

Heteronuclear Complexes. Metal Ion Induced Paramagnetism in a Metal-containing Diamagnetic Chelating Agent

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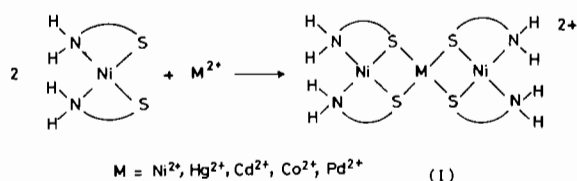
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The diamagnetic bidentate chelating agent bis-(2-mercaptoethylamine)nickel(II) forms heterometallic complexes upon reacting with various metal ions. The cadmium complexes having the general formula $[[Ni(NH_2CH_2CH_2S)_2]_2Cd]CdX_4$, are diamagnetic however the analogous mercury complexes $[[Ni(NH_2CH_2CH_2S)_2]_2Hg][HgX_4]$, where $X = Cl, Br$ are paramagnetic. The exception is $[[Ni(NH_2CH_2CH_2S)_2]_2Hg][HgI_4]$ which is diamagnetic. The electronic spectrum of this complex is consistent with a square planar environment around the nickel(II) ions. However, $[Ni(NH_2CH_2CH_2S)_2HgX_2]_n$ complexes where X is Cl or Br have the electronic spectra which are consistent with a six coordinate environment around the nickel(II) ions. The infrared spectra of the chloride complex indicated that this compound did not contain the $HgCl_4^{-2}$ anion. The X-ray powder patterns of all three complexes are different as are the infrared spectral patterns. The magnetic susceptibilities were measured from room temperature to 5 K and these complexes are ferromagnetic in character. However, the magnetic data could not be fit to any model. Comparisons are made with similar poly-metallic complexes such as $[Ni(NH_2CH_2CH_2S)_2]_2HgY_2$ where $Y = NO_3^-, Cl^-,$ and SCN^- . Based on the above data it is believed that $[Ni(NH_2CH_2CH_2S)_2HgX_2]_n$ complexes where X is Cl or Br are polymeric. However, the $[Hg[Ni(NH_2CH_2CH_2S)_2]_2]X_2$ where $X = HgI_4^{-2}, NO_3^{-}$ and Cl^{-} can be best represented as a ionic complex containing a trimetallic cation.

Introduction

Bis(2-mercaptoethylamine)nickel(II), $(Ni(MEA)_2)_2$, is a diamagnetic square planar complex [1]. This complex can function as a bidentate ligand by bonding to such metal ions as nickel(II), palladium(II), cobalt(II), copper(II), cadmium(II), and mercury(II) through the coordinated mercapto groups [1–3]. The resulting complexes are trinuclear cations (I):



The $[Ni(Ni(MEA)_2)_2]^{+2}$ cation is diamagnetic and each nickel(II) ion is in a planar environment [4]. Predictably the $[Cd[Ni(MEA)_2]_2]CdX_4$ complexes, $X = Br$ and I , are also diamagnetic [2]. However, it was reported without explanation that $[Hg(Ni(MEA)_2)_2]HgCl_4$ and $[Hg(Ni(MEA)_2)_2]HgBr_4$ are paramagnetic in the solid state while $[Hg(Ni(MEA)_2)_2]HgI_4$ was diamagnetic in the solid state [3]. Such magnetic data appears anomalous in that the metallo-ligand, $Ni(MEA)_2$, is diamagnetic and the Hg^{+2} has ten electrons in its 3d orbitals.

Results and Discussion

We have repeated the magnetic measurements on all three complexes and obtained essentially the same results as Jicha and Busch [3]. The magnetic susceptibilities of $[Ni(MEA)_2HgX_2]_n$, $X = Cl$ or Br were measured between 100 K and 6 K. The tabulated data are given in Table I. Several of the susceptibilities were tested for field dependence at selected temperatures and were found to be independent of field, (i.e., the total magnetic moment was proportional to field strength). The susceptibility data within the 30 K to 100 K range fit the Curie–Weiss law (Figs. 1 and 2). A ferromagnetic exchange is indicated both by the positive Weiss constant and by the manner in which the magnetic moment varies with temperature (Figs. 3 and 4). For example, for the complex $[Ni(MEA)_2HgCl_2]_n$, the magnetic moment per nickel ion at 102 K is $2.7 \mu_B$. The magnetic moment of $3.4 \mu_B$ is obtained at 26 K and then the magnetic moment decreases rapidly as the temperature is further lowered. At 2.1 K the μ_B is $2.26 \mu_B$. A similar profile was obtained for $[Ni(MEA)_2HgBr_2]_n$.

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TABLE I. Magnetic Susceptibilities per Gram-atom Ni^{2+} of $[\text{Ni}(\text{MEA})_2\text{HgX}_2]_n$ ($X = \text{Cl}, \text{Br}$).

X = Cl		X = Br	
T(K)	$\chi_M(\times 10^{-3})$	T(K)	$\chi_M(\times 10^{-3})$
2.1	305.00	1.8	371.38
2.5	283.66	7.5	122.16
4.2	204.05	15.0	70.27
12.0	94.36	22.0	50.78
16.0	82.42	26.0	42.05
19.0	74.95	31.0	34.22
26.0	55.14	36.0	27.72
31.0	44.08	41.0	23.10
36.0	34.95	45.0	20.34
41.0	29.42	49.5	17.85
44.0	26.02	54.0	16.06
50.0	22.04	59.0	14.29
54.0	19.42	64.0	12.86
60.0	16.80	70.0	10.73
65.0	15.34	75.0	9.83
69.0	14.18	80.0	8.94
102.0	9.03	85.0	8.23
		99.0	6.80

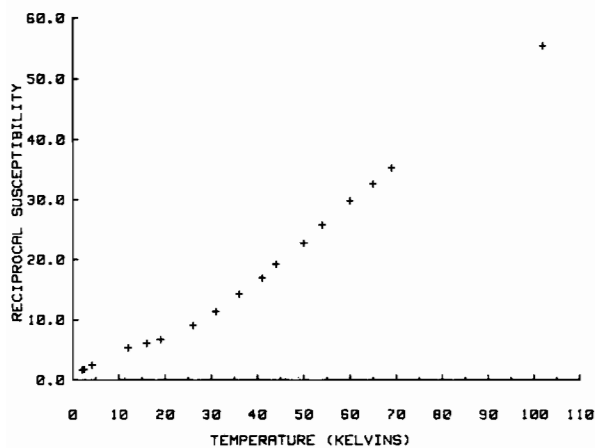


Fig. 1. Plot of reciprocal susceptibility *versus* temperature for $[\text{HgNi}(\text{MEA})_2\text{Cl}_2]_n$.

We have attempted to analyze the data in Table I in terms of various models: mean field dimer [5], isolated dimer [6], one dimensional Heisenberg [7] and Ising chains ($S = 1$), and one dimensional Ising chain with effective spin equal to $1/2$ with $g_{\perp} = 0$ [8]. All models failed to fit the experimental results in any reasonably quantitative way except the one dimensional Ising chain. However nickel(II) does not usually conform to the Ising chain model. Also in order for S_{eff} to be equal to $1/2$, one must assume a large D/K compared to T . This assumption is not likely to be valid in this case.

The electronic spectra of the solid complexes (Fig. 5) provided information with regard to the geometry of the nickel(II) ions in these complexes.

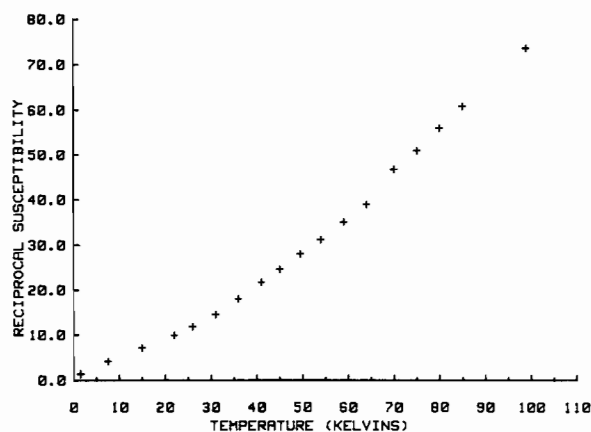


Fig. 2. Plot of reciprocal susceptibility *versus* temperature for $[\text{HgNi}(\text{MEA})_2\text{Br}_2]_n$.

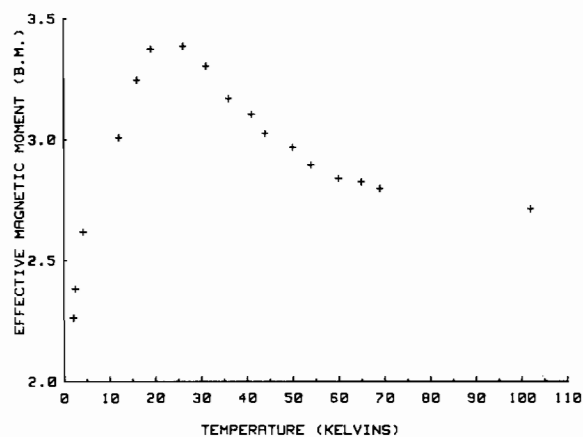


Fig. 3. Plot of μ_{eff} *versus* temperature for $[\text{HgNi}(\text{MEA})_2\text{Cl}_2]_n$.

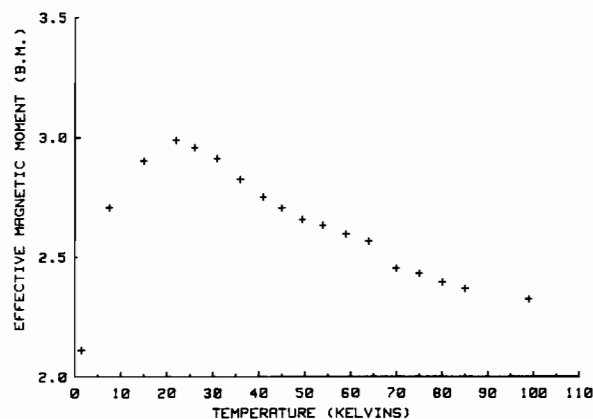


Fig. 4. Plot of μ_{eff} *versus* temperature for $\text{Hg}(\text{Ni}(\text{MEA})_2\text{Br})_n$.

The spectra of the $[\text{Ni}(\text{MEA})_2\text{HgX}_2]_n$ ($X = \text{Cl}$ or Br) complexes are consistent with six coordinate nickel(II) complexes [10]. A band in the near infrared region around 900 nm was observed for both

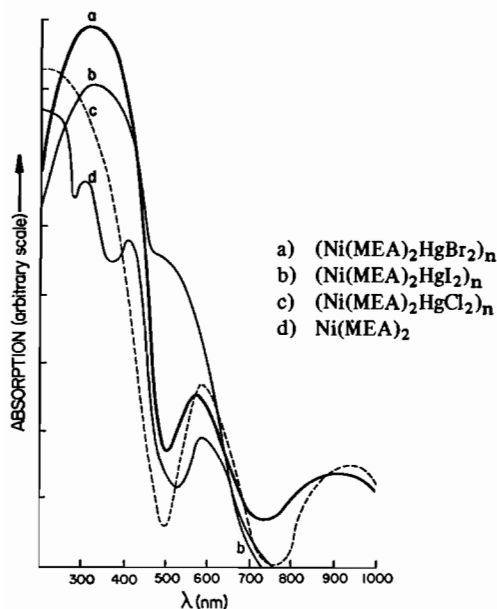


Fig. 5. Electronic spectra in Nujol 25 °C.

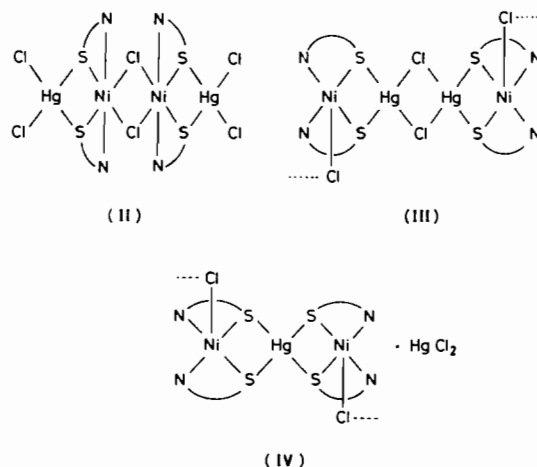
complexes. At liquid nitrogen temperature the broad band at 900 μm split. In sharp contrast, the diamagnetic $[\text{Ni}(\text{MEA})_2\text{HgI}_2]_n$ has an electronic spectrum that is diagnostic of square-planar diamagnetic nickel(II) complexes [10]. No bands were observed in the near infrared region. Therefore, we conclude that the two nickel(II) ions in $[\text{Ni}(\text{MEA})_2\text{HgI}_2]_n$ are in square planar environments while the nickel(II) ions in the other two complexes are in either a five or six coordinated environment.

All three complexes have unique X-ray powder patterns and infrared spectra suggesting that all three complexes have unique structures. Four bands have been reported for the HgCl_4^{2-} anion at 257 cm^{-1} (μ_1), 180 cm^{-1} (μ_2), 276 cm^{-1} (μ_3), and 192 cm^{-1} (μ_4) [11]. However, there are no bands observed for the complex $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_n$ from 291 cm^{-1} to 242 cm^{-1} . A band was observed at 193 cm^{-1} for $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_n$ but a band at the same energy was observed for the complex $[\text{Ni}(\text{MEA})_2\text{HgBr}_2]_n$, therefore, it is not likely that the 193 cm^{-1} band is due to the HgCl_4^{2-} anion. Finally, there are no bands between 168 cm^{-1} and 193 cm^{-1} for the complex $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_n$. Therefore we conclude that the HgCl_4^{2-} anion does not exist and $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_n$ cannot be formulated as $[\text{Hg}(\text{Ni}(\text{MEA})_2)_2]\text{HgCl}_4$. Good precedence for identifying the HgBr_4^{2-} anion via infrared spectrum is not available but we are nevertheless confident that this species does not exist as an unperturbed anion in $[\text{Hg}(\text{Ni}(\text{MEA})_2)_2]\text{HgBr}_4$. Finally, the Hg—I stretches have energies that are too low to observe with our instrumentation.

Since these are insoluble complexes it would be extremely difficult to determine the structure by X-ray techniques. However, the structure must be

consistent with the following facts: a) the nickel(II) ions have a coordination number of five or six; b) the nickel(II) ions must be linked via bridging atoms in order for the Ni(II) ions to communicate in a ferromagnetic manner. It is unlikely that the two terminal nickel(II) ions in structure I are intramolecularly coupled. All the examples that we have found in the literature of trinuclear metal complexes exhibited strong magnetic interactions between adjacent metal atoms (large J values) and weak interactions between terminal metal ions (small J values) [12, 13]. Therefore we must conclude that Ni(II) ions must communicate intermolecularly via a bridging group. However, we are assuming that only the nickel(II) ions can magnetically communicate. It has been observed that HgSalen exhibits an ESR signal [14]. Therefore, it is possible, though very unlikely, that the nickel and mercury are magnetically coupled. Because paramagnetic mercury(II) is so unlikely, this option was not further considered. c) The NiXNi bond angle where X is the bridging ligand must approach 90° for a ferromagnetic interaction.

Structure I does not conform to the first two criteria. Structure II is possible but we would expect this structure to conform to the ferromagnetic isolated dimer model having the NiCl_2Ni unit [6]. Unfortunately this is not the case. Structures III and



IV assume a NiClNi bond angle approaching 90°. These structures are consistent with our data. We would expect a relative strong magnetic interaction between nickel(II) ions bridged by a halide and a weak antiferromagnetic interaction between the terminal nickel(II) ions. This antiferromagnetic interaction may be responsible for the decrease in the magnetic moments below 40 K. A similar observation was made with the trimeric bis(acetylacetonato)nickel complex [12]. It is also possible that these complexes are metamagnets and as a result it would require a larger magnetic field strength at lower temperatures in order to induce a ferromagnetic transition [15].

In order to test whether anions other than Cl^- and Br^- could produce complexes having similar properties to $[\text{Ni}(\text{MEA})_2\text{HgX}_2]_n$ $X = \text{Cl}$ or Br , the nitrate and thiocyanate compounds were prepared. The nitrate anions in $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}](\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ are not as likely to bridge the two nickel(II) ions and also a ferromagnetic interaction through the nitrates is less likely than that of a halide. This complex has the same color as the $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}]\text{HgI}_4$. The reflectance spectrum showed bands at 480, 760, 1160 and 1320 μm . The bands in the near infrared region of the electronic spectrum as well as the magnetic moment, 0.8 BM/Ni at room temperature, suggest that either the nitrates or the water molecules are weakly bonded to the nickel(II). The two bands in the near-infrared region suggests a trans-octahedral geometry. Attempts to obtain additional evidence of coordination of the nitrate groups to the nickel by vibrational spectrum were not conclusive. Bands assigned to nitrate groups, were observed at 1350, 1378, 832 and 855 cm^{-1} . These bands can be assigned as either ionic nitrates or weakly coordinating monodentate nitrates. Based on the above data we conclude that $[\text{Ni}(\text{MEA})_2]_2\text{Hg}](\text{NO}_3)_2$ appears to have a structure similar to I, however, the nitrate groups are weakly coordinated to the nickel ions.

Potassium thiocyanate was added to an aqueous solution of $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}][\text{NO}_3]_2 \cdot 2.5\text{H}_2\text{O}$ and $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}][\text{SCN}]_2$ was isolated. The magnetic moment per nickel was 2.58 BM/Ni. Since SCN^- is a stronger ligand than the nitrate group, a stronger interaction was expected; and as a result, a higher magnetic moment was also expected. However, when KCl is added to an aqueous solution of $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}](\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ a bright red compound was isolated which analyzed as $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}]\text{Cl}_2$. The magnetic moment for this complex was approximately the same as observed for the $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}](\text{NO}_3)_2$, 0.84 BM/Ni. Based on this data it appears that the $[\text{Ni}(\text{MEA})_2\text{HgX}_2]_n$ complexes where $X = \text{Cl}^-$ or Br^- could not be simply described by structure IV because $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_2$ and $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}]\text{Cl}_2$ should have a similar structure and similar magnetic properties. It is a necessary conclusion that both mercury ions play a role in the magnetic properties of these compounds. This seems to favor structure III for the $[\text{Ni}(\text{MEA})_2\text{HgX}_2]_n$, where $X = \text{Cl}$, Br and structure I for $[(\text{Ni}(\text{MEA})_2)_2\text{Hg}]\text{X}_2$ where $X = \text{Cl}^-$, NO_3^- or HgI_4^- .

There are several questions still unanswered. Why are the mercury(II) complexes paramagnetic and the cadmium(II) complexes diamagnetic? Why are $[\text{Ni}(\text{MEA})_2\text{HgCl}_2]_n$ and $[\text{Ni}(\text{MEA})_2\text{HgBr}_2]_n$ complexes paramagnetic but the $[\text{Hg}(\text{Ni}(\text{MEA})_2)_2]\text{HgI}_4$ diamagnetic? It is known that soft metal ions such as Hg^{+2} or Cd^{+2} can form strong bonds with the coordinated mercapto group. For example, bis(2-mercaptoethylamine)nickel(II) forms stronger bonds with the

softer nonligand-field stabilized metal ion, cadmium(II) than with harder but ligand-field stabilized metal ion nickel(II) (the equilibrium constant for the reaction $[\text{Ni}(\text{Ni}(\text{MEA})_2)_2]^{+2} + \text{Cd}^{+2} = [\text{Cd}(\text{Ni}(\text{MEA})_2)_2]^{+2} + \text{Ni}^{+2}$ is $4 \times 10^{+2}$) [16]. However, the mercuric ion forms a stronger bond with a coordinated mercapto group than Cd^{+2} as evidenced by the fact that $((\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2))^{+2}$ interacted with Hg^{+2} via the coordinated sulfur but there were no reactions with Cd^{+2} [17]. Sigle, Rheinberger and Fischer's [18] research indicated that Cd^{+2} should be considered as a borderline Lewis acid in terms of its coordination tendencies toward sulfurs, while Hg^{+2} should be considered a soft metal ion. Therefore, we conclude that the Hg-S interaction is stronger than either the Ni-S or Cd-S interactions. A strong Hg-S interaction should weaken the nickel(II)-sulfur bonds in all the complexes prepared in this study. By creating a weaker ligand-field strength around the two terminal nickel(II) ions, the nickel(II) becomes a stronger electrophile and can compete for the halides on HgX_4^{-2} . Since the Cl-Hg bond is weaker than the Hg-I bond, the induced electrophilic nickel(II) ions will compete more successfully for halides in HgCl_4^{-2} than with HgI_4^{-2} . Therefore, we would expect the nickel(II) ions in $[\text{Hg}(\text{Ni}(\text{MEA})_2)_2]\text{HgI}_4$ to be diamagnetic and the chloride and bromide analogs to be paramagnetic. The weakening of the ligand-field around the nickel(II) ions by bonding the Hg^{+2} to the coordinated sulfurs, will result in the unpairing of the 3d electrons on the terminal nickel(II) ions. In doing so it allows the unpaired electrons on the nickel(II) ions to couple through the bridging halides in a ferromagnetic manner. Cadmium ion cannot form as strong a bond with the coordinated mercapto groups and as a result the bridging mercapto groups still function as a strong field ligand. Therefore all the Cd^{+2} complexes should be diamagnetic.

Experimental

Material

The $\text{Ni}(\text{MEA})_2$ and $[\text{Hg}(\text{Ni}(\text{MEA})_2)_2]\text{HgX}_4$ where $X = \text{Cl}$, Br , I were made according to a literature procedure [3]. The compounds were checked for purity by comparing magnetic moments with the literature values and by chemical analyses.

Physical Methods

The electronic spectra were run on a Perkin-Elmer Acta MIV spectrometer. Spectra of the solids were measured in a Nujol mull using diffuse transmittance techniques. The magnetic moments above 100 K of all complexes were determined by the Guoy method. Samples were compared using the $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the standard. Susceptibility mea-

surements below 100 K were made using a PAR Model 155 vibrating sample magnetometer at a field strength of 3 koe. The standard use for calibration was a MnF_2 sample traceable to NBS. The data were taken at Ohio State University in Professor P. Wigen's laboratory.

Preparation of Tetrakis-(2-aminoethanethiol)dinickel(II)mercury(II)dinitrate $[(\text{Hg}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2]_2)(\text{NO}_3)_2]$

One and seventh-five hundredths grams (0.0051 mol) of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ was dissolved in 200 ml of water and heated to approximately 50 °C on a stirrer-hot plate. To the warm solution was added with constant stirring 2.14 g (0.0102 mol) of bis-(2-aminoethanethiol)nickel(II). The resulting solution had a deep red color. One hundred milliliters of a hot, concentrated (58 g/100 g H_2O) solution of KNO_3 was added to the clear solution. Precipitation occurred immediately and the stirring was stopped 2 min after the addition of the KNO_3 solution. The mixture was allowed to stand for one-half hour and then the rose-pink precipitate was collected on a frittered glass Buchner funnel. The precipitate was washed twice with 25 ml portions of 50:50 ethanol-water mixture and finally with 25 ml of reagent grade ethanol; yield 3.07 g (81.1%). *Anal.* Calcd. for $[\text{Hg}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2]_2(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}]$: Hg, 25.53; Ni, 14.93. Found: Hg, 25.67; Ni, 14.90.

Preparation of Tetrakis-(2-aminoethanethiol)dinickel(II)mercury(II)chloride $[\text{Hg}[\text{Ni}(\text{MEA})_2]_2]\text{Cl}_2$

A tenth of a gram of $[\text{Hg}[\text{Ni}(\text{MEA})_2]_2](\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in approximately 25 ml of H_2O and 0.06 g of KCl was added to that solution. The bright red precipitate which resulted was filtered. Calc. $[(\text{Ni}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2)\text{Hg}]\text{Cl}_2$: C, 13.89; N, 8.09; H, 3.47. Found C, 13.69; N, 7.88; H, 3.56.

Preparation of Tetrakis-(2-aminoethanoethiol)dinickel(II) Thiocyanate

A similar procedure was used in the preparation of $[\text{Hg}[\text{Ni}(\text{MEA})_2]_2]\text{Cl}_2$. Calc. for $\text{Hg}[\text{Ni}(\text{SCH}_2\text{CH}_2\text{NH}_2)_2]_2(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$: C, 15.58; H, 3.6; N, 10.90. Found: C, 15.34; H, 2.92; N, 10.66.

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