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Complexes Derived from Strong Field Ligands. XIV. Heterometallic Trinuclear Complexes of β-Mercaptoethylamine

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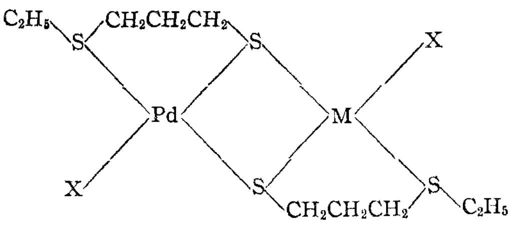
Bis-(β-mercaptoethylamine)-nickel(II) [$Ni(NH_2CH_2CH_2S)_2$] has been observed to undergo reaction with aqueous solutions of several different metal salts, resulting in the formation of adducts having the general formula $[M'\{Ni(NH_2CH_2CH_2S)_2\}_2]^{n+}$, where M′ = Cu(I), Cu(II), Pd(II), Pt(II), and Cd(II). The corresponding complex of palladium(II) [$Pd(NH_2CH_2CH_2S)_2$] behaves in an analogous manner, combining with nickel(II) ion to form a derivative of the formula $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]^{2+}$. Magnetic studies, conductivity measurements, and spectrophotometric continuous variations studies all support the assignment of a trinuclear structure in which the neutral complex serves as a chelating ligand to the unique metal atom M′. A novel material containing three different metal ions has been formulated as $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][HgI_4]$.

Introduction

In the preceding paper,[1] it was shown that β-mercaptoethylamine forms trinuclear complexes having the general formula $[M\{M(NH_2CH_2CH_2S)_2\}_2]^{2+}$ with nickel (II), palladium(II), and cobalt(II). In the case of the nickel(II) and palladium(II) complexes, the preparation could be accomplished by direct synthesis using stoichiometric quantities of ligand and metal ion, or by the solubilization of the uncharged species, [$Pd(NH_2CH_2CH_2S)_2$] and [$Ni(NH_2CH_2CH_2S)_2$], with aqueous solutions of tetrachloropalladate(II) and nickel(II) ions, respectively. The second method of preparation is of particular interest since it is reasonable to assume that such a technique may be employed for the preparation of complexes containing two different metal ions in predictable structures.

Although compounds of this general class (heterometallic polynuclear complexes) are not particularly common, the preparation of mixed metal ion complexes has been reported with the ligands 3-ethylthiopropane-1-thiol and 3-diethylarsinopropane-1-thiol. In these cases, the dimeric homonuclear complexes $[M_2\{Y(CH_2)_3S\}_2Cl_2]$, where M = Pt(II) or Pd(II) and Y = $-As(CH_3)_2$ or $-SC_2H_5$, were prepared by heating $[M\{Y(CH_2)_3S\}_2]$ with the corresponding metal halide and extracting the cooled melt with acetone or benzene.[2] Dinuclear mixed metal ion complexes were reported (for example) by heating $[Pd\{C_2H_5S(CH_2)_3S\}_2]$ with HgX_2. These were assigned structures such as that given in I. Attempts to extend that earlier study to the preparation of the corresponding complexes of platinum(II) and nickel(II), or with platinum(II) and copper(II), were unsuccessful.



I

It also should be noted that Livingstone and Plowman[3] have reported the synthesis of halogen-bridged heterometallic complexes of palladium(II) and mercury(II) with *o*-methylmercaptobenzoic acid. The mixed palladium(II)–copper(II) derivative also was reported.

These results and the findings contained herein suggest the possibility that the phenomenon of mixed metal ion complexes is more general than might be expected. The ease with which the coordinated mercaptide ion forms stable bridges appears to establish these ligands as the most promising for the preparation of compounds of this class. The present work materially augments the knowledge on the subject of heterometallic polynuclear complex ions by providing a number of additional well characterized examples.

Experimental

Materials.—Copper(I) chloride and potassium tetrachloroplatinate(II) were prepared according to the usual procedures. All other inorganic salts used in the preparations were of reagent grade. β-Mercaptoethylamine hydro-

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

[2] S. E. Livingstone, *J. Chem. Soc.*, 1994 (1956).

[3] S. E. Livingstone and R. A. Plowman, *J. Proc. Roy. Soc. N. S. Wales*, **85**, 116 (1952).

chloride was purchased from Evans Chemetics, Inc., Waterloo, New York.

Tetrakis-(β-mercaptoethylamine)-dinickel(II)-platinum-(II) Chloride, $[Pt\{Ni(NH_2CH_2CH_2S)_2\}_2)]Cl_2$, and Tetrakis-(β-mercaptoethylamine)-dinickel(II)-palladium(II) Chloride, $[Pd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$.—These derivatives of bis-(β-mercaptoethylamine)-nickel(II) were prepared in a manner analogous to Method 2 as reported earlier for the preparation of tetrakis-(β-mercaptoethylamine)-trinickel-(II) chloride.[1]

Potassium tetrachloroplatinate(II), K_2PtCl_4, (0.75 g., 0.00181 mole) was dissolved in 75 ml. of an aqueous suspension of 0.8 g. of $[Ni(NH_2CH_2CH_2S)_2]$ (0.00379 mole; 0.00017 mole excess to ensure the absence of K_2PtCl_4 during the crystallization of the final product). The suspension was warmed gently and stirred continuously during the dissolution of $[Ni(NH_2CH_2CH_2S)_2]$. A trace of undissolved starting material was removed by filtration and washed free of mother liquor with a few ml. of water. The deep red filtrate was filtered again, after reaching room temperature, and concentrated *in vacuo* with continuous pumping; yield, 1.23 g.

Microscopic examination of this product revealed the presence of potassium chloride crystals, and the sample was recrystallized from a few ml. of water and ethanol in the cold. The orange powder which formed was filtered, washed twice with a few ml. of cold absolute ethanol, and dried *in vacuo* over P_4O_{10}; yield on recrystallization, 0.95 g. (76.6%). *Anal.* Calcd. for $[Pt\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 13.96; H, 3.52; N, 8.14; S, 18.64; Cl, 10.31. Found: C, 13.70; H, 3.77; N, 7.93; S, 18.49; Cl, 10.00.

The application of this procedure to the preparation of the red palladium(II) adduct resulted in a yield of 78.6% upon recrystallization from water–ethanol. *Anal.* Calcd. for $[Pd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$: C, 16.02; H, 4.40; N, 9.35; S, 21.39; Cl, 11.83; Ni, 19.58; Pd, 17.79. Found: C, 15.81; H, 4.12; N, 9.21; S, 21.72; Cl, 12.06; Ni, 19.16; Pd, 17.70.

Tetrakis-(β-mercaptoethylamine)-dinickel(II)-copper(1) Chloride, $[Cu\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl$, and Tetrakis-(β-mercaptoethylamine)-dinickel(II)-copper(II) Chloride, $[Cu\{Ni(NH_2CH_2CH_2S)_2\}_2Cl_2$.—These compounds were isolated by a similar procedure. The copper(I) adduct was prepared from freshly prepared cuprous chloride. The product was isolated as a burnt-red crystalline solid which formed a dense matte on a sintered glass filter funnel. It was washed with water–ethanol (1:3); yield, 67.1%. *Anal.* Calcd. for $[Cu^I\}Ni(NH_2CH_2CH_2S)_2\}_2]Cl$: C, 18.44; H, 4.65; N, 10.76; S, 24.62; Cl, 6.81. Found: C, 18.28; H, 4.86; N, 10.54; S, 23.70; Cl, 7.25.

The copper(II) derivative was prepared using copper(II) chloride 2-hydrate and isolated immediately upon dissolution of the $[Ni(NH_2CH_2CH_2S)_2]$ by concentrating the filtered solution. The product was isolated as a finely divided burnt-red solid. *Anal.* Calcd. for $[Cu^{II}\{Ni(NH_2CH_2S)_2\}_2]Cl_2$: C, 17.26; H, 4.35; N, 10.07; S, 23.04; Cl, 12.74; Ni, 21.12. Found: C, 17.16; H, 4.64; N, 9.94; S, 23.10; Cl, 12.83; Ni, 20.95.

Allowing a solution of the copper(II) complex to stand for a day before concentrating resulted in a product which more closely approached the elemental analysis for the copper(I) adduct. Aqueous solutions of both compounds undergo slow decomposition over a period of a few days.

Tetrakis-(β-mercaptoethylamine)-dinickel(II)-cadmium-(II) Tetrachlorocadmate(II), $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]$-$[CdCl_4]$.—$Ni(NH_2CH_2CH_2S)_2$ (2.11 g., 0.01 mole) was solubilized in the usual manner using 2.28 g. of cadmium chloride 2.5-hydrate (0.01 mole) in 350 ml. of water. The cherry-red solution was filtered while warm, in order to remove undissolved starting material, and filtered again at room temperature. A warm saturated solution of potassium chloride (5.00 g.) in water was added slowly, resulting in the formation of a pale rose-colored solid. After allowing the solution to stand for approximately 0.5 hr., the solid was filtered, washed twice with 25-ml. portions of water–ethanol (1:1), and twice with 25-ml. portions of absolute ethanol. Drying was effected *in vacuo* over P_4O_{10} with continuous pumping. Allowing the light red filtrate to stand for a few hours at room temperature produced 0.3 g. of product; yield, 3.54 g. (89.8%). *Anal.* Calcd. for $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$: C, 12.18; H, 3.07; N, 7.11; S, 16.27; Cl, 17.98. Found: C, 12.00; H, 3.18; N, 7.04; S, 16.52; Cl, 17.70.

In the absence of added KCl, concentration of the cherry-red solution did not result in the isolation of a simple product. The coral-colored solid gave the elemental analysis: C. 13.66; H, 3.46; N, 7.93; S, 18.64; Cl, 14.06. These values are in close agreement with the formulation as an equimolar mixture of $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ and $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$: C, 13.78; H, 3.48; N, 8.04; S, 18.40; Cl, 15.26.

Both solids dissolve in water with a certain degree of difficulty and the solutions undergo substantial decomposition over a period of a few days.

Tetrakis-(β-mercaptoethylamine)-dinickel(II)-cadmium-(II) Tetraiodomercurate(II), $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]$-$[HgI_4]$.—Bis-(β-mercaptoethylamine)-nickel(II) (4.22 g., 0.02 mole) was almost completely solubilized in 350 ml. of a warm aqueous solution containing 2.28 g. of cadmium chloride 2.5-hydrate (0.02 mole). The cherry-red solution was filtered warm in order to remove traces of $[Ni(NH_2CH_2CH_2S)_2]$ and filtered again at room temperature. Seventy-five ml. of an aqueous solution containing 4.54 g. of mercury(II) iodide and a slight excess of potassium iodide over that required for the dissolving of the mercuric salt was slowly added with stirring to this solution. A pale rose-colored solid formed almost immediately and was allowed to settle before being separated from the almost colorless solution by filtration. The finely divided solid was washed twice with water, twice with absolute ethanol, and dried *in vacuo* over P_4O_{10} with continuous pumping; yield, 12.29 g. (99.0%). *Anal.* Calcd. for $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][HgI_4]$: C, 7.73; H, 1.95; N, 4.51; S, 10.32; I, 40.85; Ni, 9.45. Found: C, 7.75; H, 2.11; N, 4.90; S, 10.61; I, 36.22; Ni, 9.75.

This compound is virtually insoluble in water and other polar and non-polar solvents.

Tetrakis-(β-mercaptoethylamine)-dipalladium(II)-nickel-(II) Chloride Dihydrate, $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2 \cdot 2H_2O$.—The procedure employed for the preparation of this compound is analogous to that used for the preparation of the palladium(II) and platinum(II) adducts of $[Ni(NH_2CH_2CH_2S)_2]$. Solubilization of the $[Pd(NH_2CH_2CH_2S)_2]$ was effected in aqueous solution using nickel chloride 6-hydrate. The red-orange $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$ was recrystallized from a small quantity of cold

TABLE I

CORRECTED MOLAR MAGNETIC SUSCEPTIBILITIES, MAGNETIC MOMENTS, AND MOLAR CONDUCTANCES

Compound	$\chi_M \times 10^{-6}$ complex	T, °K.	μ_{eff} (B.M. per metal ion)	λ_M (ohm^{-1})
$[Ni(NH_2CH_2CH_2S)_2]$	−98.70	300	...	...
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$[a]	−16.22	300	...	242
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$[b]	−338.98	300	...	...
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Br_2$	−282.24	305	...	245
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]I_2$	−205.40	305	...	246
$[Pd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$	−86.88	302	...	244
$[Cu^{II}\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$	+452.06	305	1.03	184
$[Cu^{I}\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl$	−75.90	305	...	127
$[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$	−291.95	303	...	442
$[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][HgI_4]$	−216.25	305	...	...
$[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2 \cdot 2H_2O$	−142.10	302	...	258
$[Co\{Co(NH_2CH_2CH_2S)_2\}_2]Cl_2$	+7324.91	304	2.49	148[c]
$[Pt\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$	...	...	...	238
$[Pd\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$	...	...	...	238
$[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2]CdCl_4$	...	...	...	423

[a] Prepared by Method 1. [b] Prepared by Method 2. [c] Molar conductance determined in methanol.

water–ethanol; yield after recrystallization for the Ni(II) adduct, 68.1%. *Anal.* Calcd. for $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2Cl_2 \cdot 2H_2O$: C, 14.05; H, 4.14; N, 8.20; S, 18.76; Cl, 10.37; Ni, 8.58; Pd, 31.21. Found: C, 14.26; H, 4.41; N, 7.84; S, 18.49; Cl, 11.32; Ni, 8.81; Pd, 31.62.

Spectrophotometric Measurements.—The method of continuous variations was used to establish the existence of metal ion adducts of $[Ni(NH_2CH_2CH_2S)_2]$ and $[Pd(NH_2CH_2CH_2S)_2]$ in aqueous solution. All spectra were obtained by means of a Beckman D.U. spectrophotometer using quartz cells. Stock solutions (10^{-3} *M*) of analyzed samples of $[Ni(NH_2CH_2CH_2S)_2]$ and $[Pb(NH_2CH_2CH_2S)_2]$ were prepared by gentle heating on a steam bath and vigorous shaking in order to completely dissolve the samples. Wave lengths of maximum absorption for $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]^{2+}$ and $[Cu\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}$ were selected from the spectra of aqueous solutions (5×10^{-4} *M*) of these complexes.

The enhancement of absorption was determined by a graphical method[4] for each system and was plotted against the mole % of $[M(NH_2CH_2CH_2S)_2]$ in solution in order to determine the complex-to-metal ion ratio.

Magnetic Measurements.—Magnetic moments were obtained as described earlier.[1] Magnetic data for the complexes are listed in Table I.

Conductivity Measurements.—Molar conductances were determined as before[1] and the data are summarized in Table I.

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

Discussion

The reaction of the neutral, square planar complexes, $[Ni(NH_2CH_2CH_2S)_2]$ and $[Pd(NH_2CH_2CH_2S)_2]$, with appropriate metal salts or complexes in aqueous media has resulted in the isolation of these new substances: $[Pd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, $[Cu^{II}\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, $[Pt\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, $[Cu^{I}\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$, $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]CdCl_4$, $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]HgI_4$, $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2 \cdot 2H_2O$, and $[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2]CdCl_4$.

The materials containing Cu(II) or Cd(II) as the unique metal ion were prepared by the reaction of $[Ni(NH_2CH_2CH_2S)_2]$ with the hydrated metal ion (eq. 1), while the derivatives of Pd(II) and

$$2[Ni(NH_2CH_2CH_2S)_2] + M^{2+} \longrightarrow [M\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+} \quad (1)$$

Pt(II) were synthesized by the reaction of aqueous solutions of tetrachloropalladate(II) and tetrachloroplatinate(II), respectively, with the very slightly soluble nickel(II) complex (eq. 2).

$$2[Ni(NH_2CH_2CH_2S)_2] + MCl_4^{2-} \longrightarrow [M\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+} + 4Cl^- \quad (2)$$

The very great tendency of these reactions to proceed may be judged from the fact that although both $[Ni(NH_2CH_2CH_2S)_2]$ and $Cu^{I}Cl$ are only very slightly soluble, stoichiometric amounts dissolve totally upon reaction (eq. 3).

$$2[Ni(NH_2CH_2CH_2S)_2] + CuCl \longrightarrow [Cu^{I}\{Ni(NH_2CH_2CH_2S)_2\}_2]^+ + Cl^- \quad (3)$$

The single derivative of $[Pd(NH_2CH_2CH_2S)_2]$ reported here is readily prepared by the dissolution of the neutral complex in a solution of Ni^{2+}.

The expected structure of β-mercaptoethylamine complexes having the stoichiometry $[M_3(NH_2CH_2CH_2S)_4]^{2+}$ has been suggested previously as shown in II below.[1] This proposed structure has

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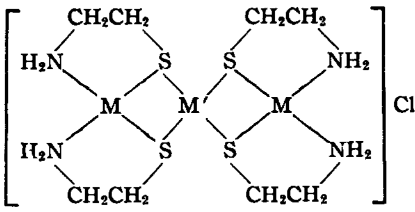
[4] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

served as the basic hypothesis leading to the synthesis of the compounds of immediate interest. The centermost metal ion M′ is *primed* to emphasize the fact that it is this metal ion which has been permuted in the course of the present investigations. The successful synthesis of six derivatives in which M is Ni(II) and M′ is either Pd(II), Pt(II), Cd(II), Cu(I), or Cu(II) clearly vindicates the hypothesis. Further, the synthesis of [Ni{Pd(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$]Cl$_2$·2H$_2$O shows the even greater generality of structure II, for here M is Pd(II) and M′ is Ni(II).



II

The inferred structures are further supported by physical data. The magnetic moments have been determined for these materials (Table I). The nickel ion is invariably found to be diamagnetic in these compounds, regardless of the site it occupies in structure II. Thus, [Pd{Ni(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$]$^{2+}$, [Ni{Pd(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$]$^{2+}$, and [Ni{Ni(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$]$^{2+}$ all are essentially diamagnetic, implying that the chelate and bridge sites both involve planar coördination of the nickel(II) ions. The expected conformation of the bridging sulfur atoms leads to an interesting structural consideration. The sulfur atoms should be pyramidal, not trigonal planar. Consequently, the trinuclear ion is expected to be bent at each pair of sulfur bridges, yielding a chair conformation. Presumably, the ions containing Cu(II), Pt(II), or Pd(II) at the unique site also are of structure II. With the exception of the Cu(II) adduct, these compounds all exhibit molar conductance (Table I) within the narrow range from 238 to 258 ohm^{-1}. These values are consistent with the formulation of the complex salts as di-univalent electrolytes.

The method of continuous variations has been utilized in a few cases to establish the existence of compounds of the same stoichiometry in solution as has been found by analysis of pure solids. As shown in Fig. 1, a plot of enhancement *vs.* mole fraction for varying ratios of the concentrations of [Pd(NH$_2$CH$_2$CH$_2$S)$_2$] and NiCl$_2$ indicates the formation of [Ni{Pd(NH$_2$CH$_2$CH$_2$S)$_2$}$_2$]$^{2+}$ in dilute aqueous solution.

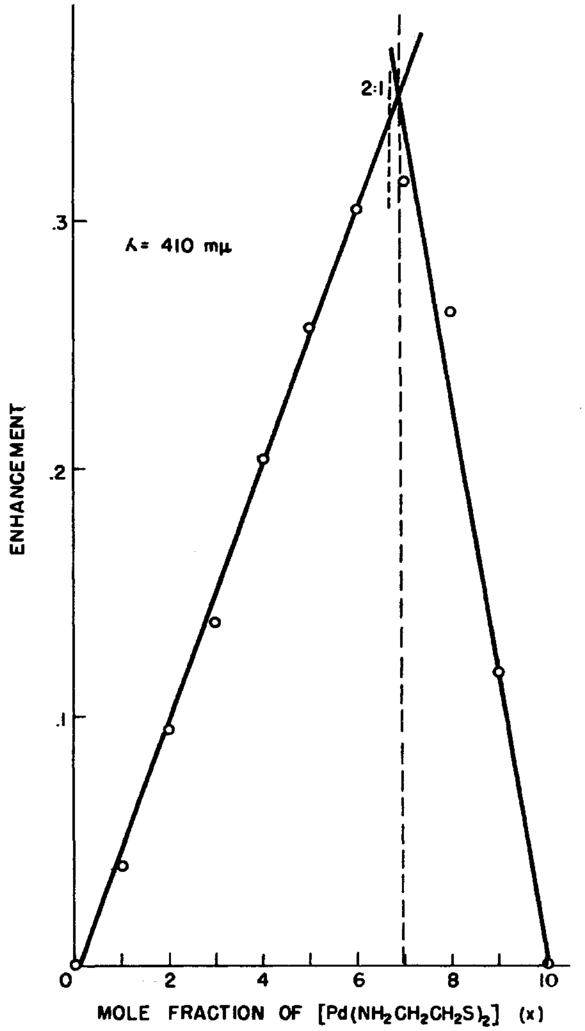


Fig. 1.—Continuous variations study of bis-(2-aminoethanethiolo)-palladium(II) (x) and Ni^{2+} ($1 - x$) in 10^{-3} *M* solutions.

$$2[\mathrm{Pd(NH_2CH_2CH_2S)_2}] + \mathrm{Ni^{2+}} \rightarrow \{\mathrm{Ni[Pd(NH_2CH_2CH_2S)_2]_2}\}^{2+}$$

The reaction involving the formation of the copper(II) adduct presents a rather interesting example of the stabilization of a lower oxidation state, resulting in the formation of a stable copper(I) species. Although a plot of enhancement *vs.* mole fraction of [Ni(NH$_2$CH$_2$CH$_2$S)$_2$] and CuCl$_2$ (Fig. 2), employing the method of continuous variations, substantiates the formation of a copper adduct, the significant variation in optical density observed over a period of several hours is indicative of at least partial contribution from the Cu(I) species. This contribution also is evident in the low molar conductivity of 184 ohm^{-1} measured for an analyzed sample of the copper(II) adduct. Moreover, this value decreases considerably over a period of time upon allowing the solution to stand at 25°. This phenomenon can be associated

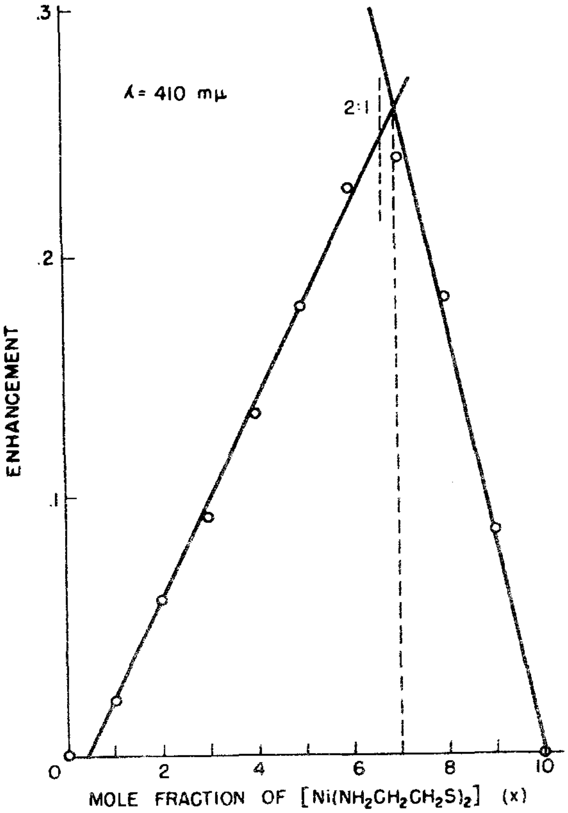


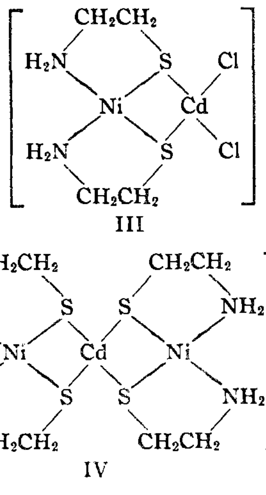
Fig. 2.—Continuous variations study of bis-(2-aminoethanethiolo)-nickel(II) (x) and Cu^{2+} ($1 - x$) in 10^{-3} M solutions.

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

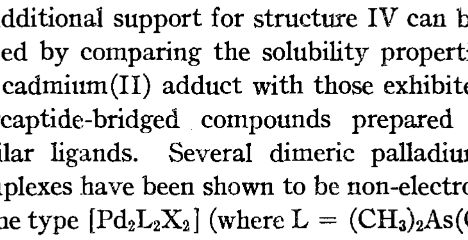
with the oxidation of the ligand to the corresponding disulfide. Precluding the possibility of appreciable dissociation of the $[Ni(NH_2CH_2CH_2S)_2]$ in aqueous solution at the concentrations employed, it is interesting that the coördinated mercaptide group parallels the normal behavior of mercaptide ligands in the presence of cupric salts.[5]

The copper(I) adduct, $[Cu^I\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl$, which can be isolated in a pure state by solubilizing $[Ni(NH_2CH_2CH_2S)_2]$ with cuprous chloride, is representative of a second stuctural class of mixed metal ion complexes formed by β-mercaptoethylamine. The observed diamagnetism and molar conductivity of 127 ohm^{-1} are consistent with a uni-univalent electrolyte comprised of a tetrahedral copper(I) ion bonded to two square planar bis nickel(II) complexes.

A cadmium(II) adduct might be expected to exhibit the same structural properties as the copper(I) derivative because of the preference of both metal ions for a tetrahedral configuration. However, chemical analysis of the solid isolated from an aqueous solution containing excess chloride ion reveals a stoichiometry of 1 ligand and 1 chloride per metal ion, which is in agreement with two alternate formulations (structures III and IV).



III



IV

The slow dissolving of the complex in water and its virtual insolubility in less polar solvents would appear to favor the electrolyte (structure IV).

Additional support for structure IV can be obtained by comparing the solubility properties of the cadmium(II) adduct with those exhibited by mercaptide-bridged compounds prepared from similar ligands. Several dimeric palladium(II) complexes have been shown to be non-electrolytes of the type $[Pd_2L_2X_2]$ (where L = $(CH_3)_2As(CH_2)_3SH$, CH_3-SC_6H_4SH, $C_2H_5S(CH_2)_3SH$, or $H_2NC_6H_4SH$, and X is a monodentate group such as Cl^-).[6] Most of these compounds are insoluble in water, but exhibit some solubility in non-polar solvents, particularly chloroform. In the case of the cadmium(II) adducts of $[Ni(NH_2CH_2CH_2S)_2]$, a significant solubility was observed only for water as the solvent medium. The molar conductivity (assuming structure IV) in water was found to be 442 ohm^{-1}, which is explainable in terms of extensive dissociation of the tetrachlorocadmate anion in dilute solution. Evidence in support of this suggestion arises from the stability constants determined by Vandergee and Dawson.[7] A similar conclusion can be reached from the analytical results obtained for samples prepared in the absence of excess chloride ion. The apparent stoichiometry, $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]_2CdCl_6$, can be interpreted in terms of the formation of a lattice compound comprised of $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ and $[Cp\{Ni(NH_2CH_2CH_2S)_2\}_2][Cd$-

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(5) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, p. 159.

(6) S. E. Livingstone, *J. Chem. Soc.*, 1989 (1956).

(7) C. E. Vandergee and H. J. Dawson, Jr., *J. Am. Chem. Soc.*, **75**, 5689 (1953).

$Cl_4]$. The presence of excess chloride ion favors the formation of $[CdCl_4]$ and precipitation of the corresponding salt. Moreover, the existence of a lattice compound is definitely favored over the formation of a salt containing the anion $[CdCl_6]^{4-}$.

An attempt was made to establish the structure of the cadmium(II) adduct by isolating the proposed complex cation, $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}$, in the form of the tetraiodomercurate salt. The addition of an aqueous solution of potassium tetraiodomercurate to an aqueous solution of the cadmium adduct resulted in the formation of an insoluble coral-colored precipitate. Analysis of this finely divided solid is in close agreement with the formulation $[Cd\{Ni(NH_2CH_2CH_2S)_2\}_2][HgI_4]$. Considerable difficulty was encountered, particularly in obtaining reproducible metal analyses because of the complexity of the compound. The observed diamagnetism of this complex is consistent with the behavior of the adducts of $[Ni(NH_2CH_2CH_2S)_2]$ as previously discussed. It also should be mentioned that a more thorough investigation of this compound was hampered by its virtual insolubility in both polar and non-polar solvents. The association of structure IV with the cadmium(II) complex appears reasonable on the basis of present evidence.

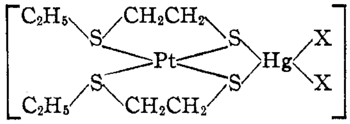
A similar situation appears to exist for a compound of the stoichiometry 1 metal ion : 1 ligand: 1 chloride in which all of the metal sites are occupied by cadmium(II).[1] This compound can easily be prepared using stoichiometric quantities of cadmium chloride and ligand in the presence of excess chloride. It 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, 423 ohm^{-1}, is consistent with that observed for the cadmium(II) adduct of $[Ni(NH_2CH_2CH_2S)_2]$.

A novel demonstration of the greater lability associated with the bridged nickel(II) ion as compared to that of heavier metals resulted during the investigation of the behavior of an aqueous solution of $[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2$ in the presence of the tetrachloromercurate anion. The insoluble pale yellow solid which separated from solution was analyzed and found to be in excellent agreement with either of the two possible formulations given in the equation

$$[Ni\{Pd(NH_2CH_2CH_2S)_2\}_2]Cl_2 + 2[HgCl_4]^{2-} \longrightarrow [Hg\{Pd(NH_2CH_2CH_2S)_2\}_2][HgCl_4] \text{ or } [Hg\{Pd(NH_2CH_2CH_2S)_2\}Cl_2]$$

Because of the great complexing ability of palladium(II), the likelihood of exchanging ligands is small. Therefore, structures in which the mercaptoamine is chelated to the mercury(II) are not considered to be very probable.

At this point, it is well to consider again the dimeric mercury(II)–platinum(II) complex of 3-ethylthiopropane-1-thiol $[PtHgL_2X_2]$ which exhibits the same stoichiometry as the mercury(II) adduct of $[Pd(NH_2CH_2CH_2S)_2]$. Livingstone[2] has suggested a symmetrical structure (structure I) for this compound, although an alternate structure (structure V) may be based on the mode of formation. This also is in agreement with its behavior as a non-electrolyte in nitrobenzene. This compound is soluble in benzene, chloroform, and to a lesser extent in acetone and alcohol. The fact that the mercury(II) adduct of $[Pd(NH_2CH_2CH_2S)_2]$ is insoluble in these solvents tends to provide additional support for the electrolyte structure, $[Hg\{Pd(NH_2CH_2CH_2S)_2\}_2][HgCl_4]$. Attempts to prepare simple salts containing the cation $[Hg\{Pd(NH_2CH_2CH_2S)_2\}_2]^{2+}$ failed.



V

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