From the data in Table III, it is concluded that the position of $PO[N(CH_3)_2]_3$ in the spectrochemical series relative to N_3^- and NCO^- is: $Cl^- \sim PO[N(CH_3)_2]_3 < N_3^- < NCO^-$.

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Complexes Derived from Strong Field Ligands. XIII. The Complexes of β-Mercaptoethylamine with Nickel(II), Palladium(II), Cobalt(II), and Cadmium(II)

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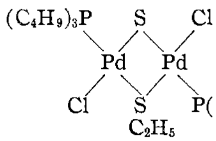
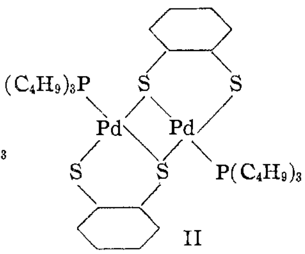
β-Mercaptoethylamine forms two distinct types of compounds with transition metal ions. One type is represented by the well defined monomeric complexes bis-(β-mercaptoethylamine)-nickel(II) and bis-(β-mercaptoethylamine)-palladium(II), ML_2. Nickel(II) and palladium(II) also form a second compound, $[M(ML_2)_2]Cl_2$. The nickel(II) trimer is diamagnetic, indicating that all three nickel atoms are contained in planar coördination polygons. The trimer exhibits the usual properties of a salt and is readily prepared from aqueous solution, either by reaction of the ligand and metal ion or by the solubilization of NiL_2 with nickel chloride. A structure involving a third nickel atom utilizing to full advantage the strong donor properties of two *cis*-NiL_2 molecules is consistent with the preparation and properties of this compound. A cobalt(II) trimer, $[Co(CoL_2)_2]Cl_2$, which exhibits a magnetic moment of 2.49 B.M. per cobalt(II) atom, has been isolated. A cadmium(II) complex also has been isolated and has been assigned the formulation $[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$.

Introduction

One of the most distinguishing properties associated with the mercaptide group is its ability to react readily with many metals to form complexes containing sulfur bridges. The initial investigations involving compounds of this class were carried out by Chatt and Mann,[1] who prepared dichlorobis-(tri-*n*-butylphosphine)-μ-ethylthiolodipalladium(II) (structure I) and bis-(tri-*n*-butylphosphine)-μ-bis-(*o*-phenylenedithiolo)-dipalladium(II) (structure II).



I



II

The fact that the former compound and the platinum(II) analog[2] can be isolated in both *cis* and *trans* forms is a measure of the stability of the mercaptide bridge when compared to the chlorine-bridged analog which forms only the stable *trans* isomer. The great stability of the coördinated mercaptide group also is apparent from the inability of these compounds to undergo reactions with strong donor ligands. In contrast to this behavior, the chloro-bridge is quite labile in the presence of the same ligands. Recently, bridged compounds of platinum(II) and palladium(II) have been reported for *o*-methylthiobenzenethiol, 3-dimethylarsinepropane-1-thiol, 3-ethylthiopropane-1-thiol, and *o*-aminobenzenethiol.[3,4]

Jensen has observed this same bridge-forming tendency for the nickel(II) complex with ethyl mercaptan, which he established to be a diamagnetic polymetallic complex.[5] The formation of polymeric species is prevalent for mercaptan ligands in the absence of other donor atoms of comparable strength. The influence of an additional donor atom, which fulfills this requirement, upon the extent of bridging in mercaptan com-

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[1] J. Chatt and F. C. Mann, *J. Chem. Soc.*, 1949 (1936).

[2] J. Chatt and F. A. Hart, *ibid.*, 2363 (1953).

[3] S. E. Livingstone, *ibid.*, 437 (1956).

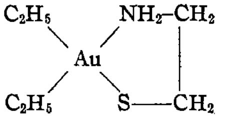
[4] S. E. Livingstone, *ibid.*, 1989 (1956).

[5] K. A. Jensen, *Z. anorg. allgem. Chem.*, **252**, 227 (1944).

plexes may be exemplified by the mercapto amine ligands.

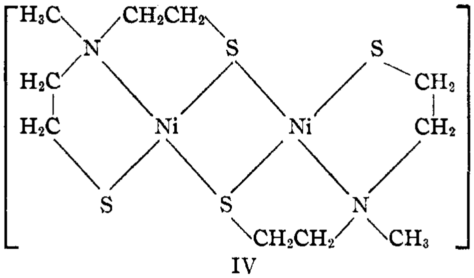
β-Mercaptoamine ($NH_2CH_2CH_2SH$), the simplest ligand of this class, was first studied by K. A. Jensen,[6] who observed the formation of two nickel(II) complexes in solution. One compound was isolated from strongly basic solution and was identified as the slightly soluble bis-(β-mercaptoethylamine)-nickel(II). The second nickel(II) derivative was obtained from neutral or slightly acidic solution; however, a definite stoichiometry was not assigned to it. Jensen assumed that this water-soluble product contained the coördinated *zwitter* ion; however, the sole evidence in support of his conclusion was the presence of chloride ion in the sample.

Several years passed before further investigations of the chelating ability of β-mercaptoethylamine were reported. The second investigation involved the preparation of a rather novel gold compound, (β-mercaptoethylamine)-diethylgold (structure III). As in the case of the previously mentioned nickel(II) complex, the coördinated mercaptide ion was not found to undergo bridge formation. These investigators[7] also mentioned the formation of well defined complexes of this ligand with palladium, copper, and cobalt; however, the stoichiometries and properties of these compounds were not published. The few remaining reports concerned with the complexes formed by β-mercaptoethylamine are confined, for the most part, to solution studies.[8-11]



III

Nickel(II) complexes of two additional mercaptoamines, 2,2′-dimercaptodiethylamine, $HN(CH_2CH_2SH)_2$, and methyl-2,2′-dimercaptodiethylamine, $CH_3N(CH_2CH_2SH)_2$, have been reported.[12] In view of the great tendency for nickel(II) to form four-coördinate complexes, a dimeric bridged structure was proposed for these compounds. Cryoscopic molecular weight studies provide support for this structural representation (structure IV).



IV

The present work records a detailed investigation of the complexes formed by nickel(II), palladium(II), and cobalt(II) with β-mercaptoethylamine.

Experimental

Spectrophotometric Measurements.—The method of continuous variations was used to establish the existence of the nickel(II) adduct of $[Ni(NH_2CH_2CH_2S)_2]$ in aqueous solution. Spectra were obtained by means of a Beckman D. U. spectrophotometer and a Cary Model 10 recording spectrophotometer using quartz cells. A stock solution (10^{-3} *M*) of an analyzed sample of $[Ni(NH_2CH_2CH_2S)_2]$ was prepared by gentle heating on a steam bath and vigorous shaking in order to completely dissolve the sample. The wave length of maximum absorption characteristic of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ was selected from the spectrum of an aqueous solution (5×10^{-4} *M*) of this complex.

The enhancement of absorption was determined by a graphical method[13] and was plotted against the mole % of $[Ni(NH_2CH_2CH_2S)_2]$ in solution in order to determine the complex-to-metal ion ratio.

Magnetic Measurements.—Magnetic moments were obtained for solid samples by the Gouy method using iron(II) ammonium sulfate 6-hydrate as the standard. The values given by Selwood[14] were used for the diamagnetic susceptibilities of the anions. Pascal's constants[15] were used to calculate the diamagnetism of the ligands. The values utilized are: $NH_2CH_2CH_2S^-$, -50.13×10^{-6}; Cl^-, -26×10^{-6}; Br^-, -36×10^{-6}; I^-, -52×10^{-6}. Magnetic data for the complexes are listed in Table I.

Conductivity Measurements.—Molar conductances were determined from resistance measurements using a Model RC-16B conductivity bridge manufactured by Industrial Instruments, Inc., and a cell with a constant of 2.042 cm.$^{-1}$. The cobalt(II) trimer undergoes decomposition in aqueous solution; therefore, the molar conductance for this compound was determined in methanol solution. All other measurements were made in water at 25°. The molar conductances for the compounds studied are listed in Table II.

Analyses.—Microanalyses were performed by Schwarzkopf Microanalytical Laboratories and by Galbraith Microanalytical Laboratories.

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(6) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 265 (1936).

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(8) R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, **78**, 4891, 4893 (1956); *ibid.*, **79**, 518 (1957).

(9) E. Felder, A. Resigno, and R. Radica, *Gazz. chim. ital.*, **85**, 453 (1955).

(10) N. C. Li and R. A. Manning, *J. Am. Chem. Soc.*, **77**, 5225 (1955).

(11) I. M. Klotz, G. H. Czerlinski, and H. A. Feiss, *ibid.*, **80**, 2920 (1958).

(12) J. Harley-Mason, *J. Chem. Soc.*, 146 (1952).

(13) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

(14) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 26.

(15) P. W. Selwood, *ibid.*, p. 92.

TABLE I

CORRECTED MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL IONS

Compound	$\chi_M \times 10^{-6}$ complex	*T*, °K.	μ_{eff} (B.M. per metal ion)
$[Ni(NH_2CH_2CH_2S)_2]$	−98.70	300	...
$[Ni\{Ni(NH_2CH_2CH_2S_2)\}_2]Cl_2$[a]	−16.22	300	...
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$[b]	−338.98	300	...
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Br_2$	−282.24	305	...
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2$	−205.40	305	...
$[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$	+7324.91	304	2.49

[a] Prepared by Method 1. [b] Prepared by Method 2.

TABLE II

MOLAR CONDUCTANCES OF COMPLEXES OF β-MERCAPTOETHYLAMINE AT 25°

Compound	λ_M (ohm^{-1})
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$	242
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Br_2$	245
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2$	246
$[Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$	238
$[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$[a]	148
$[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$	423

[a] Molar conductance determined in methanol.

Bis-(β-mercaptoethylamine)-nickel(II) $[Ni(NH_2CH_2CH_2S)_2]$.— β-Mercaptoethylamine hydrochloride (11.93 g., 0.105 mole) and 8.00 g. of sodium hydroxide (0.20 mole) were dissolved in 200 ml. of water. This solution was added slowly with stirring to 11.89 g. of nickel chloride 6-hydrate (0.05 mole) in 200 ml. of warm water. A deep red color developed initially but quickly faded upon the addition of all the ligand solution, at which point the formation of light green crystals was observed. Stirring was continued for several minutes and the solution was allowed to cool to room temperature before isolating the crystalline solid by filtration. The crystals were washed twice with 50-ml. portions of water, followed by two 50-ml. portions of abolute ethanol, and dried *in vacuo* over P_4O_{10} with continuous pumping; yield, 9.45 g. (89.5%). *Anal.* Calcd. for $[Ni(NH_2CH_2CH_2S)_2]$: C, 22.77; H, 5.73; N, 13.28; S, 30.39; Ni, 27.83. Found: C, 22.75; H, 5.72; N, 13.07; S, 30.09; Ni, 28.28.

Aternatively, this compound can be prepared from strongly ammoniacal solutions of nickel salts, by the direct addition of β-mercaptoethylamine hydrochloride.

Bis-(β-mercaptoethylamine)-palladium(II) $[Pd(NH_2CH_2CH_2S)_2]$.—β-Mercaptoethylamine hydrochloride (2.38 g., 0.021 mole) and 1.60 g. of sodium hydroxide (0.04 mole) were dissolved in 75 ml. of water. This solution was added slowly with stirring to 3.27 g. of potassium tetrachloropalladate(II) (0.01 mole) in 75 ml. of warm water. The deep red solution quickly turned bright yellow, and continued stirring at room temperature resulted in the precipitation of a small quantity of lemon-yellow crystals. More of the product crystallized from solution after cooling for several hours. The product was collected by filtration and washed twice with 20-ml. portions of water, twice with 20-ml. portions of ethanol, and dried *in vacuo* over P_4O_{10} for several hours; yield, 2.12 g. (81.8%). *Anal.* Calcd. for $[Pd(NH_2CH_2CH_2S)_2]$: C, 18.79; H, 4.68; N, 10.82; S, 24.76. Found: C, 18.54; H, 4.68; N, 10.65; S, 24.85.

Tetrakis-(β-mercaptoethylamine)-trinickel(II) Chloride, $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$. Method 1.—β-Mercaptoethylamine hydrochloride (15.03 g., 0.132 mole) was dissolved in 125 ml. of absolute ethanol. Sodium hydroxide (10.56 g., 0.264 mole) in 50 ml. of aqueous ethanol (3 parts absolute ethanol to 2 parts water by volume) was added and the sodium chloride formed during the neutralization reaction was removed by filtration. The clear ligand solution was added slowly with stirring to 150 ml. of a warm aqueous solution containing 23.53 g. (0.099 mole) of nickel chloride 6-hydrate. A deep red solution formed, and dark crystals separated from solution almost immediately. The solution was allowed to stand for approximately 2 hr. in the cold to allow further crystallization. The dark green plates which crystallized from solution were isolated by filtration, washed three times with 25-ml. portions of cold ethanol, and dried *in vacuo* over P_4O_{10}; yield, 16.50 g. Concentration of the mother liquor to about 50 ml. yielded 0.57 g. of product; total yield, 17.27 g. (93.8 %). *Anal.* Calcd. for $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 17.42; H, 4.39; N, 10.16; S, 23.25; Cl, 12.86. Found: C, 17.50; H, 4.55; N, 10.15; S, 23.48; Cl, 12.67.

The product cannot be recrystallized conveniently from water because of the rapid formation of the slightly soluble $[Ni(NH_2CH_2CH_2S)_2]$, particularly from concentrated solutions. The complex also is soluble, but to a lesser degree, in absolute methanol and ethanol. In these solvents there is no indication of decomposition. The unrecrystallized product does not exhibit a sharp melting point; however, it is thermally stable below 285°.

Tetrakis-(β-mercaptoethylamine)-trinickel(II) Chloride. Method 2.—Ten g. of bis-(β-mercaptoethylamine)-nickel(II) $[Ni(NH_2CH_2CH_2S)_2]$ (0.0474 mole) was added to an aqueous solution of nickel chloride 6-hydrate in 400 ml. of water. The resulting suspension was heated with constant stirring for slightly more than 1 hr., during which time partial solubilization of $[Ni(NH_2CH_2CH_2S)_2]$ occurred. Separation of the resulting deep red solution from the unreacted starting material (2.2 g.) was effected by filtration. The deep red filtrate then was heated on a hot water bath and concentrated *in vacuo* to about 50 ml. A dark, highly crystalline product separated from solution and was filtered, washed twice with 25-ml. portions of cold ethanol, and dried *in vacuo* over P_4O_{10} for several hours; yield, 6.85 g. (52.3 %). *Anal.* Calcd. for $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 17.42; H, 4.39; N, 10.16; S, 23.25; Cl, 12.86. Found: C, 17.22; H, 4.41; N, 10.14; S, 23.04; Cl, 12.52.

The product isolated by this procedure is identical in every respect with that prepared by Method 1.

The corresponding bromide and iodide salts were isolated by adding a twofold excess of potassium bromide or potassium iodide to an aqueous solution which was approximately 0.033 *M* in the chloride salt. The solution was cooled for approximately 2 hr.; the crystalline product which formed was isolated by filtration and washed twice with 25-ml. portions of cold methanol. The product then was dried *in vacuo* over P_4O_{10} for several hours. Allowing the filtrate to stand in the cold overnight resulted in the crystallization of a small amount of product. The yields were 80.9 and 92.1 % for the bromide and iodide salts, respectively. *Anal.* Calcd. for $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Br_2$: C, 15.00; H, 3.78; N, 8.75; S, 20.02; Br, 24.95; Ni, 27.49. Found: C, 14.85; H, 3.94; N, 8.86; S, 19.90; Br, 25.19; Ni, 27.69. Calcd. for $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2$: C, 13.08; H, 3.30; N, 7.63; S, 17.46; I, 34.56; Ni, 23.97. Found: C, 13.28; H, 3.30; N, 7.54; S, 17.11; I, 34.41; Ni, 23.67.

The solubilities of the three salts in water, methanol, and ethanol decrease sharply from the chloride to the iodide; however, this solubility trend is reversed in the solvent dimethylformamide.

Tetrakis-(β-mercaptoethylamine)-tripalladium(II) Chloride, $[Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$.—The procedure employed for the preparation of this compound is analogous to Method 2 used for the preparation of the nickel(II) adduct of $[Ni(NH_2CH_2CH_2S)_2]$. Solubilization of the $[Pd(NH_2CH_2CH_2S)_2]$ was effected in aqueous solution using potassium tetrachloropalladate(II). The yellow $[Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$ was recrystallized from a small quantity of cold water–ethanol; yield after recrystallization for the Pd(II) adduct, 76.6%. *Anal.* Calcd. for $[Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 13.81; H, 3.48; N, 8.05; S, 18.44; Cl, 10.29. Found: C, 13.70; H, 3.57; N, 7.84; S, 18.13; Cl, 9.89.

Tetrakis-(β-mercaptoethylamine)-tricadmium(II) Tetrachlorocadmate(II), $[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$.—β-Mercaptoethylamine hydrochloride (5.68 g., 0.05 mole) was added to a solution of 4.00 g. of sodium hydroxide in 250 ml. of water. A solution of 10.03 g. of cadmium chloride 2.5-hydrate (0.0438 mole) in 150 ml. of water was added slowly with stirring to the ligand solution. A white solid formed during the addition but dissolved upon continued stirring. After slightly more than two-thirds of the cadmium chloride solution had been added, the solid began to accumulate. Rapid stirring was essential at this point to prevent the white solid from adhering to the bottom of the beaker. The white suspension was stirred for an additional 15 min. without heating; the finely divided solid was filtered, washed twice with 25-ml. portions of water, twice with 25-ml. portions of methanol, and dried *in vacuo* over P_4O_{10} with continuous pumping; yield, 7.75 g. Concentration of the filtrate to approximately one-fourth the original volume produced 0.28 g. of white powder; total yield, 8.03 g. (81.8%). *Anal.* Calcd. for $[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$: C, 10.72; H, 2.70; N, 6.25; S, 14.32; Cl, 15.83. Found: C, 11.29; H, 2.84; N, 6.86; S, 14.31; Cl, 15.35.

Recrystallization of the product could not be accomplished because of its very slight solubility in water and methanol and virtual insolubility in less polar organic solvents. Upon extended contact with light, the white solid slowly turns dark.

Tetrakis-(β-mercaptoethylamine)-tricobalt(II) Chloride, $[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$.—This compound was prepared using a slight modification of Method 1 employed for the preparation of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$. Absolute methanol was used as the solvent in place of a water–ethanol mixture, and the sodium chloride produced during the neutralization of the ligand hydrochloride was removed by filtration before the addition of the ligand solution to the cobalt chloride solution. The entire reaction was carried out under a blanket of dry nitrogen to prevent the possible air oxidation of cobalt(II) to cobalt(III). The dark green solid which formed almost immediately upon the addition of the ligand solution was filtered under nitrogen, washed with several 25-ml. portions of absolute ethanol, and dried *in vacuo* over P_4O_{10}. The dry product did not appear to undergo any chemical alterations on standing; yield, 88.6%. *Anal.* Calcd. for $[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 17.39; H, 4.39; N, 10.14; S, 23.23; Cl, 12.84. Found: C, 17.11; H, 4.46; N, 10.02; S, 23.52; Cl, 12.68.

Results and Discussion

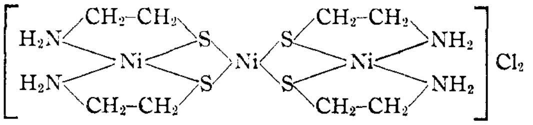
Previous investigators have reported the isolation of uncharged monomeric complexes of β-mercaptoethylamine with nickel(II) and cobalt(III) ions. However, little information concerning properties of these compounds can be derived from the early studies.

During the course of this investigation, bis-(β-mercaptoethylamine)-nickel(II) and bis-(β-mercaptoethylamine)-palladium(II) were prepared. These compounds share the common property of being only sparingly soluble in both polar and nonpolar solvents and are readily deposited from a strongly basic solution containing stoichiometric amounts of ligand and metal salt. The nickel(II) complex was found to be diamagnetic, which is consistent with a square planar configuration for nickel(II).

It is well established that treatment with pyridine usually results in the expansion of the coördination number of planar four-coördinate nickel(II) complexes to six. However, the reaction of pyridine with $[Ni(NH_2CH_2CH_2S)_2]$ failed to produce such a derivative, the starting material being reclaimed unchanged. This behavior serves to illustrate the high stability of this planar species. Moreover, although the uncharged complexes are stable in basic solution, they can be dissolved in dilute hydrochloric acid without complete dissociation to the free ligand and metal salt.

The unsymmetrical nature of β-mercaptoethylamine conceivably could lead to geometric isomerism among its metal complexes. However, during the course of the preparation of various samples in which experimental conditions were varied, no evidence of such isomerism was apparent. The methods usually employed in the separation of two geometric isomers are experimentally impractical in view of the very slight solubilities of these uncharged species.

The initial phases of the investigation on the complexes formed by β-mercaptoethylamine with bivalent nickel resulted in the isolation of dark green crystalline solids displaying the rather unusual stoichiometry of 4 ligands for every 3 metal ions. A reasonable structure for this compound involves a third nickel ion utilizing to full advantage the strong donor properties of the coördinated sulfur atoms of two uncharged *cis*-bis-(β-mercaptoethylamine)-nickel(II) molecules (structure V).



V

Despite the uncertainty associated with the actual geometric form for the uncharged species, the configurational stability of the *cis* isomer receives some theoretical justification from the premise that two π-bonding sulfur atoms would not be expected to enter into competition for the d-π electrons of the nickel(II) ion as would be required for the *trans* isomer. As has been pointed out in the case of platinum(II),[16] the two metal d-π orbitals d_{xz} and d_{yz} are properly oriented for the formation of orthogonal π bonds to two ligands in *cis* positions in the planar structure.

Assuming the validity of this structure, it is conceivable that tetrakis-(β-mercaptoethylamine)-trinickel(II) chloride, $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, could be synthesized from the neutral bis complex, $[Ni(NH_2CH_2CH_2S)_2]$. Evidence for this reaction arises from the apparent ease of solubilization of the ordinarily difficultly soluble bis complex by an aqueous solution of nickel chloride.

$$2[Ni(NH_2CH_2CH_2S)_2] + Ni^{2+} \longrightarrow [Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}$$

This procedure permits the subsequent isolation of a highly crystalline compound which displays the same stoichiometry and properties associated with the trimeric complex. The incomplete solubilization observed when stoichiometric quantities of complex and metal salt are used and the ready precipitation of the uncharged bis complex $[Ni(NH_2CH_2CH_2S)_2]$ upon dissolution of the trimer in water suggest a high degree of lability for this compound. These effects were counteracted by the presence of excess nickel chloride in the aqueous solutions used in the synthesis of the bromide and iodide salts of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}$. The lower solubility of these salts in water facilitated their isolation in states of high purity and high yield.

Magnetic measurements (Table I) indicate that this novel cation contains only diamagnetic nickel(II), a result certainly in agreement with the proposed structure. In water, the molar conductivities of the chloride, bromide, and iodide salts are 242, 245, and 246 ohm^{-1}, respectively (Table II). These values fall within the range 234 to 268 ohm^{-1} given by Werner and Miolati[17] for a variety of di-univalent amine complexes. As would be expected on the basis of the large cation size, the molar conductivity of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]X_2$ occurs at the lower extremity of this range.

Additional evidence arises from spectrophotometric continuous variations studies which normally involve the observation of changes in the optical density at a particular wave length in the visible region as a function of the mole fraction of metal ion and ligand. A modification of this method was used in establishing the existence of the trimeric complex in aqueous solution. In this experiment the bis-(β-mercaptoethylamine)-nickel(II) was used in place of the ligand. A plot of enhancement against the mole fraction of reactants (Fig. 1) indicates the formation of a maximum absorbing species at a complex–metal ion ratio of 2:1. This corresponds to the stoichiometry of the proposed trimeric species. In addition, it also can be seen that the legs of the plot very closely approach linearity, indicating the formation of a predominant, rather stable polymetallic complex.

It is interesting to note that the metal–sulfur bonds can be considered as being formed using tetrahedral sulfur orbitals. This would assure the absence of coplanarity for the coördination spheres of two adjacent nickel atoms. Moreover, this situation bears a strong resemblance to the strainless configurations assigned to cyclohexane, which are commonly referred to as the boat (or C) form and the chair (or Z) form. As in the case of cyclohexane, the chair conformation would be expected to possess the greater thermodynamic stability in view of the minimization of repulsion between atoms of the coördinated ligands.

An extension of this work to include other possibilities has been made in order to determine whether this bridge-forming tendency exists for other metal ion complexes of β-mercaptoethylamine. In this connection, the bis-(β-mercaptoethylamine)-palladium(II) complex was observed to behave in a manner analogous to that of the corresponding nickel(II) compound. The neutral

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(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 251.

(17) A. Werner and A. Miolati, *Z. physik. Chem.*, **14**, 508 (1894).

complex dissolved in an aqueous solution of potassium tetrachloropalladate(II), with reaction, as shown below. The palladium(II) adduct of $[Pd(NH_2CH_2CH_2S)_2]$ was recrystallized from water–

$$2[Pd(NH_2CH_2CH_2S)_2] + PdCl_4^{2-} \longrightarrow [Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2 + 2Cl^-$$

ethanol and excellent agreement with the stoichiometry expected for the trimeric complex was found upon analysis.

Although simple monomeric complexes of cobalt(II) and cadmium(II) with this ligand were isolated, these metal ions form stable trimeric complexes when stoichiometric quantities of metal chloride and ligand are employed. It was necessary to employ an excess of chloride ion in the case of the cadmium(II) adduct in order to obtain a solid of definite stoichiometry. The cadmium(II) trimer is only slightly soluble in both polar and non-polar solvents, but dissolves in water over a period of a few hours, resulting in a solution whose molar conductance is 423 ohm^{-1}. This behavior is consistent with that expected of a tetrachlorocadmate salt of the trimeric species in view of the large dissociation experienced by the tetrachlorocadmate ion in dilute solution. However, it should be noted that this behavior also is in agreement with the formulation as a non-electrolyte $[Cd_2(NH_2CH_2CH_2S)_2Cl_2]$ since hydrolysis of such a substance would produce a di-univalent electrolyte. Additional evidence for the formulation of this compound as an electrolyte will be discussed in another paper.[18]

The last example in the series of compounds displaying a stoichiometry of three metal ions and four ligands is the homometallic cobalt(II) trimer, $[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$. The usual ease of oxidation of complexes of cobalt(II) to cobalt(III) in aqueous systems, which was in evidence during the preparation of the tris-(β-mercaptoethylamine)-cobalt(III), necessitated the use of a non-aqueous solvent and protection from air. Methanol was chosen because of the ionic nature of both the reactants and product, and the reaction and isolation of the final product were conducted under dry nitrogen. The resulting dark green solid apparently does not display a tendency to undergo oxidation when dry. It dissolves readily in water, forming a deep reddish brown solution which slowly deposits $[Co(NH_2CH_2CH_2S)_3]$ upon the addition of aqueous ammonia. In methanol this compound exhibits a molar conductivity of 147 ohm^{-1}, which approximates the values expected for di-univalent electrolytes. Stoufer has observed a range of 145–176 ohm^{-1} for di-univalent electrolytes in this solvent.[19]

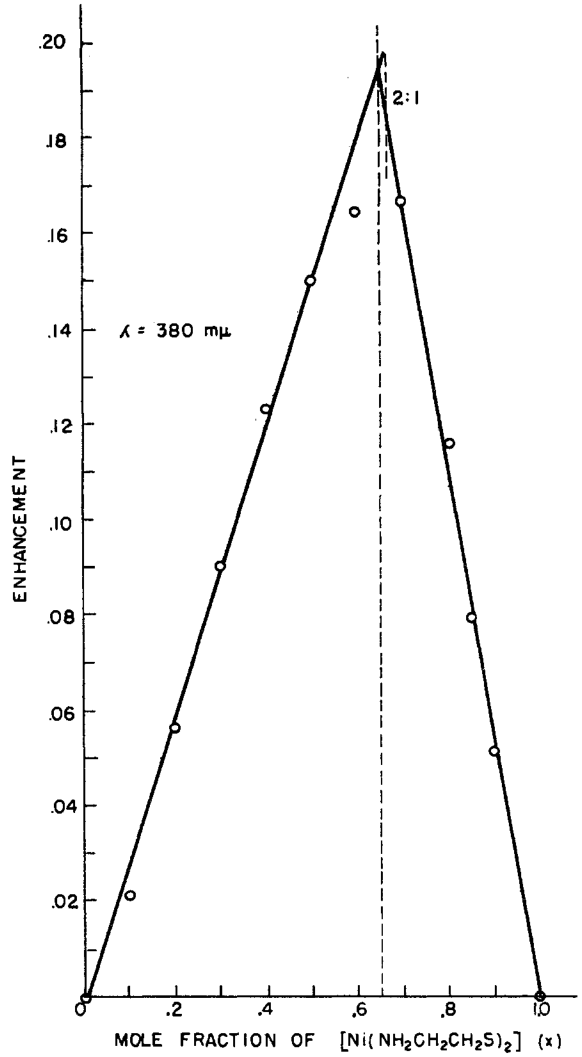

Fig. 1.—Continuous variations study of bis-(β-mercaptoethylamine)-nickel(II) (x) and nickel(II) in 10^{-3} *M* solutions.

$$2[Ni(NH_2CH_2CH_2S)_2]^0 + Ni^{2+} \longrightarrow [Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}$$

The compound has a magnetic moment of 2.49 B.M. calculated per cobalt(II) atom. This is consistent with the values observed for the cobalt(II) complexes of other sulfur-containing ligands. This substance would be expected to involve square planar cobalt(II).

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