The Effect of NNS Type Ligands on the Stereochemistry and Electronic Properties of Nickel(II) Complexes

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A series of complexes of the general stoichiometry of $(NiLX)_n$ have been prepared where L is NH_2-$(CH_2)_nNH(CH_2)_2S$ and n is 2, 3, 4 and X is a chloride or $B(C_6H_5)_4$. All the complexes in which the anion is a chloride are diamagnetic, while the $B(C_6H_5)_4$ complexes have magnetic moments varying from 1.07 BM to 1.29 BM. These complexes containing the tetraphenylborate counteranion adhere to the Curie–Weiss law from 300 K–77 K. In solution most of these complexes appear to be dimers. However, in the solid form the $NiLB(C_6H_5)_4$ complexes appear to be more polymeric. Based on spectral and magnetic data these complexes appear to have both square planar diamagnetic sites and paramagnetic sites in which the nickel(II) has a coordination number greater than four.

Introduction

There has been little systematic research on how the stereochemistry, and electronic properties of metal complexes are affected by varying the nature and position of certain donor atoms within a given polydentate ligand [1]. For example, there is no systematic study available of metal complexes containing tetradentate ligands that have two nitrogens and two sulfur donors in which the number and the position of these donors are varied, (NH_2CH_2-$CH_2SCH_2CH_2SCH_2CH_2NH_2$ (NSSN), $NH_2CH_2CH_2$-$SCH_2CH_2NHCH_2CH_2SH$ (NSNS), $HSCH_2CH_2NH$-$CH_2CH_2NHCH_2CH_2SH$ (SNNS), $HSCH_2CH_2SCH_2$-$CH_2NHCH_2CH_2NH_2$ (SSNN), *etc*). Nevertheless, complexes containing many of these ligands have been prepared and characterized [1–3]. We have initiated such an systematic investigation by studying nickel(II) complexes containing saturated tridentate ligands with only nitrogen (amines) and sulfur (mercapto or thioether groups) donor atoms. Tridentate ligands are the smallest polydentate in which one can vary both the number and position of the donor atoms. Also, since nickel(II) complexes can be found in many different types of geometries, a study of nickel(II) complexes containing mixed donor triden-

tate ligands is an obvious place to initiate such an investigation.

Presently, it is known that nickel(II) complexes of both diethylenetriamine (NNN) and bis(2-aminoethyl)sulfide (NSN) [4, 5] are paramagnetic and the coordination number of the nickel(II) is six. The general formulas of these complexes are $Ni(NNN)_2^{+2}$ or $Ni(NSN)_2^{+2}$. Thus it appears that a tridentate ligand with two terminal primary amines groups and either a nitrogen or sulfur in the central position will function as a relatively weak field ligand [4] (in fact the thioether group on the NSN ligand may be so weak that it has been recently suggested that this group may not even be bonded to the nickel(II) [5]). In contrast, tridentate ligands containing two mercapto groups in the terminal positions and either a nitrogen or sulfur in the central position will function as strong field ligands toward nickel(II) producing square planar diamagnetic, dimeric complexes [6–9]. Examples of tridentate ligands which can cause nickel(II) to have such a square planar environment include 2,2′-dimercaptodiethyl sulfide (SSS), 2,2′-dimercaptodiethylmethylamine (SCH_3NS) and 2,2′-dimercaptodiethylamine (SNS). The general formula for complexes of this type is $Ni_2(SXS)_2$ [6–9].
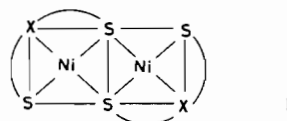
In summary, the two terminal groups (the primary amines or mercapto groups) are more influential in determining both the stereochemistry and electronic properties of the nickel(II) than is the nature of the central donor atom in the above saturated tridentate ligands. Also the degree of oligomer formation appears to be a function of the nature of the terminal donor groups in these tridentate ligands. In order to have oligomer formation a terminal mercapto group is required [2, 10, 11]. It has already been reported that saturated SSS type ligands can coordinate to various metal ions resulting in dimeric and trimeric complexes [12]. We would like to report

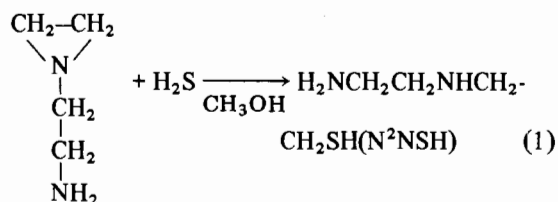TABLE I. Conductance Data for Nickel(II) Complexes of 2-(n-amino$(CH_2)_n$)-aminoethanethiol.

Complex	Solvent	Λ^a	Onsager slope
$[Ni(N^2NS)Cl \cdot \frac{1}{2}CH_3OH]_n$	CH_3OH	134	533
$[Ni(N^2NS)B(C_6H_5)_4]_n$	CH_3NO_2	141	349
	CH_3CN	256	608
	$(CH_3)_2CO$	203	691
$[Ni(N^3NS)(B(C_6H_5)_4)H_2O]_n$	CH_3NO_2	160	268
	CH_3CN	273	544
	$(CH_3)_2CO$	231	–

[a]Values at 10^{-3} molar concentration. Assumed all complexes were dimers.   [b]Slope of the plot $(\Lambda_o - \Lambda_e)$ vs. $\sqrt{c}$ where Λ_o is the y-intercept of the plot of Λ_e vs. $\sqrt{c_e}$ and Λ_e is the equivalent conductance.
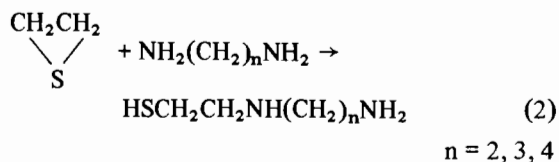
the results of our studies on nickel(II) complexes containing a series of tridentate ligands with a weak field functional group at one end of the ligand (the primary amine), and one strong field group at the other end of the ligand (the mercapto group). Our initial goals were to prepare nickel(II) complexes having unusual stereochemistry and electronic properties. We were also interested in determining how a polydentate ligand containing a terminal mercapto and weak field donor atoms can affect the degree of oligomerization.

Results

The 2-(2-aminoethyl)aminoethanethiol (N^2NS) was prepared by two methods. The method providing the best yield (~70%) involved the cleavage of an aziridine ring in N-(2-aminoethyl)-aziridine by hydrogen sulfide at low temperature [13].

$$
\begin{array}{c}
CH_2\text{--}CH_2 \\
\diagdown N \diagup \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
NH_2
\end{array}
+ H_2S \xrightarrow{\ CH_3OH\ } H_2NCH_2CH_2NHCH_2\text{-} \\
CH_2SH(N^2NSH) \qquad (1)
$$

The second method involved the ring cleavage of ethylenesulfide by ethylenediamine (yields 25%) [14].

$$
\begin{array}{c}
CH_2CH_2 \\
\diagdown \diagup \\
S
\end{array}
+ NH_2(CH_2)_nNH_2 \rightarrow \\
HSCH_2CH_2NH(CH_2)_nNH_2 \qquad (2) \\
n = 2, 3, 4
$$

Method 2 was employed to prepare 2-(3-aminopropyl)aminoethanethiol (N^3NS). A large excess of

diamine was required in Method 2 and the reaction was carried out in a dilute solution in order to prevent polymerization. Because of the high reactivity of ethylenesulfide, the reaction was carried out under a dry, oxygen free environment. These ligands were characterized by chemical analysis and infrared spectra.

Two nickel(II) compounds were isolated from $NiCl_2 \cdot 6H_2O$ and N^2NSH in methanol; a black crystalline compound $[Ni(N^2NS)Cl \cdot \frac{1}{2}CH_3OH]_n$ and a light brown powder $[(Ni(N^2NS)Cl]_n$. The pink powdery $[Ni(N^2NS)B(C_6H_5)_4]_n$ was prepared by the reaction of $NaB(C_6H_5)_4$ and $[Ni(N^2NS)Cl \cdot \frac{1}{2}CH_3OH]_n$ in H_2O. Also the pink powder $[Ni(N^3-NS)B(C_6H_5)_4 \cdot H_2O]_n$ was isolated by reacting $NiCl_2 \cdot 6H_2O$, and N^3NSH in a one to one mol ratio and then adding $NaB(C_6H_5)_4$ to this mixture. However, a similar reaction employing $NiCl_2 \cdot 6H_2O$ and N^4NSH with $NaB(C_6H_5)_4$ resulted in the isolation of a complex mixture. While all the compounds isolated with the tetraphenylborate anion were pink, all the other complexes had colors between black or reddish black and brown. All the complexes prepared in this study are stable in air and were not hydroscopic.

Solubilities of the complexes were varied. The reddish brown solid $[Ni(N^2NS)Cl \cdot \frac{1}{2}CH_3OH]_n$, was fairly soluble in methanol, hot ethanol and water. However, the brown powder $[Ni(N^2NS)Cl]_n$ was found to be only soluble in water. $[Ni(N^{2\,or\,3}NS)(B(C_6H_5)_4)]_n$ complexes were found to be very soluble in nitromethane, acetone, and acetonitrile. However, the tetraphenylboron complexes were not soluble in water and only slightly soluble in methanol. These solubility observations are easily explained by the organic nature of the large anion. All complexes soluble in water will decompose in water within an hour after the solids were dissolved. In all solvents except pyridine, the solid dissolved to give red solutions. All the above complexes were also slightly soluble in pyridine; however, a color change from red to yellow was noted as a

TABLE II. Magnetic Data for Nickel(II) Complexes of 2-(n-amino(CH$_2$)$_n$)aminoethanethiol.

Complex	Solvent[a]	μ_{eff}.	T K
[Ni(N^{2}NS)Cl·½CH$_3$OH]$_n$	Solid	0.37	299
[Ni(N^{2}NS)Cl]$_n$	Solid	0.52	297
[[Ni(N^{2}NS)] [B(C$_6$H$_5$)$_4$]]$_n$	C$_5$H$_5$N	1.10	306
	Solid	1.07	298
[[Ni(N^{3}NS)] B(C$_6$H$_5$)$_4$]$_2$·H$_2$O]$_n$	C$_5$H$_5$N	1.90	293
	Solid	1.29	293

[a]NMR solution moments were taken in 3% t-butyl alcohol.

TABLE III. Electronic Spectral Data for Nickel(II) Complexes of (2-(n-aminoalkyl)aminoethanethiol.

Complex–Solvent	ν_{max}, cm^{-1}	ϵ, l/mol cm
[Ni$_2$(N^{2}NS)$_2$]Cl$_2$·CH$_3$OH		
CH$_3$OH	19,800	593
	28,200	1510
	32,900	5290
H$_2$O	19,800	338
diffuse transmittance	11,200	15.7
	20,410	
	28,000	
Ni$_2$(N^{2}NS)$_2$Cl$_2$		
H$_2$O	20,330	75
	36,620	870
	41,152	1070
diffuse transmittance	19,410	
[Ni$_2$(N^{2}NS)$_2$] [B(C$_6$H$_5$)$_4$]$_2$		
CH$_3$NO$_2$	19,400	250
C$_5$H$_5$N	10,400	14.4
	17,600	48.5
	22,500	690
diffuse transmittance	21,265	
[Ni$_2$(N^{3}NS)$_2$] [B(C$_6$H$_5$)$_4$]$_2$·2H$_2$O		
(CH$_3$)$_2$CO	19,590	10460
	27,701	2156
C$_5$H$_5$N	10,800	6.27
	17,600	35
	24,100	172
CH$_3$NO$_2$	19,305	286.2
	26,667	715.4
diffuse transmittance	19,600	

methanol solution of this salt was diluted with pyridine.

The infrared spectra of all the above complexes show no SH stretching frequency around 2500 cm^{-1} which was present in the free ligands thereby indicating the loss of the proton during coordination. The N–H stretching frequencies are at somewhat lower energies than was observed for the free ligand.

TABLE IV. Temperature Dependent Magnetic Data of $[(\text{Ni}_2\text{-}(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{S})_2]\text{B}[(\text{C}_6\text{H}_5)_4]_2\cdot2\text{H}_2\text{O}$.

T [K]	χ_M [1×10^{-6} cqs units]	μ_{eff} [BM]
77	2819	1.32
93	2288	1.31
121	1732	1.30
170	1218	1.29
300	668	1.27

Fig. 1. A plot of $1/\chi_m$ versus T for $[\text{Ni}(\text{N}^3\text{NS})(\text{B}(\text{C}_6\text{H}_5)_4)]_2$.

Such data suggest that both the mercapto group and the amine groups are coordinated [5].

The molar conductivities (Table I) do not distinguish between [ML] [X], a 1:1 electrolyte and $[\text{M}_n\text{L}_n]\text{X}_n$, a n:1 electrolyte. However, Onsager slopes are more valuable in distinguishing true electrolyte types [15]. In methanol, the Onsager slope for $[\text{Ni}(\text{N}^2\text{NS})\text{Cl}\cdot\text{CH}_3\text{OH}]_n$ is suggestive of a two to one electrolyte (533) (Table I) (Onsager slopes for 1 to 1 electrolytes in methanol were found to be around 250 and for 2 to 1 electrolytes around 515) [15, 16]. Also, based on Onsager slopes in $\text{CH}_3\text{-CN}$ it appears that $[\text{Ni}(\text{N}^2\text{NS})(\text{B}(\text{C}_6\text{H}_5)_4)]_n$ and the $[\text{Ni}(\text{N}^3\text{NS})(\text{B}(\text{C}_6\text{H}_5)_4]_n$ approach a two to one electrolyte. Therefore we conclude that these compounds might be dimeric in these solvents (I). However $(\text{Ni}[\text{N}^2\text{NS}]) [\text{B}(\text{C}_6\text{H}_5)_4])_n$ and $([\text{Ni}(\text{N}^3\text{NS})]\text{-}[\text{B}(\text{C}_6\text{H}_5)_4])_n$ in CH_3NO_2 have Onsager slopes between a one to one electrolyte and a two to one electrolyte (Onsager slopes for 1 to 1 electrolytes in CH_3CN and CH_3NO_2 are approximately 340 and 200 respectively and for 2 to 1 electrolytes the values are approximately 750 and 450) [15–17].

The diffuse transmittance spectra of these complexes at room temperature indicate that the nickel-(II) ion is in a square planar environment (Table III). Similar spectra were observed in weakly coordinating solvents such as CH_3OH, CH_3NO_2, $(\text{CH}_3)_2\text{CO}$ (Table III). However, in strongly coordinating solvents such as pyridine or water, a weak intensity band in the near infrared region was observed along with the more intense band in the visible region. Bands in the near infrared region of the electronic spectrum having low values are usually attributed to nickel(II) in a six coordinate environment while the bands in the visible region, 19.000 cm^{-1}–22.000 cm^{-1} having higher values are indicative of square planar nickel(II) [18]. A diffuse transmittance spectrum of $[\text{Ni}(\text{N}^3\text{NS})\text{B}(\text{C}_6\text{H}_5)_4]_n$ at 77° was taken and a broad weak band was observed at 900 mu suggesting that some of the nickel ions had a coordination number greater than four.

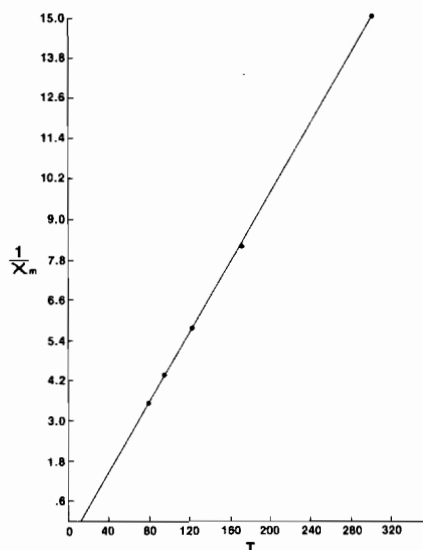The magnetic moments of the solid $[\text{Ni}(\text{N}^2\text{NS})\text{Cl}\cdot\frac{1}{2}\text{CH}_3\text{OH}]_n$ is essentially diamagnetic suggesting that the nickel(II) ions in these complexes are in square planar environments (Table II). The nickel(II) complexes containing the tetraphenylboron anion had magnetic moments between 1.07 and 1.30 BM in the solid state (Table II). Such magnetic moments for nickel(II) are considered anomalous [19]. The magnetic moment did not vary significantly between 77 K and 300 K for the complex $[\text{Ni}(\text{N}^3\text{NS})\text{B}(\text{C}_6\text{H}_5)_4]_n$ in the solid state, however, in acetone this magnetic data did not follow the Curie–Weiss Law (Table IV).

Discussion

Based on most the spectral and magnetic evidence it appears that a linear tridentate ligand containing only one terminal mercapto group and two amine groups is a strong enough ligand to cause most of the resulting nickel(II) complexes to be square planar in the solid state. Therefore it is likely that the stereochemistry around the nickel(II) ion is square planar. Other nickel(II) complexes containing ligands with two nitrogens and a terminal sulfur as donor atoms gave similar results. For example Vance, Warner and Seff observed that 2-(pyridylethyl)aminoethylthiolo ligand formed binuclear square planar complexes with nickel(II) [20]. Sacconi and Speroni [21] prepared monomeric diamagnetic square planar nickel(II) complexes by also employing an NNS type ligand (II).
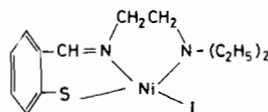
However, both sets of researchers employed stronger field nitrogen ligands such as a pyridine nitrogen or imine nitrogen, than the amine nitrogens employed in this research (a terminal thioether group in contrast to a terminal mercapto group must be a relatively weak field ligand as evidenced by the fact that the nickel(II) complexes containing the Schiff base derived from *o*-methylthiobenzaldehyde and N,N-diethylethylenediamine are 5 coordinated in the solid state [21]).

Although the $Ni(N^2NS)Cl$ appears to be diamagnetic, the magnetic data for the $Ni(N^n-NS)B(C_6H_5)_4$ complexes in the solid state are anomalous. The magnetic moments observed for the complexes are between 1.07 and 1.29 BM. Since it is not likely that $B(C_6H_5)_4^-$ is a stronger coordinating group than Cl^-, these magnetic moments cannot be explained by assuming that $B(C_6H_5)_4^-$ is coordinating to the nickel(II). The magnetic moment for $Ni(N^3NS)B(C_6H_5)_4$ in the solid state (Fig. 1) is relatively constant over a 200 K temperature range.

The above data argues in favor of the coexistence of two different types of stereochemistries for the nickel ions either within the unit cell or within the complexes. Should these anomalous magnetic moments been due to antiferromagnetic interactions, a flattened tetrahedral geometry, a spin equilibrium or direct nickel to nickel bonding, the μ_{eff} would vary with temperature [19]. However, since the magnetic data fits the Curie–Weiss law, this suggests the coexistence of high and low spin nickel(II) in a constant ratio of approximately one paramagnetic nickel(II) per six nickel(II) ions over the entire experimental temperature range. These paramagnetic nickel(II) ions are likely to have a coordination number of five or six. The diffuse reflectance spectra showed no bands in the near infrared which would be indicative of six coordinate nickel(II) at room temperature nor is there any spectral evidence for tetrahedral nickel(II). However at 77 K a weak band was observed at 900 mm. This band is characteristic of high spin nickel(II). Therefore both the magnetic data and the low temperature spectral data suggest that $(Ni(N^3NS)B(C_6H_5)_4)_n$ has two different stereochemical nickel(II) sites.

Similar observations were made with the nickel(II) complexes containing the tridentate Schiff ligand -N-salicylidenargine [22]. These complexes also have anomalously low magnetic moments which obey the Curie–Weiss law. It was speculated that a octahedral form coexisted with a square planar form. The electronic spectrum of this complex is similar to the electronic spectrum of $[Ni(N^3NS)B(C_6H_5)_4]_n$. Similar results were also obtained in a series of nickel(II) complexes containing the Schiff bases formed from 5-chloro-2-hydroxybenzophenone and a series of alkanediamines [23].

There are several different ways in which the nickel ions could obtain a coordination number greater than four in these complexes. Direct nickel–nickel bonding is possible. Wei and Dahl [24] showed such bonding in the $[Ni(Ni(NH_2CH_2CH_2S)_2)_2]Cl_2$ complex. However, complexes having a metal to metal bond should not conform to the Curie–Weiss law. Also it is possible that several $Ni_n(N^nNS)_n^{n+}$ units may interact via the bridging sulfurs. Such a structure would require some mercapto groups to be bonded to three nickel(II) ions. Such interactions have been demonstrated for analogous complexes [25, 26].

The basic interacting unit is likely to be a dimer, $Ni_2(N^nNS)_2^{+2}$ based on our conductivity data. One model consistent with the magnetic and electronic spectral data is that a dimer(III) and a tetramer cluster (IV) coexist in a one to one ratio in the unit cell.
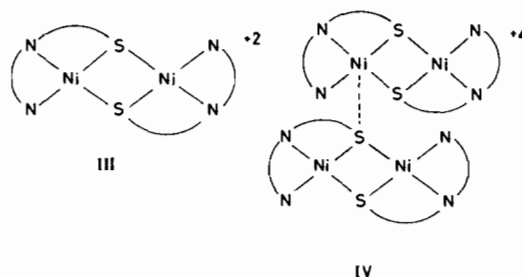
The two nickel(II) ions in structure III are square planar and diamagnetic and three out of the four nickel ions in structure IV would be in a square planar stereochemistry and diamagnetic. Therefore only one nickel ion per six would be paramagnetic.

In relatively polar solvents such as CH_3CN, CH_3NO_2 or CH_3OH, structure IV should break up into the basic $Ni_2(NNS)_2^{+2}$ units. This would explain why the Onsager slopes indicated that these complexes appear to be two to one electrolyte types in CH_3CN and CH_3NO_2. Since $[Ni_2(N^3NS)_2]^{+2}$ and $[Ni_2(N^3NS)_2]_2^{4+}$ exist in a one to one ratio, an equilibrium between these two species should not alter adherence to the Beer–Lambert law. The Beer–Lambert law does hold over a wide concentration range for the complex $[Ni(N^3NS)B(C_6H_5)_4]_n$ in acetone at 513 mμ. However at 360 mμ, the Beer–Lambert Law is adhered to at low concentrations but not at high concentrations. At a concentration of 5×10^{-4} M there is a peak maximum at 360 mn however, upon increasing the concentration of $Ni_2(N^3NS)_2(B(C_6H_5)_4)_2$ to 5×10^{-3} M the peak maximum moves steadily to 376 mμ. Apparently the higher energy band is influenced by solute–solute interactions but the lower energy band is not. A plot of the mol ratio of $[[Ni(N^3NS)]-[B(C_6H_5)_4]]_2$ to pyridine in acetone *versus* the optical density at 19.590 cm^{-1} and 27.701 cm^{-1} gave similar results to those in just acetone. We

therefore conclude that the pyridine does not form an adduct with the metal complexes at low pyridine concentrations.

A possible explanation of why the solid [Ni(N^n-NS)B(C$_6$H$_5$)$_4$]$_x$ complexes are paramagnetic while the solid [Ni(N^{n}NS)]$_y$X$_y$ (X = halide) are essentially diamagnetic may be due to hydrogen bonding in the halide complexes which prevents association of the Ni$_2$(N^{n}NS)$_2^{+2}$ unit. It has been well established that the bridging sulfurs should orient the two planes in Ni$_2$(N^{n}NS)$_2^{+2}$ into a V shape due to the tetrahedral bonding of the bridging sulfurs [12, 27]. This V-shape will partially block one side of the dimer from entrance of another donor. In the dimeric complex Ni$_2$(S(CH$_2$)$_2$S(CH$_2$)$_2$S)$_2$ the two nickel ions are within 2.73 Å of each other [12, 28]. This bond distance is almost within the distance expected for a nickel–nickel bond. Therefore unless the dihedral angle increases, the inside of the V is essentially blocked. If the secondary amine hydrogen is oriented so that this hydrogen is oriented on the outside of the V, the halide can hydrogen bond to hydrogens on both nitrogens and prevent association of the Ni$_2$-(N^{n}NS)$_2^{+2}$ groups.

In conclusion, we know that by varying only the number and positions of the nitrogens and sulfur donors in simple tridentate ligands we can dramatically control the electronic and stereochemical properties of the resulting nickel(II) complexes as well as these complexes' ability to form either oligomers or clusters.

Experimental

Physical Measurements

The equivalent molar conductance measurements were determined using an American Instrument Co., Model 5-2050 conductivity bridge in conjunction with a Beckman conductivity cell. Solvents used for making measurements were water, methanol acetonitrile acetone and nitromethane. The mass susceptibility was determined by the Evans method using a Varian A-60 NMR with coaxial NMR tubes. The solvent was water with 2% t-butyl alcohol as an inert reference or acetone in CD$_3$COCD$_3$. The complex dissolved in solvent was placed in the outer tube and solvent alone was placed in the inner tube. Diamagnetic corrections were made using Pascal's constants. A Perkin Elmer model 337 spectrophotometer was used to record all infrared spectra. The spectra of complexes were obtained in both Nujol mulls and KBr pressed pellets. The spectra were calibrated using standard polystyrene spectra. A Beckman Acta MIV UV–Visible IR spectrophotometer and Beckman DK-2 with 1 cm and 10 cm matched cells were used to obtain visible and near infrared spectra. The visible spectra of solids were

measured in Nujol mulls. The mull was placed on Sharkskin filter paper in the sample beam and a similar piece of filter paper with Nujol was placed in the reference beam. The electronic spectra was taken at 77 K on Cary 14 using Nujol mulls at the University of Toledo.

Syntheses of 2-(2-aminoethyl)aminoethanethiol Via N-(2-aminoethyl)aziridine and Hydrogen Sulfide

The synthesis was achieved by the general ring cleavage reaction given by Rosenthal [13]. Approximately 250 ml of methanol were cooled to isopropyl alcohol–dry ice temperature after which hydrogen sulfide gas from a compressed gas tank was bubbled through the solution. After several minutes the flask was weighed and it was determined that 11.5 grams (0.337 mol) of hydrogen sulfide gas had been dissolved. To this solution was added 18.8 grams (0.218 mol) of N-(2-aminoethyl)aziridine drop by drop over a five minute period with vigorous stirring. Stirring was continued for one hour at the lowered temperature. The reaction mixture was then brought to room temperature over a period of approximately one hour. The solvent was removed at room temperature by vacuum distillation at 6–10 mm Hg. The product was collected at 40–50 °C/6 mm Hg and 21 grams (80 per cent yield) were obtained.

Synthesis of 2-(Y)aminoethanethiol, where Y = 2-Aminoethyl and 3-Aminopropyl and 4-Aminobutyl

One mol of diamine in 250 ml of benzene was refluxed in a 3-neck, 500 ml flask fitted with a stirrer, Dean-Stark trap, condenser, and a pressure equalizing addition funnel through which nitrogen was introduced. The solution was refluxed with stirring for two hours to azeotropically remove any water. The water which collects in the Dean-Stark trap should be removed before continuing. Following the two hour reflux 0.124 mol of ethylenesulfide in 150 ml of benzene were added drop by drop through the addition funnel over a 1.25 hour period while the refluxing and stirring were continued. The reflux was continued for a two-hour period following the completion of the addition of ethylenesulfide. After cooling the solvent was removed by vacuum distillation and the products collected by vacuum distillation.

Synthesis of Bis(2-(2-aminoethyl)aminoethanethiolo)-dinickel(II) Chloride [Ni$_2$(NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$-S)$_2$] Cl$_2$·CH$_3$OH and Ni$_2$[NCH$_2$CH$_2$NHCH$_2$CH$_2$S]$_2$-Cl$_2$

To a solution of 2.886 grams (2.41 × 10^{-2} mol) of 2-(2-aminoethyl)aminoethanethiol dissolved in fifty ml of methanol was added a solution of 6.60 grams (2.41 × 10^{-2} mol) nickel(II) chloride hexahydrate dissolved in 200 ml of hot methanol. The ligand solution became deep red on the addition of

the metal salt. The mixture was stirred for ten minutes and was placed in a refrigerator for one hour. After this period a solid product was observed. The solution was filtered, yielding a fine brown powder which was recrystallized from a 1:1:1 mixture of butanol, ethanol and methanol and dried, *in vacuo* over P_2O_5. *Anal.* calcd. $[Ni_2(NH_2CH_2CH_2NHCH_2\text{-}CH_2S)_2]Cl_2$: N, 13.13; C, 22.52; H, 5.20; Cl, 16.62. Found: N, 13.31; C, 22.45; H, 5.44; Cl, 18.88. Immediately after the first filtration the filtrate was returned to the refrigerator. After several hours, further precipitation was noticed. The solution was again filtered through a medium fritted glass funnel and a dark black crystalline precipitate was obtained. The crystals were recrystallized employing a mixed solvent method with methanol and benzene and a dark reddish-brown powder was obtained. *Anal.* calcd. for $[Ni_2(NH_2CH_2CH_2NHCH_2CH_2S)_2]Cl_2 \cdot CH_3OH$: N 12.21; C, 23.56; H, 5.71. Found: N, 12.18; C, 23.21; H, 5.75.

Synthesis of Bis[2-(2-aminoethyl)aminoethanethiolo] dinickel(II) Tetraphenylboron, $[Ni_2(NH_2CH_2CH_2\text{-}NHCH_2CH_2S)_2][B(C_6H_5)_4]_2$

One hundred sixteen milligrams of *bis*[2-(2-aminoethyl)aminoethanethiolo] dinickel(II) chloride was dissolved in ten ml of water, giving a deep red solution. To this solution was added, drop by drop, and with stirring, a saturated, aqueous solution of sodium tetraphenylboron. The resulting pale pink, water insoluble precipitate was vacuum filtered, washed several times with water and dried *in vacuo* over P_2O_5. *Anal.* calcd. for $[Ni_2(NH_2CH_2CH_2NHCH_2\text{-}CH_2S)_2][B(C_6H_5)_4]_2$: N, 5.64; C, 67.65; H, 6.29. Found: N, 5.79; C, 57.84; H, 6.53.

Synthesis of Bis(2-(3-aminopropyl)aminoethanethiolo)dinickel(II) Tetraphenylboron, $[Ni_2(NH_2CH_2\text{-}CH_2CH_2NHCH_2CH_2S)_2][B(C_6H_5)_4]_2 \cdot 2H_2O$

To a solution of 3.30 grams (0.0139 mol) of nickel(II) chloride hexahydrate in 100 ml of water was added 1.865 grams (0.0139 mol) of 2-(3-aminopropyl)aminoethanolthiol. The solution was stirred for 10 minutes and filtered. To the filtrate was added a saturated aqueous solution of sodium tetraphenylboron. A pink precipitate was obtained and was dried *in vacuo* and P_2O_5. *Anal.* calcd.: $[Ni_2\text{-}(NH_2CH_2CH_2CH_2NHCH_2CH_2S)_2]]B(C_6H_5)_4]_2 \cdot 2H_2O$: C, 65.82; H, 6.67; N, 5.29. Found: C, 65.69; H, 6.74; N, 5.13.

Acknowledgements

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