394 (1907).

(10) P. C. Ray, *ibid.*, **109**, 131 (1916).

(11) P. C. Ray, *ibid.*, **109**, 603 (1916).

(12) P. C. Ray, *ibid.*, **111**, 101 (1917).

(13) P. C. Ray and P. C. Guha, *ibid.*, **115**, 261, 541, 548, 1148 (1919).

(14) R. V. G. Ewens and C. G. Gibson, *ibid.*, 431 (1949).

(15) D. C. Jicha and D. H. Busch, Abstracts, 135th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 15N.

(16) D. H. Busch, J. A. Burke, Jr., D. C. Jicha, M. C. Thompson, and M. L. Morris, ref. 1, p. 125.

(17) R. Adams, W. Reischneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957); *cf. Chem. Abstr.*, **53**, 16,145 (1959).

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(19) D. Spinelli and A. Salvemini, *Ann. Chim.* (Rome), **51**, 1296 (1961); *cf. Chem. Abstr.*, **56**, 15,530*d* (1962).

(20) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **84**, 1762 (1962).

(21) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

(22) D. C. Jicha and D. H. Busch, *ibid.*, **1**, 878 (1962).

(23) D. H. Busch and D. C. Jicha, *ibid.*, **1**, 884 (1962).

(24) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 213 (1964).

(25) J. W. Wrathall and D. H. Busch, *Inorg. Chem.*, **2**, 1182 (1963).

of unreacted $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ was removed by filtration, and the solution was concentrated *in vacuo*. Heating the solution in a hot water bath during concentration facilitated the removal of the solvent without affecting the final product. The green oil which remained could not be induced to crystallize upon further concentration; however, the addition of a small quantity of cold ethanol produced a light green solid which was collected by filtration and washed twice with 25-ml. portions of cold ethanol. Failure to remove a sufficient amount of the dimethylformamide before the addition of ethanol prevented the formation of the green solid; however, upon concentration of the resulting solution *in vacuo* followed by cooling for a few hours, the product crystallized in the form of green plates. The solid is somewhat soluble in ethanol and concentration of the combined filtrate and wash solution followed by cooling for several hours resulted in the crystallization of more product. Final drying was effected *in vacuo* with continuous pumping; yield 5.42 g. (72.9%). *Anal.* Calcd. for $[\mathrm{Ni(NH_2CH_2CH_2SCH_3)_2I_2}]$: C, 14.56; H, 3.66; N, 5.66; S, 12.95; I, 51.29; N. 11.85. Found: C, 14.65; H, 3.64; N, 5.59; S, 13.12; I, 51.35; Ni, 11.61.

This compound is soluble in chloroform, benzene, ethanol, and methanol, but undergoes decomposition in water.

Reaction of $[\mathrm{Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2}$ with Methyl Iodide. The Preparation of $[\mathrm{Ni(NH_2CH_2CH_2SCH_3)_2I_2}]$.—$[\mathrm{Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2}$ (3.67 g.) was partially dissolved in 350 ml. of dimethylformamide, and 1.35 ml. of methyl iodide (0.10 ml. in excess of 0.02 mole) was added slowly by means of a syringe. After 20 min. of constant stirring at room temperature, the dark starting material had almost completely dissolved, resulting in a deep red solution. After approximately 40 min., the color of the solution had changed to a clear emerald-green. The solution was filtered twice and concentrated *in vacuo* to a few milliliters. Solidification of the green oil which remained was induced by the addition of a small amount of cold ethanol. Further concentration of the green filtrate yielded more product. The crystals were collected by filtration and washed twice with 25-ml. portions of cold ethanol and dried for several hours *in vacuo* over P_4O_{10}; yield 3.87 g. (78.2%). *Anal.* Calcd. for $[\mathrm{Ni(NH_2CH_2CH_2SCH_3)_2I_2}]$: C, 14.56; H, 3.66; N, 5.66; S, 12.95; I, 51.29; Ni, 11.85. Found: C, 14.78; H, 3.73; N, 5.76; S, 12.71; I, 51.30; Ni, 11.71.

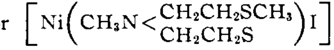
It was noted that the addition of dry benzene in place of cold ethanol resulted in the formation of a brick-red solid which turned green upon extended contact with the atmosphere. The presence of dimethylformamide in the sample was confirmed by the infrared absorption spectrum. Removal of the solvent could not be accomplished by drying at 78° *in vacuo* for 2 hr.; however, stirring of the solid with absolute ethanol resulted in the formation of $[\mathrm{Ni(NH_2CH_2CH_2SCH_3)_2I_2}]$ free of dimethylformamide.

Reaction of $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ with Benzyl Iodide. The Preparation of $[\mathrm{Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2I_2}]$.—The procedure employed for the preparation of the benzylated derivatives of $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ is analogous to that used in the methyl iodide reactions. Benzyl iodide was prepared fresh by the method of Coleman and Hansen.[26] $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ (3 g., 0.0142 mole) was suspended in 200 ml. of dimethylformamide and 3.8 ml. of benzyl iodide (0.2 ml. in excess of 0.0284 mole, colorless liquid, m.p. 24°.). A deep red solution formed almost immediately. The suspension was stirred for approximately 2 hr. during which time almost all of the $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ reacted and the color of the solution changed from a deep red to an emerald-green. This solution was filtered and concentrated *in vacuo* until a green oil remained. The addition of cold absolute ethanol to this green oil produced a light green solid which was filtered, washed twice with 25-ml. portions of absolute ethanol, and dried *in vacuo;* yield 4.6 g. Concentration of the filtrate and ethanol washings produced 1.1 g. of product; total yield 5.7 g. (63.3%). *Anal.* Calcd. for $[\mathrm{Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2I_2}]$: C, 33.41; H, 4.06; N, 4.33; S, 9.91; I, 39.23. Found: C, 33.80; H, 4.25; N, 4.61; S, 9.68; I, 38.75.

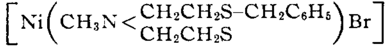
Reaction of $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ with Benzyl Bromide and Benzyl Chloride.—The reaction of $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ with benzyl bromide and benzyl chloride was observed to proceed in a manner similar to that previously reported using benzyl iodide. A larger volume of dimethylformamide was required to dissolve the $[\mathrm{Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]X_2}$ ($X = Cl^-$ or Br^-) which formed as a stable intermediate during the alkylation reaction, in view of the lower solubility of these salts in this solvent as compared to the corresponding iodide. In the case of the alkylation reaction using benzyl chloride, stirring the reaction mixture overnight failed to dissolve all of the $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$. The blue $[\mathrm{Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Br_2}]$ and the powder blue $[\mathrm{Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Cl_2}]$ were isolated by concentration of the dimethylformamide solution to an oil and the subsequent addition of cold ethanol which promoted crystallization; yield, for benzyl bromide derivative, 68.9%; yield, for benzyl chloride derivative, 43.9%. *Anal.* Calcd. for $[\mathrm{Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Cl_2}]$: C, 46.58; H, 5.65; N, 6.04; S, 13.81; Cl, 15.28. Found: C, 46.79; H, 5.60; N, 6.02; S, 13.79; Cl, 15.32.

All of the benzylated derivatives of $[\mathrm{Ni(NH_2CH_2CH_2S)_2}]$ are soluble in methanol, ethanol, chloroform, and benzene, but undergo rapid decomposition in water.

Reaction of $[\mathrm{Pd(NH_2CH_2CH_2S)_2}]$ with Methyl Iodide. The Preparation of $[\mathrm{Pd(NH_2CH_2CH_2SCH_3)I_2}]$.—Methyl iodide (0.53 ml., 0.10 ml. in excess of 0.00772 mole) was added slowly by means of a syringe to a suspension of 1.00 g. of $[\mathrm{Pd(NH_2CH_2CH_2S)_2}]$ in 200 ml. of dimethylformamide. The reaction flask was stoppered and the mixture was allowed to stir slowly overnight. After approximately 12 hr., the yellow starting material had almost completely dissolved, resulting in the formation of a cherry red solution. A small amount of residue ($[\mathrm{Pd(NH_2CH_2CH_2S)_2}]$) was removed by filtration, and the filtrate was concentrated to a heavy red oil *in vacuo*. The addition of a small quantity of cold absolute ethanol to the oil resulted in the formation of a finely divided red solid which was isolated by filtration. The product was washed twice with 20-ml. portions of cold ethanol and dried *in vacuo* with continuous pumping; yield 1.2 g. An additional 0.25 g. was obtained by concentration of the filtrate; total yield 1.45 g. (83.3%). *Anal.* Calcd. for $[\mathrm{Pd(NH_2CH_2CH_2SCH_3)I_2}]$: C, 7.98; H, 2.01; N, 3.10; S, 7.10; I, 56.19. Found: C, 8.10; H, 1.91; N, 3.05; S, 7.42; I, 55.06.

Reaction of $[\mathrm{Ni_2\{CH_3N(CH_2CH_2S)_2\}_2}]$ with Methyl Iodide.—$[\mathrm{Ni_2\{CH_3N(CH_2CH_2S)_2\}_2}]$ (2.08 g., 0.005 mole) was dissolved in 200 ml. of warm chloroform. The deep red solution was allowed to reach room temperature and 0.88 ml. of methyl iodide (0.2 ml. in excess of 0.01 mole) in 10 ml. of chloroform was added. The flask was stoppered and the solution was stirred for 4.5 hr. At this point the temperature of the solution was raised to approximately 40° and stirring was continued for an additional 30 min. A small amount of brown residue was removed by filtration and the deep red solution was concentrated almost to dryness *in vacuo*. The concentrate (a few milliliters) was triturated with a small quantity of benzene and ethanol in the cold, resulting in the formation of a red-brown powder. After filtration, the product was washed with a few milliliters of cold benzene (slightly soluble in this solvent) and dried *in vacuo;* yield 1.86 g. Concentration of the filtrate and cooling resulted in the isolation of 0.3 g. of product; total yield 2.24 g. (60.2%). *Anal.* Calcd. for  $\left[\mathrm{Ni}\left(\mathrm{CH_3N}<\begin{matrix}\mathrm{CH_2CH_2SCH_3}\\ \mathrm{CH_2CH_2S}\end{matrix}\right)\mathrm{I}\right]$: C, 20.59; H, 4.04; N, 4.00; S, 18.33; I, 36.27. Found: C, 20.73; H, 4.25; N, 4.13; S, 18.46; I, 36.10.

Alternatively, this complex can be isolated more easily from chloroform solution by the addition of ether or from dichloroethane upon concentrating the solution.

Reaction of $[\mathrm{Ni_2\{CH_3N(CH_2CH_2S)_2\}_2}]$ with Benzyl Bromide.—$[\mathrm{Ni_2\{CH_3N(CH_2CH_2S)_2\}_2}]$ (1.04 g., 0.0025 mole) was dissolved in 200 ml. of chloroform and 0.80 ml. of benzyl bromide (0.2 ml. in excess of 0.005 mole) in 10 ml. of chloroform was added. The flask was stoppered and the solution stirred for 4.5 hr., and then stirred for an additional 30 min. at approximately 40°. A trace of residue was removed by filtration, and the filtrate was concentrated almost to dryness. The addition of a small quantity of ether resulted in the formation of a brown powder which was isolated by filtration and washed with cold benzene. The product was dried *in vacuo* with continuous pumping to remove traces of benzyl bromide; yield 1.55 g. (67.3%). *Anal.* Calcd. for  $\left[\mathrm{Ni}\left(\mathrm{CH_3N}<\begin{matrix}\mathrm{CH_2CH_2S{-}CH_2C_6H_5}\\ \mathrm{CH_2CH_2S}\end{matrix}\right)\mathrm{Br}\right]$: C, 38.02; H, 4.80; N, 3.70; S, 16.92; Br, 21.08. Found: C, 37.85; H, 5.05; N, 3.52; S, 16.69; Br, 21.27.

This compound exhibited the same solubility properties previously mentioned for the methylated derivative.

Reaction of Bis[2-(2-mercaptoethyl)pyridino]palladium(II) with Dimethyl Sulfate. Preparation of Tetrakis[2-(2-mercaptoethyl)-pyridino]tripalladium(II) Methyl Sulfate Dihydrate.—One gram (2.61×10^{-3} mole) of $\mathrm{Pd(C_5H_4NCH_2CH_2S)_2}$ was suspended in

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[26] G. H. Coleman and C. R. Hansen, *J. Am. Chem. Soc.*, **50**, 1196 (1928).

100 ml. of chloroform. To this suspension was added 0.5 ml., 0.69 g. (5.5 × 10^{-3} mole), of dimethyl sulfate. The mixture was stirred for 4 hr., during which time the $Pd(C_5H_4NCH_2CH_2S)_2$ dissolved, giving an orange solution. The solvent was removed *in vacuo*, giving an orange sirup. A small amount of cold ethanol was added to the sirup, whereupon a yellow precipitate formed which was collected by filtration, washed with small amounts of cold ethanol and ether, and dried *in vacuo* over H_2SO_4; yield 0.2 g. (17%). *Anal.* Calcd. for $C_{30}H_{42}N_4O_{10}Pd_3S_6$: C, 31.9; H, 3.7; N, 5.0; S, 17.0. Found: C, 32.5; H, 3.7; N, 4.8; S, 17.4.

Reaction of Bis[2-(2-mercaptoethyl)pyridino]nickel(II) with Benzyl Bromide. Preparation of Dibromobis[2-(2-μ-mercaptoethyl)pyridino]dinickel(II).—$Ni(C_5H_4NCH_2CH_2S)_2$ (0.7 g., 2.09 × 10^{-3} mole) was suspended in 100 ml. of chloroform. To this suspension was added 0.53 ml., 0.76 g. (4.46 × 10^{-3} mole), of benzyl bromide. The mixture was stoppered and stirred for 16 hr. at room temperature. During this time the solid dissolved, giving a red-brown solution. The solution was reduced in volume to about 20 ml., whereupon red-brown crystals formed. These were collected by filtration, washed with chloroform and ether, and dried *in vacuo* over H_2SO_4. A second fraction was obtained by adding ether to the filtrate; total yield 0.55 g. (96%). *Anal.* Calcd. for $C_{14}H_{16}Br_2N_2Ni_2S_2$: C, 30.4; H, 2.9; N, 5.1; Br, 28.9. Found: C, 30.4; H, 3.1; N, 5.3; Br, 28.0.

Reaction of Bis[2-(2-mercaptoethyl)pyridino]palladium(II) with Benzyl Bromide. Preparation of Dibromobis[2-(2-μ-mercaptoethyl)pyridino]dipalladium(II).—$Pd(C_5H_4NCH_2CH_2S)_2$ (0.68 g., 1.77 × 10^{-3} mole) was suspended in 50 ml. of chloroform. To this mixture was added 0.54 ml., 0.78 g. (4.54 × 10^{-3} mole), of benzyl bromide. The mixture was stirred for 2 hr., whereupon the solid dissolved, giving an orange solution. Evaporation over steam produced orange crystals which were collected by filtration, washed with methanol and ether, and dried *in vacuo* over H_2SO_4. A second fraction was obtained by evaporation of the filtrate; total yield 0.5 g. (87%). *Anal.* Calcd. for $C_{14}H_{16}Br_2N_2Pd_2S_2$: N, 4.4. Found: N, 4.2.

Attempted Reaction of Dichlorobis[2-(2-μ-mercaptoethyl)-pyridino]dinickel(II) with Benzyl Bromide.—One gram (2.15 × 10^{-3} mole) of $Ni_2(C_5H_4NCH_2CH_2S)_2Cl_2$ was suspended in 100 ml. of chloroform. To this suspension was added 0.56 ml., 0.81 g. (4.71 × 10^{-3} mole), of benzyl bromide in 20 ml. of chloroform. A solution resulted which was stirred for 4 hr. and refluxed for 11 hr. with no apparent reaction. The volume of the solution was reduced by evaporation *in vacuo* to about 15 ml., and a black crystalline material formed. This was collected by filtration, washed with chloroform and ether, and dried *in vacuo* over H_2SO_4; yield 0.9 g. The infrared spectrum of the product was identical with that of the starting material. *Anal.* Calcd. for $C_{14}H_{16}Cl_2N_2Ni_2S_2$: N, 6.0. Found: N, 5.8, 6.1.

Reaction of Bis[2-(2-mercaptoethyl)pyridino]nickel(II) with Dimethyl Sulfate. Preparation of Tetrakis[2-(2-mercaptoethyl)-pyridino]trinickel(II) Methyl Sulfate Dihydrate.—One gram (2.97 × 10^{-3} mole) of $Ni(C_5H_4NCH_2CH_2S)_2$ was suspended in 100 ml. of chloroform. To this suspension was added 0.66 ml., 0.91 g. (7.3 × 10^{-3} mole), of dimethyl sulfate. The $Ni(C_5H_4NCH_2CH_2S)_2$ dissolved in a short time and, after a few minutes, a precipitate formed. The mixture was stirred for 4 hr., after which the red solid was collected by filtration, washed with chloroform and ether, and dried *in vacuo* over H_2SO_4; yield 0.7 g. (60%). *Anal.* Calcd. for $C_{30}H_{42}N_4Ni_3O_{10}S_6$: C, 36.5; H, 4.3; N, 5.7; S, 19.5. Found: C, 36.4; H, 4.4; N, 5.6; S, 19.2.

Reaction of Biacetylbis(mercaptoethylimino)nickel(II), Ni(BE), with Methyl Iodide.—Ni(BE) (1.30 g., 0.005 mole) was dissolved in $CHCl_3$ (100 ml.) and 1.45 g. (0.0102 mole) of methyl iodide was added to the solution. The solution was stirred for 1 hr. During this time the solution changed from a deep magenta color to green-brown. The solution was evaporated to dryness *in vacuo*, and the solid was recrystallized from ethanol. The product was isolated and dried *in vacuo* over P_2O_5. The product was dark brown crystals. *Anal.* Calcd. for $Ni(C_{10}H_{20}N_2S_2)I_2$: C, 22.04; H, 3.70; N, 5.14; S, 11.77; I, 46.58. Found: C, 22.13; H, 3.87; N, 5.27; S, 11.89; I, 46.14.

Reaction of Biacetylbis(mercaptoethylimino)nickel(II), Ni(BE), with Benzyl Bromide.—This reaction was analogous to the previous one except that 1.75 g. (0.0102 mole) of benzyl bromide was used instead of methyl iodide. The product was light brown in color. *Anal.* Calcd. for $Ni(C_{22}H_{28}N_2S_2)Br_2$: C, 43.81; H, 4.68; N, 4.65; S, 10.63; Br, 26.50. Found: C, 43.93; H, 4.88. N, 4.73; S, 10.51; Br, 26.73.

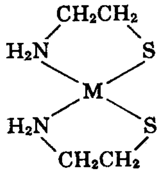
Reaction of 2,3-Pentanedionebis(mercaptoethylimino)nickel(II), Ni(PE), with Methyl Iodide and Benzyl Bromide.—These reactions and separations were analogous to the ones for Ni(BE) except that 1.38 g. (0.01 mole) of Ni(PE) was the substance alkylated. *Anal.* Calcd. for $Ni(C_{11}H_{22}N_2S_2)I_2$: C, 23.63; H, 3.97; N, 5.01; S, 11.47; I, 45.41. Found: C, 23.62; H, 3.82; N, 5.05; S, 11.60; I, 45.47. *Anal.* Calcd. for $Ni(C_{23}H_{30}N_2S_2)Br_2$: C, 44.75; H, 4.90; N, 4.54; S, 10.39; Br, 25.89. Found: C, 44.94; H, 4.84; N, 4.40; S, 10.25; Br, 25.83.

Reaction of 2,3-Octanedionebis(mercaptoethylimino)nickel(II), Ni(OE), with Methyl Iodide and Benzyl Bromide.—These reactions and separations were analogous to the ones for (NiBE) except that 1.59 g. (0.01 mole) of Ni(OE) was the substance alkylated. *Anal.* Calcd. for $Ni(C_{14}H_{28}N_2S_2)I_2$: C, 27.98; H, 4.70; N, 4.66; S, 10.67; I, 42.24. Found: C, 28.13; H, 5.00; N, 4.40; S, 10.51; I, 42.04. *Anal.* Calcd. for $Ni(C_{26}H_{36}N_2S_2)Br_2$: C, 47.37; H, 5.51; N, 4.25; S, 9.73; Br, 24.25. Found: C, 47.11; H, 5.77; N, 3.92; S, 9.80; Br, 24.01.

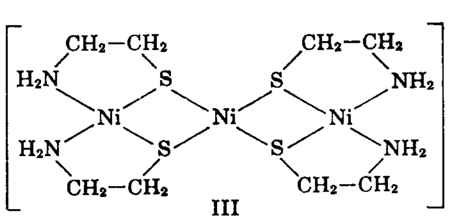
Physical Measurements.—Molecular weights were obtained with a Mecrolab osmometer. Infrared spectra were determined by the KBr pellet technique and in Nujol mulls on Perkin-Elmer Model 21 and Model 337 recording spectrophotometers. A Cary Model 14 spectrophotometer was used for measurements in the ultraviolet, visible, and near-infrared spectral ranges. Magnetic measurements were performed at room temperature by the Gouy method.

Results and Discussion

Complexes of 2-Aminoethanethiol.—The least complicated complexes formed by 2-aminoethanethiol are the square-planar nickel(II) and palladium(II) derivatives. Other investigations with this ligand and its N-substituted analogs strongly suggest structure II. The nickel complex is insoluble or only sparingly soluble in most solvents; however, in the presence of methyl iodide, benzyl bromide, or similar alkylating agents it slowly dissolves in dimethylformamide with reaction. The reaction with methyl iodide proceeds to completion in approximately 2 hr., forming an emerald-green solution of the product. Initial dissolution produces the deep red color typical of the bridged trimer[21] having structure III. This strongly suggests that the bridged Ni–S bond is formed by displacement of the newly formed thioether group (eq. 5 and 6). Such a result is not surprising in view of the



II



III

$$[Ni(NH_2CH_2CH_2S)_2] + 2CH_3I \xrightarrow{DMF} [Ni(NH_2CH_2CH_2SCH_3)_2I_2] \quad (5)$$

$$[Ni(NH_2CH_2CH_2SCH_3)_2I_2] + 2[Ni(NH_2CH_2CH_2S)_2] \longrightarrow [Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2 + 2NCH_2H_2CH_2SCH_3 \quad (6)$$

fact that the central nickel ion in structure III, although bound only to bridged sulfur atoms, is spin-paired, while, as will be shown shortly, the nickel atom in the alkylated complex is spin-free. This suggests that bridging sulfur atoms are stronger ligands than thioether groups. As expected, the trimer may be isolated if the reaction is interrupted at the appropriate time.

Removal of the dimethylformamide *in vacuo*, after complete reaction, produces a green oil which can be induced to crystallize upon the addition of cold absolute ethanol, yielding a light green solid. Analysis of this material reveals a stoichiometry of: one nickel(II) to two $NH_2CH_2CH_2SCH_3$ to two iodides. The infrared spectrum displays two sharp bands of medium intensity at 3263 and 3216 cm.$^{-1}$ which are characteristic of the "coordinated" $-NH_2$ asymmetric and symmetric stretching frequencies.[27] A third band of comparable intensity occurs at 1578 cm.$^{-1}$ with a shoulder at 1588 cm.$^{-1}$ which can be attributed to the $-NH_2$ deformation mode. The appearance of these bands confirms the presence of a primary amine. In contrast, a secondary amine usually exhibits only extremely weak absorption in the "deformation" region and a single NH stretching frequency.[28]

On the basis of these spectral observations, the electrophilic nature of the attacking alkyl group, and the usual inability of the coordinated amine nitrogen to undergo chemical reactions, it would appear that methylation of the ligand has occurred at the coordinated sulfur atom, as indicated in eq. 5. Moreover, alkylation of the sulfur atom is consistent with the results obtained by Ewens and Gibson for the reaction of (2-aminoethanethiolo)diethylgold with ethyl bromide.

The alkylation of $[Ni(NH_2CH_2CH_2S)_2]$ was also carried out using benzyl halides under the same conditions, and salts of the dibenzylated complex were isolated; $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2X_2]$ where X = Cl^-, Br^-, or I^-.

In these cases, the rate of alkylation might be expected to be dependent upon the particular benzyl halide used. Indeed, a significant variation was observed, with the rate of benzylation increasing in the order: $C_6H_5CH_2Cl < C_6H_5CH_2Br < C_6H_5CH_2I$.

The reaction of tetrakis(2-aminoethanethiolo)trinickel(II) iodide, $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2$, with methyl iodide was found to result in the formation of a product which is identical with that obtained by methylation of $[Ni(NH_2CH_2CH_2S)_2]$.

In this case the greater solubility of the trimeric complex in dimethylformamide produces a smoother reaction without apparent contamination of the product. Similarly, $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Cl_2]$ and $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Br_2]$ can be prepared by reaction of the chloride and bromide salts of the trimeric complex with benzyl chloride and benzyl bromide, respectively. However, the chloride and bromide salts of the trimeric species are considerably less soluble in DMF than is the corresponding iodide.

Two coordination structures are in agreement with the stoichiometries exhibited by these alkylation products. These are $[Ni(NH_2CH_2CH_2SR)_2X_2]$ and $[Ni(NH_2CH_2CH_2SR)_2]X_2$. The solid products obtained using methyl iodide and benzyl iodide exhibit magnetic moments of 3.18 and 3.09 Bohr magnetons, respectively. These magnetic moments correspond to values typical of two unpaired electrons in structures involving octahedral nickel(II). Consequently, these compounds are formulated as octahedral materials, $[Ni(NH_2CH_2CH_2SCH_3)_2I_2]$ and $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2I_2]$. The (admittedly limited) solubilities of these compounds in chloroform and other less polar organic solvents are in agreement with their formulation as nonelectrolytes. In methanol at 25°, the molar conductivities of 166 and 167 ohm^{-1} for $[Ni(NH_2CH_2CH_2SCH_3)_2I_2]$ and $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2I_2]$, respectively, are characteristic of di-univalent electrolytes in this solvent, indicating almost complete solvolysis of the coordinated iodide ions in this relatively polar solvent. Decomposition of these complexes was observed upon dissolving in water.

The visible and near-infrared spectra of the methyl iodide and benzyl bromide derivatives have been investigated under a variety of conditions and are summarized in Table I. The absorption bands are of low intensity and the envelopes are surprisingly symmetrical in view of the highest possible symmetry of the six-coordinate complexes. The occurrence of just three bands of low intensity strongly suggests that the local symmetry posed by the ligand field behaves rather like O_h despite the conclusion by Maki[29] that the spectra of complexes containing mixed ligands more often conform to patterns predicted for lower symmetry. Accordingly, the assignments in the pseudo-octahedral complexes are ν_1, $^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2, $^3A_{2g} \rightarrow {}^3T_{1g}$; ν_3, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$.[30]

The substantial solvent dependence of the spectra is readily attributed to variations in the composition of the complex resulting from displacement of the halide ions by solvent. The spectrum of the benzyl bromide derivative in the nonpolar solvent chloroform is most ideal and a reasonable *Dq* value of 860 cm.$^{-1}$ can be assigned to the average ligand field made up of the two primary amines, two thioethers, and two bromides. In dimethylformamide, the molar conductance of this substance is 93.2 ohm.$^{-1}$, a value intermediate between those observed for typical uni-univalent and di-univalent electrolytes in that solvent.[31] Insofar as solvolysis has occurred, the stronger ligand DMF has displaced the bromide ion and the average ligand field strength is increased ($Dq \simeq 915$ cm.$^{-1}$ in DMSO and ~930 cm.$^{-1}$ in DMF).

The spectral properties of the methyl iodide derivative are completely parallel. Although the data for chloroform solutions of this compound are inaccurate, it is sufficient to confirm the expected lower average ligand field, as required by replacing the bromides with iodides, $Dq \simeq 830$ cm.$^{-1}$. The apparent higher *Dq* for the iodide (982 cm.$^{-1}$) over the corresponding benzyl bromide derivative (930 cm.$^{-1}$) in solution in DMF is easily accounted on the basis of the molar conductance data. The molar conductance for the methyl iodide derivative is 141.7 ohm^{-1}, a value consistent with complete replacement of the iodides by DMF molecules.[31] As mentioned earlier, the bromides are

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[27] M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 1521 (1960).

[28] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[29] G. Maki, *J. Chem. Phys.*, **29**, 162 (1959).

[30] C. K. Jørgensen, *Acta. Chem. Scand.*, **9**, 1362 (1955).

[31] P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, **2**, 282 (1963).

TABLE I

ELECTRONIC SPECTRA OF $[Ni(NH_2CH_2CH_2SR)_2X_2]$

		ν_1		ν_2		ν_3	
RX	Solvent	$1/\lambda$, cm.$^{-1}$	ϵ_{max}	$1/\lambda$, cm.$^{-1}$	ϵ_{max}	$1/\lambda$, cm.$^{-1}$	ϵ_{max}
$C_6H_5CH_2Br$	DMF	9300	10.8	15,700	11.0	25,400	25.0
$C_6H_5CH_2Br$	DMSO	9150	4.56	14,900	3.60	25,000	9.13
$C_6H_5CH_2Br$	$CHCl_3$	8600	3.65	16,200	5.41	25,400	11.3
$C_6H_5CH_2I$	DMF	9640	13.3	15,400	9.00	~28,600	105.0
$C_6H_5CH_2I$	DMSO	9260	8.29	15,200	6.55	25,400	19.4
CH_3I	DMF	9823	7.34	16,330	5.36	27,470	138.0
CH_3I	DMSO	9414	5.70	15,240	3.60	25,806	13.7
CH_3I	$CHCl_3$[a]	~8330	?	16,300	?	(~19,000)	?

[a] Very limited solubility, concentration unknown, and data inaccurate.

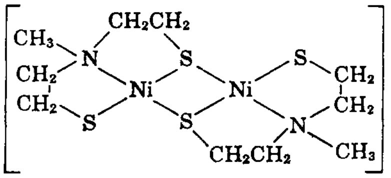
not totally replaced by DMF. Thus the average *Dq* for the average complex derived from $[Ni(NH_2CH_2CH_2SCH_3)_2I_2]$ is greater than the corresponding values for species derived by solvation from $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Br_2]$. The molar conductance for $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2I_2]$ is 127 ohm^{-1}, also approximating the behavior of a di-univalent electrolyte. Variations in the intensity of the third band are probably related to the presence of intense absorptions in the ultraviolet region.

On the basis of electrostatics, the halide ions would be expected to occupy mutually *trans* positions. However, such an arrangement should produce deviations in the spectral properties in accord with C_{2v} or, at best, D_{4h} symmetry. Since the lower symmetry is not apparent in the spectrum of $[Ni(NH_2CH_2CH_2SCH_2C_6H_5)_2Br_2]$ in chloroform, one might suspect that the bromides are mutually *cis*, and simultaneously *trans* to the amino groups. It is doubtful that any experiment short of total structure determination could resolve this question.

From the experiments summarized above it may be concluded that planar nickel(II) complexes of mercaptoamines react with alkyl halides forming octahedral products in which the alkyl group has been added to the mercapto function, producing a thioether, while the halide ion has become bound to the nickel(II) ion. It is interesting that the formation of the carbon–sulfur bond is attended by substantial diminution in the intensity of the metal–ligand interaction.

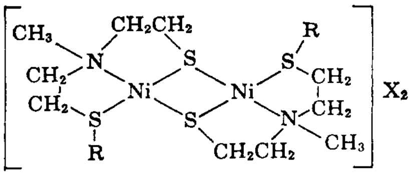
Alkylation of the uncharged bis palladium(II) complex, $[Pd(NH_2CH_2CH_2S)_2]$, proceeds somewhat differently under the conditions employed for the corresponding nickel(II) complex. Allowing the reaction mixture to stir for several hours at slightly above room temperature results in the formation of a red solution which, upon concentration and the addition of cold ethanol, yields a red solid having a stoichiometry of one Pd(II) to one $NH_2CH_2CH_2SCH_3$ to two I^-. This compound is only slightly soluble in ethanol and chloroform but may be recrystallized from the warm ethanol. The formulation of this compound as the nonelectrolyte, $[Pd(NH_2CH_2CH_2SCH_3)I_2]$, is in agreement with these solubility properties and the coordination number of four for palladium(II). The ease of formation of the monoalkylated complex is also dependent upon the particular alkyl halide employed. The reaction of benzyl bromide with $[Pd(NH_2CH_2CH_2S)_2]$ results in the isolation of a solid having a composition suggestive of a mixture of $[Pd(NH_2CH_2CH_2SCH_2C_6H_5)_2]Br_2$ and $[Pd(NH_2CH_2CH_2SCH_2C_6H_5)Br_2]$. This behavior is in accord with the lesser coordinating ability (toward palladium(II)) of bromide ion as compared to iodide ion.

Complexes of N-Methyl-2,2′-dimercaptodiethylamine.—The report[32] that nickel(II) forms a dimeric complex of structure IV with N-methyl-2,2′-dimercaptodiethylamine has been confirmed[33] in these laboratories. The compound is diamagnetic,[33] indicating planar coordination about the two nickel atoms. This compound is highly soluble in chloroform and similar solvents. In view of the poor coordinating tendencies of these solvents, they are well suited to substantiate the contention that alkylation of the mercaptide function does not require its prior dissociation from the metal ion. If that were the case a vanishingly slow reaction would be expected in these solvents. In fact, the reactions proceed at moderate rates, giving good yields in a few hours at room temperature or slightly above.



IV

Both benzyl bromide and methyl iodide produce compounds of the composition $Ni\{CH_3N(CH_2CH_2S)_2\}RX$. The red-brown methylated derivative and the brown benzylated derivative can be isolated with a certain degree of difficulty. Molecular weight determination on the benzyl bromide derivative reveals it to be dimeric: mol. wt., calcd. for $[Ni_2\{CH_3N(CH_2CH_2S)_2\}_2(C_6H_5CH_2Br)_2]$, 758; found, 767 ± 29. Ignoring, for the moment, the function of the halides, these data suggest partial structure V. Of particular significance is the implication that only the *terminal* sulfur atoms have reacted with the alkyl halide. That is, the bridge sulfur atoms have failed to react with the excess of reagent or in competition with the terminal groups. The reaction proceeds further in the presence of large



V

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[32] J. Harley-Mason, *J. Chem. Soc.*, 146 (1952).

[33] D. C. Jicha, Thesis, The Ohio State University, 1960.

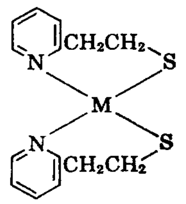
excesses of alkyl halide or under forcing conditions; however, only poorly defined, intractable materials have been isolated from these systems. The inconsistencies apparent among the atom ratios in these products imply destruction of the complex.

The dimeric, dialkylated products of partial structure V are formed from highly reproducible procedures and, in fact, may be formed under a variety of conditions. The compositions of the products as revealed by elemental analyses are in excellent agreement with theory and consistently reproducible. Despite this happy situation, the magnetic moment has been observed to vary from sample to sample, over the range from 1.9 to 3 B.M., for materials of essentially identical gross composition. The absence of a field strength dependence in the case of samples having high moments eliminates the possibility of minute amounts of ferromagnetic impurities. It appears that careful purification of solvents and exclusion of air and moisture minimize the moment; however, samples exhibiting values below 2 B.M. have not been prepared with high reproducibility. The visible and ultraviolet spectra exhibit a number of absorption bands, but the complexity of the structure is such that this does not provide an adequate route to the solution of the unresolved questions.

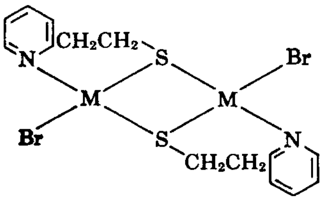
Although the electronic structure and the manner of binding of the halide ions remain open to question, the synthesis of these compounds reveals two most significant facts. Mercaptide ions coordinated to a single metal ion react with alkyl halides even in solvents of very low coordinating power, strongly indicating that they react while remaining bound to the metal ion. Further, mercaptide groups bound to two metal ions (bridge sulfurs) are much less reactive.

Complexes of 2-(2-Mercaptoethyl)pyridine.—Three structural classes of complex have been prepared with this ligand.[25] They are illustrated by bis[2-(2-mercaptoethyl)pyridino]nickel(II) (VI), dibromobis[2-(2-mercaptoethyl)pyridino]nickel(II) (VII), and tetrakis[2-(2-mercaptoethyl)pyridino]trinickel(II) cation (VIII). The existence of the sulfur-bridged complexes confirms the nucleophilic character of the coordinated sulfur atom in the bis complex (VI). Consequently, it was expected that these reactions would be straightforward and typical of the reactions of the coordinated mercaptide group. In particular, the reaction of eq. 7 was expected.

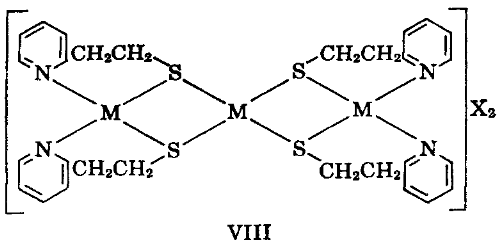
$$\mathrm{Ni(C_5H_4NCH_2CH_2S)_2 + 2RX \longrightarrow Ni(C_5H_4NCH_2CH_2SR)_2X_2} \quad (7)$$



VI



VII



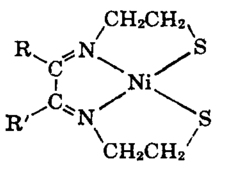
VIII

Attempts to form alkylated complexes by the reaction of benzyl bromide with NiL_2 and PdL_2 (L is the subject ligand) gave, surprisingly, complexes of stoichiometry $M_2L_2Br_2$ (VII). Attempts to carry the reaction further, to alkylate the bridged sulfur atoms, were unsuccessful. In this connection, attempts to alkylate $Ni_2L_2Cl_2$ resulted in almost quantitative recovery of the starting material. It appears that in the reaction of benzyl bromide with complexes of the type ML_2, alkylation of the ligand weakens the metal–sulfur bond so much that the newly formed thioether cannot compete with the remaining mercaptan for the metal ion. Furthermore, it seems that the difference in reactivity between the bridged and unbridged mercapto sulfur is great enough to prevent further alkylation after bridging takes place.

In an attempt to avoid the formation of bridged complexes, such as $N_2L_2Br_2$, an alkylating agent which does not contain halogen, *i.e.*, dimethyl sulfate, was used. The only products from these reactions, however, were bridged complexes of the type $M_3L_4(CH_3SO_4)_2$ (VIII). Once again, the bridged structure was shown to have much greater stability than the complex of the alkylated sulfur compounds and less reactivity than nonbridged sulfur complexes. It should also be pointed out that the reaction of dimethyl sulfate with PdL_2 provided the only route by which a complex containing the ion $Pd_3L_4^{+2}$ could be obtained.[25] Reactions of this type may, thus, provide a useful synthetic technique.

The behavior of alkylating agents with these complexes strikingly emphasizes two of the outstanding characteristics of mercapto complexes: (1) the strong tendency of this group to form bridged complexes and (2) the great difference in reactivity of bridged and unbridged sulfur.

Complexes of α-Diketobismercaptoethylimines.—A novel synthetic method has led to the synthesis of the nickel(II) complexes of a variety of α-diketobismercaptoethylimines.[20,24] The square-planar complexes have been assigned structure IX. Unlike a number of other complexes containing coordinated mercaptide groups, these complexes show no tendency to bind by sulfur bridges to additional metal ions. Consequently, there was some question concerning the reactivity of these functions toward alkylating agents such as methyl iodide, benzyl bromide, and ethyl bromide. The proposed reaction is illustrated in eq. 8. The reaction of 2 moles of methyl iodide or benzyl bromide with 1 mole of the complex proceeds at a fairly rapid rate in $CHCl_3$. The color change is usually

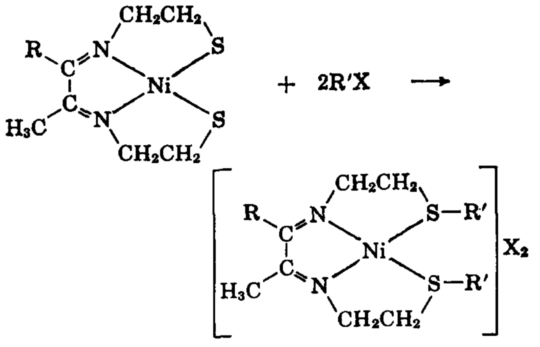


IX

found to be complete within 15 to 20 min. Reactions were allowed to proceed for approximately 1 hr. to assure complete reaction. Since the products are highly soluble in chloroform, it is necessary to remove the chloroform (rotary evaporator) and recrystallize from ethanol. In all cases a single brown crystalline product formed. The expected compositions of these products were confirmed by elemental analyses. The infrared spectra of the products show the absorptions expected of the alkylated ligands. The molecular weights of these products show them to be monomeric in 1,2-dichloroethane (Table II). Further, the halide ions remain coordinated in this solvent. Conductivity measurements on aqueous solutions provide molar conductance values that are within the range usually expected of di-univalent electrolytes (Table II). This demonstrates the fact that the halide ions have been displaced from the alkyl groups by reaction with the sulfur atoms. The complexes diiodo-S,S′-dimethyl-2,3-octanedionebis(mercaptoethylimine)nickel(II) and dibromo-S,S′-dibenzyl-2,3-octanedionebis(mercaptoethylimine)nickel(II) are not soluble in water, so it was necessary to determine their conductivities in methanol. These values are somewhat lower than expected for di-univalent electrolytes. Thus, although the halide ions are coordinated to the metal ions in solvents of low polarity, they are readily displaced by highly polar solvents. The reaction in water (eq. 9) being complete, while

$$Ni(LR_2)X_2 + 2H_2O \longrightarrow Ni(LR_2)(H_2O)_2^{2+} + 2X^- \quad (9)$$

the analogous reaction in methanol presumably does not go to completion, but produces a mixture of unipositive and dipositive cations.



(8)

TABLE II

MOLECULAR WEIGHTS AND MOLAR CONDUCTIVITIES OF THE PRODUCTS FROM THE REACTION OF α-DIKETONEBIS(MERCAPTOETHYLIMINE)NICKEL(II) COMPLEXES WITH MONOFUNCTIONAL ALKYLATING AGENTS

Compound[a]	Molecular weight[b] Theory	Molecular weight[b] Found	Conductivity[c] H_2O	Conductivity[c] Methanol
$Ni(BEB)Br_2$	603	607	219	...
$Ni(BEM)I_2$	545	545	222	...
$Ni(PEB)Br_2$	617	627	212	...
$Ni(PEM)I_2$	559	579	221	...
$Ni(OEB)Br_2$	659	655	...	96.6
$Ni(OEM)I_2$	601	618	...	113

[a] Abbreviations are: BEB = S,S′-dibenzylbiacetylbis(mercaptoethylimine); BEM = S,S′-dimethylbiacetylbis(mercaptoethylimine); PEB = S,S′-dibenzyl-2,3-pentanedionebis(mercaptoethylimine); PEM = S,S′-dimethyl-2,3-pentanedionebis(mercaptoethylimine); OEB = S,S′-dibenzyl-2,3-octanedionebis-(mercaptoethylimine); OEM = S,S′-dimethyl-2,3-octanedionebis(mercaptoethylimine). [b] Molecular weights were obtained using 1,2-dichloroethane as solvent.

The molecular weight data and magnetic susceptibilities of the alkylated complexes show that the anions are coordinated to the metal ion in 1,2-dichloroethane solution and in the solid state. Magnetic susceptibilities show the ground state to be a triplet state (Table III). Further inferences regarding structure may be derived from the electronic spectra of these interesting compounds.

TABLE III

MAGNETIC SUSCEPTIBILITIES OF PRODUCTS FROM THE REACTION OF α-DIKETOBIS(MERCAPTOETHYLIMINE)NICKEL(II) COMPLEXES WITH MONOFUNCTIONAL ALKYLATING AGENTS

Compound[a]	T, °K.	X_m	μ_{eff}
$Ni(BEB)Br_2$	300	3446×10^{-6}	3.01
$Ni(BEM)I_2$	299	3521×10^{-6}	3.01
$Ni(PEB)Br_2$	300	3470×10^{-6}	3.03
$Ni(PEM)I_2$	300	3395×10^{-6}	2.98
$Ni(OEB)Br_2$	297	3640×10^{-6}	3.10
$Ni(OEM)I_2$	297	3718×10^{-6}	3.08

[a] Abbreviations are given in footnote *a* to Table II.

The ligand field strengths of the anions above and below the plane of the tetradentate ligand are expected to be smaller than those of the in-plane donor atoms. Further, the donor strengths of the dimethine function and the thioether groups are not expected to be identical. In fact, the true symmetry of the compounds, $Ni(LR_2)X_2$, is essentially C_{2v}. This presumes that the halide ions are mutually *trans; i.e.*, the reactions of Ni(BE), Ni(PE), and Ni(OE) with alkyl halides do not alter the basic symmetry about the metal ion. However, if one directs his attention to the in-plane donors, the deductions of Maki provide some useful considerations.[29,34] In her theoretical treatment of tetragonal nickel(II), Maki shows that the energy diagram for D_{4h} is approximately the same as that for C_{2v}, differing mainly because of a few changes in notation which are required by the symmetry relationships. Maki has derived these energy diagrams[34] and applied them to show that the model is suitable for the explanation of solvation effects.[29,35] Ballhausen and Liehr[36] have also carried out calculations involving tetragonal nickel(II) complexes, but these are not as consistent with the data at hand as is the treatment due to Maki.[34]

The complexes diiodo-S,S′-dimethyl-α-diketobis(mercaptoethylimine)nickel(II) and dibromo-S,S′-dibenzyl-α-diketobis(mercaptoethylimine)nickel(II) exhibit slightly different spectra (Tables IV and V) in 1,2-dichloroethane due to the difference in the ligand field strengths of the two anions, Br^- and I^-. The iodides exhibit two charge-transfer bands at 24,400–25,300 and 27,800–31,000 cm.$^{-1}$. The bromides exhibit only one charge-transfer absorption at 35,700–36,200 cm.$^{-1}$. The occurrence of these intense absorptions at higher energy in the case of bromides is consistent with the assumption that the transfer of an electron from the halide to the nickel constitutes a significant aspect of the transition. Further, the difference in energy between the lowest energy charge-transfer bands for the bromide and iodide cases is about 4.6 kcal. as compared to a difference in electron affinity between iodine and bromine of 6.9 kcal. It is known that, with the

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(34) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

(35) G. Maki, *ibid.*, **29**, 1129 (1958).

(36) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

same acceptor, the charge-transfer energy changes with the halide ion and is proportional to the electron affinity of the halogen.[37-39]

TABLE IV

ELECTRONIC SPECTRA OF METHYLATED α-DIKETOBIS(MERCAPTOETHYLIMINE)NICKEL(II) COMPLEXES OBTAINED WITH 1,2-DICHLOROETHANE SOLUTIONS[a]

Band		Ni(BEM)I$_2$	Ni(PEM)I$_2$	Ni(OEM)I$_2$
I	λ_{max}, mμ	1,063	1,082	....
	$\bar{\nu}$, cm.$^{-1}$	9,410	9,240	....
	ϵ_{max}	40.9	27.6	....
II	λ_{max}, mμ	794 (sh)	782 (sh)	....
	$\bar{\nu}$, cm.$^{-1}$	12,500	12,800	....
	ϵ_{max}	$\sim$80.7	$\sim$50.9	....
III	λ_{max}, mμ	532 (sh)	546 (sh)	563 (sh)
	$\bar{\nu}$, cm.$^{-1}$	18,800	18,300	17,800
	ϵ_{max}	$\sim$398	$\sim$327	$\sim$1070
IV	λ_{max}, mμ	411	411	395 (sh)
	$\bar{\nu}$, cm.$^{-1}$	24,400	24,400	25,300
	ϵ_{max}	6,870	7,320	$\sim$5,770
V	λ_{max}, mμ	323	323	360
	$\bar{\nu}$, cm.$^{-1}$	31,000	31,000	27,800
	ϵ_{max}	6,700	6,800	6,470
VI	λ_{max}, mμ	....	....	293
	$\bar{\nu}$, cm.$^{-1}$	....	....	34,100
	ϵ_{max}	....	....	11,400

[a] Abbreviations are the same as in footnote *a* to Table II.

TABLE V

ELECTRONIC SPECTRA OF BENZYLATED α-DIKETOBIS(MERCAPTOETHYLIMINE)NICKEL(II) COMPLEXES OBTAINED WITH 1,2-DICHLOROETHANE SOLUTIONS[a]

Band		Ni(BEB)Br$_2$	Ni(PEB)Br$_2$	Ni(OEB)Br$_2$
I	λ_{max}, mμ	961	964	960 (sh)
	$\bar{\nu}$, cm.$^{-1}$	10,400	10,400	10,400
	ϵ_{max}	26.7	26.0	$\sim$28.5
II	λ_{max}, mμ	834	828	758 (sh)
	$\bar{\nu}$, cm.$^{-1}$	12,000	12,100	13,200
	ϵ_{max}	45.0	45.8	$\sim$67.2
III	λ_{max}, mμ	592 (sh)	580 (sh)	607 (sh)
	$\bar{\nu}$, cm.$^{-1}$	16,900	17,200	16,500
	ϵ_{max}	$\sim$67.3	$\sim$81.7	$\sim$156
IV	λ_{max}, mμ	447	454	446 (sh)
	$\bar{\nu}$, cm.$^{-1}$	22,400	22,000	22,400
	ϵ_{max}	261	270	$\sim$533
V	λ_{max}, mμ	278	280	276
	$\bar{\nu}$, cm.$^{-1}$	36,000	35,700	36,200
	ϵ_{max}	9,380	9,610	8,760

[a] Abbreviations are the same as in footnote *a* to Table II.

The diiodo complexes ($Ni(LR_2)I_2$, Table IV) exhibit three d–d transitions: band I, 9200–9400 cm.$^{-1}$, band II, 12,500–12,800 cm.$^{-1}$, and band III, 17,800–18,800 cm.$^{-1}$, the last two being shoulders. Extinction coefficients, although higher in value than observed by Venanzi[40] in somewhat similar systems, correspond in that the first absorption (low frequency) is the weakest and the last absorption is much greater in intensity than either of the first two absorptions. The bands are all assumed to involve triplet–triplet transitions and, in pseudo-tetragonal symmetry, the assignments are: band I, $^3B_{2g} \rightarrow {}^3E_g$; band II, $^3B_{2g} \rightarrow {}^3A_{2g}$, $^3B_{1g}$; band III, $^3B_{2g} \rightarrow {}^3E_g$. In the case of the bromides, corresponding assignments are made, but here four bands are observed since the low energy charge-transfer bands no longer obscure weaker transitions in the short wave length part of the visible spectrum. Band IV is assigned to the transition $^3B_{2g} \rightarrow {}^3A_{2g}$. The difference between bands I and II should provide a crude estimate of the axial distortion of the six-coordinate complex. On this basis, the axial distortion of the diiodo complexes is much greater than that of the dibromo compounds, as expected.

It may be concluded that all the properties of the products formed by the reaction of α-diketobis(mercaptoethylimine)nickel(II) complexes with alkyl halides are consistent with the predictions of eq. 8. Further, the products are properly formulated as six-coordinate with the halide ions above and below the plane of the tetradentate ligand.

Conclusions

A number of new transition metal complexes have been prepared by a novel synthesis utilizing ligand reactions. In all cases the ligand reaction transforms the coordinated mercapto group into a bound thioether function.

It may be generally concluded that the mercaptide function retains much of its nucleophilic character when bound to a single metal ion, for a variety of nickel(II) and palladium(II) complexes containing this group react smoothly with electrophiles in both coordinating and noncoordinating solvents. When the mercaptide group is bound to two metal ions; *i.e.*, when it is a bridging group, it is much less reactive. In fact, compounds containing only bridging sulfur atoms have been observed to react with electrophiles only in systems where they are in equilibrium with unbridged substances. The reaction may be used to distinguish between *bridged* and *terminal* mercapto groups and, under favorable circumstances, it can be used to show the relative numbers of the two kinds of sulfur atoms in a complex.

The systems investigated provide useful information concerning the relative complexing ability (toward Ni(II) and Pd(II)) of the thioether group as compared to the bridged sulfur bond. It has generally been observed that thioether groups are displaced by coordinated mercapto units to form sulfur-bridged products. Also, although bridged sulfur often leads to diamagnetic square-planar structures for nickel(II), the thioether complexes of nickel(II) are invariably spin-free and six-coordinate even though the mercaptoamine compounds from which they are derived are low-spin square-planar in structure. It is interesting that the ligand reaction may be utilized to weaken metal–donor bonds without substitution at the metal ion.

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