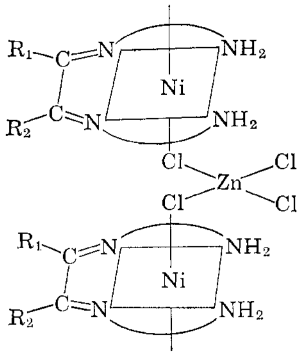
may be used to calculate the ligand field strength of the axial groups (Dq^z) by the relation[22–26]

$$Dq^z = (2\nu_1 - 10Dq^{xy})/10$$

The spectra appear to be consistent with the above model. The transition to $^3B_{2g}$ is essentially constant as would be predicted if the complexes have the same structure in solution as in the solid state. A value of 1228 (average of all ν_2 bands) is quite reasonable for Dq^{xy} since tris(ethylenediamine)nickel(II) and tris-(1,10-phenanthroline)nickel(II) have Dq values of 1120 and 1270, respectively.[28] Values of Dq^z for $ZnCl_4^{2-}$ and NCS^- in these complexes have been calculated using the equation given above. A Dq^z value of 220 for $ZnCl_4^{2-}$ was found. This very low Dq value is not too surprising in view of the fact that the chlorides are serving as bridges



The Dq^z value for NCS^- of 920 is in good agreement with Dq^z values for NCS^- obtained with other in-plane ligands containing similar nitrogen donors.[25]

Acknowledgment.—This investigation was supported in part by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences. The assistance of Mr. Ron Lewis in this investigation is gratefully acknowledged.

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Complexes Derived from Strong-Field Ligands. XXI. Nickel(II) Complexes of N-Substituted β-Mercaptoethylamines

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Received August 30, 1967

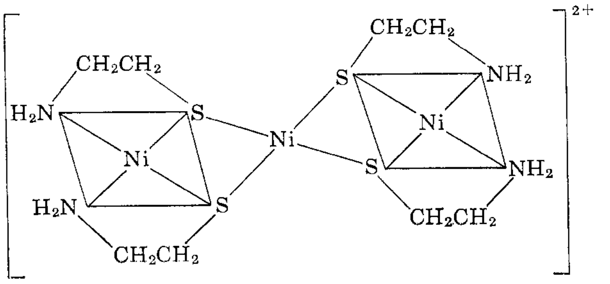
The nickel(II) complexes of ten N- and N,N-disubstituted β-mercaptoethylamines have been prepared and characterized. All are strong-field ligands, producing low-spin, four-coordinate nickel(II). Four classes of complex have been found, and the species produced in a given system is dependent on steric considerations and the reaction conditions. All ligands studied except N,N-diethyl-β-mercaptoethylamine and N-*t*-butyl-β-mercaptoethylamine form the monomeric *trans*-planar complexes NiL_2. The latter two ligands bind through sulfur alone, forming diamagnetic planar complexes that exist as insoluble polymers. Ligands of limited steric requirements form the trinuclear, sulfur-bridged cations $Ni[NiL_2]_2^{2+}$. Highly hindered ligands can form only the dimers $Ni_2L_2X_2$.

Introduction

β-Mercaptoethylamine (MEA) forms two classes of complexes with nickel(II)—planar, diamagnetic $Ni(MEA)_2$ and the trinuclear complex $Ni[Ni(MEA)_2]_2^{2+}$ which also contains only diamagnetic nickel(II) (structure I).[1] A crystal structure[2] shows the presence of three planar nickel(II) atoms, held in the trinuclear ion by sulfur bridges. The trinuclear complex has been prepared by reaction of bis(β-mercaptoethylamine)-nickel(II)

$$2Ni(MEA)_2 + Ni^{2+} \longrightarrow Ni[Ni(MEA)_2]_2^{2+} \qquad (1)$$

Similar complexes containing various other metal ions in the center metal ion site have been prepared[3] by the reaction of $Ni(MEA)_2$ with different metal salts, *i.e.*, $M[Ni(MEA)_2]_2^{n+}$, where $M^{n+} = Cu^+$, Cu^{2+}, Pd^{2+}, Pt^{2+}, and Cd^{2+}. Bis(β-mercaptoethylamine)-palladium(II) reacts in an analogous fashion and $Ni[Pd(MEA)_2]_2^{2+}$ has been prepared. Related bridged complexes are formed by tris(β-mercaptoethylamine)-cobalt(III),[4] but in this case triple bridges are formed, producing sulfur-bonded octahedral nickel(II) in $Ni[Co(MEA)_3]_2^{2+}$.



I

Bis(β-mercaptoethylamine)nickel(II) has only very limited solubility in polar solvents, and its structure

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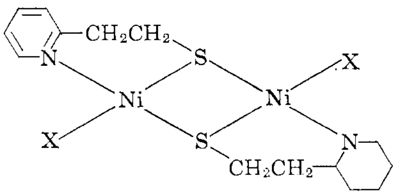
(1) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

(2) L. Dahl, paper presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(3) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 878 (1962).

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

and reactions have not been studied extensively, despite a substantial interest in the complexes of sulfur donors and their chemistries. The presence of substituents on the nitrogen atoms was expected to produce compounds of more tractable properties. Earlier studies[4] led to the characterization of three kinds of nickel(II) complexes with 2-(2-mercaptoethyl)pyridine. In addition to the monomeric and trinuclear complexes, a dimer[5,6] $Ni_2L_2X_2$ was characterized and assigned structure II.



II

Uhlig and Heinrich[6] also reported the synthesis of dinitratobis(2-(2-mercaptoethyl)pyridine)nickel(II) which contains a neutral, protonated ligand.

Dichlorobis(N,N-diethyl-β-mercaptoethylamine)dinickel(II) has been reported.[7,8] A structure analogous to II has been assumed.

The present investigation has involved the synthesis and characterization of the nickel(II) complexes of a broad range of N-substituted β-mercaptoethylamines. The ligands used and a useful system of abbreviations are summarized in Table I. The stoichiometries and structures of the complexes formed depend on the steric and electronic properties of the ligand and, to some extent, on the reaction conditions. The ligands studied offer a wide variation in their steric requirements and include both secondary and tertiary amines.

TABLE I

FORMULAS AND ABBREVIATIONS FOR LIGANDS

Formula	Abbreviation	Formula	Abbreviation
$H_2NCH_2CH_2S^-$	MEA	$n\text{-}C_6H_{13}NHCH_2CH_2S^-$	HxL
$(CH_3)_2NCH_2CH_2S^-$	Me_2L	$n\text{-}C_8H_{17}NHCH_2CH_2S^-$	OcL
$(C_2H_5)_2NCH_2CH_2S^-$	Et_2L	$n\text{-}C_{10}H_{21}NHCH_2CH_2S^-$	DcL
$n\text{-}C_3H_7NHCH_2CH_2S^-$	n-PrL	$C_6H_5CH_2NHCH_2CH_2S^-$	BzL
$i\text{-}C_3H_7NHCH_2CH_2S^-$	i-PrL	$C_6H_5CH_2CH_2NHCH_2CH_2S^-$	PeL
$t\text{-}C_4H_9NHCH_2CH_2S^-$	BuL		

Results and Discussion

Each of the ligands studied forms a neutral bis(N-substituted β-mercaptoethylamine) complex with nickel(II). By their physical appearances these complexes can be separated into three classifications and an attempt has been made to determine what electronic and structural properties are responsible for the marked differences among the classes. Two of the nickel(II) complexes, $[Ni(Et_2L)_2]$ and $[Ni(BuL)_2]$, are brown powders which are only very slightly soluble in halocarbons or dimethyl sulfoxide and virtually insoluble in water, alcohols, and hydrocarbons. Six of the bis(mercaptoamine) complexes are isolated as green solids, $[Ni(n\text{-}PrL)_2]$, $[Ni(HxL)_2]$, $[Ni(OcL)_2]$, $[Ni(DcL)_2]$, $[Ni(BzL)_2]$, and $[Ni(PeL)_2]$. None of these complexes is nicely crystalline, and, as the length of the alkyl substituent increases, the solids become more talc-like in nature. This may be attributed to the difficulty of packing the long hydrocarbon chains into a lattice. The green complexes are soluble in halocarbons, slightly soluble in benzene, and only sparingly soluble in water for the shorter N-alkyl substituents. The two remaining bis(mercaptoamine) complexes with nickel(II), $[Ni(Me_2L)_2]$ and $[Ni(i\text{-}PrL)_2]$, are maroon crystalline solids which have appreciable solubility in both polar and nonpolar solvents. It is emphasized that the classification of these complexes is not submitted as evidence of a difference in electronic or molecular structure; however, the apparent distinction leads one to study the chemical and physical properties more closely.

The magnetic susceptibilities of all the bis(N-substituted β-mercaptoethylamine)nickel(II) complexes are either negative or small. The higher susceptibilities observed give magnetic moments of about 0.6 BM, a value in the range often observed for spin-paired ions.[9] For the d^8 electronic configuration of nickel(II), diamagnetism commonly means that the metal ion is four-coordinate with the strong donor atoms situated approximately at the corners of a square plane. The mercaptide ion acts as a strong-field ligand in virtually all of its complexes. In fact, even when bridging between two metal ions, it often stabilizes the spin-paired configuration in both of those metal ions. This is well illustrated by the diamagnetism of the polymeric simple mercaptides of nickel(II).[10] Indeed, mercaptide sulfur atoms in transition metal complexes usually occur as bridges between metal ions, and the metal ions are usually in their spin-paired configurations. The presence of another moderately strong ligand appears to be the most general way of producing an unbridged, coordinated mercaptide ion. In the case of the mercaptoethylamines, the amine nitrogen generally coordinates in preference to the coordinated mercaptide. When the steric requirements of the amine end of the mercaptoethylamine ligand are increased, it might be expected that formation of a nitrogen–metal bond will become less favorable as has been found in complexes of N-substituted ethylenediamines.[11-17]

The molecular weights of all of the bis(N-substituted β-mercaptoethylamine)nickel(II) complexes have been measured except for the brown $[Ni(BuL)_2]$ and $[Ni(Et_2L)_2]$ which are only very slightly soluble in any

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

[6] E. Uhlig and G. Heinrich, *Z. Anorg. Allgem. Chem.*, **330**, 40 (1964).

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[8] C. A. Root, M.S. Thesis, The Ohio State University, 1962.

[9] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 147.

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[11] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952).

[12] H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).

[13] D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

[14] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

[15] D. M. L. Goodgame and L. M. Venanzi, *ibid.*, 5909 (1963).

[16] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

[17] D. W. Meek, *ibid.*, **4**, 250 (1965).

media, Table II. The green and maroon complexes give values close to the theoretical value for [Ni(ligand)$_2$]. This is strong evidence that both the nitrogen and the sulfur atoms on the ligand are coordinated and that sulfur bridging does not occur. It is interesting that, in the series of green complexes with unbranched N substituents, there is no gross alteration in the properties of the bis complexes as the alkyl substituent is varied in length. From this it is concluded that increasing the steric requirements without increasing the bulk in the immediate vicinity of the coordinated nitrogen does not alter the manner of chelation to the metal ion.

TABLE II
MOLECULAR WEIGHT DATA FOR THE BIS(N-SUBSTITUTED β-MERCAPTOETHYLAMINE)NICKEL(II) COMPLEXES

Compound[a]	Theory	Found	Solvent
[Ni(Me$_2$L)$_2$]	267	288	$C_2H_4Cl_2$
[Ni(*i*-PrL)$_2$]	295	272	$CHCl_3$
[Ni(*n*-PrL)$_2$]	295	305	$CHCl_3$
[Ni(OcL)$_2$]	435	390	$CHCl_3$
[Ni(DcL)$_2$]	491	485	$CHCl_3$
[Ni(BzL)$_2$]	391	409	$CHCl_3$

[a] Ligand abbreviations are listed in Table I.

The electronic spectra of the bis(N-substituted β-mercaptoethylamine)nickel(II) complexes confirm the assignment of square-planar structures for the whole series. The spectra consist of two weak bands in the visible region, having extinction coefficients of 32–48 and about 150 l. mole^{-1} cm^{-1}, and very intense bands in the near-ultraviolet region. There are no absorption bands at wavelengths longer than about 700 mμ in the spectra of the complexes. Thus, five-coordinate structures are ruled out.[18,19] The spectral bands (absorption maxima in kK) are: [Ni(MEA)$_2$], refl: 16.4, 21.4, 26.6. [Ni(Me$_2$L)$_2$], refl: 14.2, 20.2, 26.7; in H_2O: 14.8 (ϵ 38.4), 19.8 (ϵ 89.4), 30.5 (ϵ 11,700), 42.9 (ϵ 9240); in $CHCl_3$: 14.0 (ϵ 38.5), 20.0 (ϵ 104), 29.2 (ϵ 14,200), 42.4 (ϵ 12,800); in C_6H_6: 13.9 (ϵ 34.7), 20.1 (ϵ 111), 28.6 (ϵ 12,400), 36.4 (ϵ 3650); in $C_2H_4Cl_2$: 13.9 (ϵ 37.6), 20.0 (ϵ 110), 28.9 (ϵ 13,000). [Ni(*i*-PrL)$_2$], refl: 15.6, 19.9, 26.7; in $C_2H_4Cl_2$: 15.4 (ϵ 48.4), 20.5 (ϵ 244), 31.9 (ϵ 7370). [Ni(*n*-PrL)$_2$], refl: 15.8, 20.6, 26.8; in C_6H_6: 15.3 (ϵ 47.2), 20.8 (ϵ 228); in $C_2H_4Cl_2$: 15.3 (ϵ 40.0), 21.0 (ϵ 135), 30.5 (ϵ 12,500); in CH_3OH: 15.9 (ϵ 42.6), 20.2 (ϵ 235). [Ni(HxL)$_2$], in $C_2H_4Cl_2$: 15.3 (ϵ 41.6), 20.9 (ϵ 152), 30.6 (ϵ 11,500). [Ni(OcL)$_2$], refl: 15.7, 21.0, 28.6; in $C_2H_4Cl_2$: 15.5 (ϵ 32.0), 20.9 (ϵ 139), 30.6 (ϵ 7880). [Ni(DcL)], in $CHCl_3$: 15.6 (ϵ 35.8), 20.9 (ϵ 121), 30.9 (ϵ 10,200), in $C_2H_4Cl_2$: 15.5 (ϵ 36.0), 20.9 (ϵ 159), 30.6 (ϵ 9680). [Ni(BzL)$_2$], refl: 20.8, 26.2, 28.2. [Ni(PeL)$_2$], refl: 15.7, 20.8, 26.6. [Ni(Et$_2$L)$_2$], refl: 18.5, 23.3. [Ni(BuL)$_2$], refl: 18.9.

The brown complexes, [Ni(Et$_2$L)$_2$] and [Ni(BuL)$_2$], show two very broad, intense bands between 18,500 and 23,300 cm^{-1} in their reflectance spectra. Both the green and maroon complexes show two bands attributable to d–d transitions in 1,2-dichloroethane solutions. The low-energy band occurs at 15,300–15,500 cm^{-1} for [Ni(*n*-PrL)$_2$], [Ni(HxL)$_2$], [Ni(OcL)$_2$], and [Ni(DcL)$_2$]. [Ni(BzL)$_2$] and [Ni(PeL)$_2$] are not soluble enough in dichloroethane to permit the measurement of their spectra in this solvent, but in the reflectance spectrum of [Ni(PeL)$_2$] a band is observed at 15,700 cm^{-1}. It must be mentioned that, on standing, solutions of the green bis complexes undergo reaction and gradually become deep red. Therefore the spectral data reported here were obtained from freshly prepared solutions or from solid samples. The maroon complexes also have absorption bands in this region. [Ni(*i*-PrL)$_2$] has a band at 15,400 cm^{-1} in 1,2-dichloroethane solution, and the corresponding band in [Ni(Me$_2$L)$_2$] occurs at lower energy, 13,900 cm^{-1}. This decrease in energy of the first transition is probably a manifestation of the added steric requirements of a coordinated tertiary amine over that of a secondary amine. This effect has been observed by several workers who have studied the relative stability constants and spectra of metal complexes of secondary and tertiary amines.[14-17]

The second d–d band has a molar extinction coefficient 2–3 times larger than the low-energy band in all of the green and maroon complexes. This transition occurs at 20,900–21,000 cm^{-1} for all of the green *n*-alkyl-substituted complexes and at 20,600 and 20,000 cm^{-1} for maroon [Ni(*i*-PrL)$_2$] and [Ni(Me$_2$L)$_2$], respectively. This shift may reflect either a steric or a symmetry difference in the complexes. Although the isopropyl derivative is a secondary amine, its branching provides much more bulk near the metal ion than do the straight-chain substituents.

There is a very intense band ($\epsilon \cong 10{,}000$) in the near-ultraviolet region for all of the bis(N-substituted β-mercaptoethylamine)nickel(II) complexes. This is a charge-transfer band.

The two maroon complexes, [Ni(Me$_2$L)$_2$] and [Ni(*i*-PrL)$_2$], have considerable solubility in both polar and nonpolar solvents. The magnetic and molecular weight data for these compounds lead to the assignment of monomeric, square-planar structures. These two complexes are the only ones in the series which can be obtained in marcrocrystalline form. Upon solution in benzene, there is no change in the visible spectrum of [Ni(Me$_2$L)$_2$], and sufficient solubility is obtained to permit dipole moment measurement. The data for this measurement were not obtained under ideal conditions owing to the necessarily narrow range of concentrations which had to be used. Therefore, the limits of the measurements were estimated and an error treatment was carried out allowing it to be said with certainty that the dipole moment of [Ni(Me$_2$L)$_2$] is less than 3 D. If the complex has the *cis* structure, a moment of 8–9 D is expected on the basis of Jensen's work with the *cis-trans* isomers of d^8 planar metal com-

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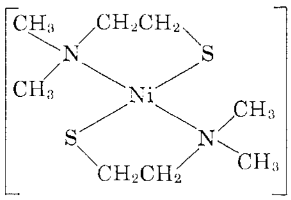
(18) L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964).

(19) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

plexes.[20] On the strength of this measurement, [Ni($Me_2L)_2$] is assigned a *trans*-square-planar structure (III), in benzene solution



III

Amma and Girling[21] have reported a crystal structure for this compound showing it to have structure III in the solid state. Clearly dissolution in various solvents occurs without a gross change in structure.

The lack of major variations in the visible spectrum on going from polar to more nonpolar solvents implies that there is no structural change, such as geometric isomerization, taking place due to changes in solvent polarity. The similarity of the spectrum and physical appearance of [Ni(*i*-PrL$)_2$] suggests that these two maroon complexes have related structures.

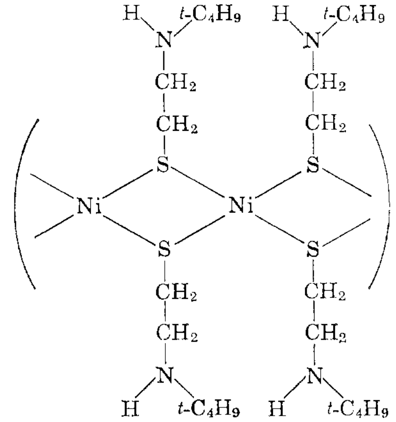
The infrared spectra of the bis(mercaptoamine)-nickel(II) complexes have been recorded from 4000 to 400 cm^{-1} on a high-resolution instrument. The most useful portion of the spectrum is the N–H stretching region. Table III lists the positions of the N–H stretching band for all the secondary amine complexes and two of the free ligands N-*n*-octyl- and N-benzyl-β-mercaptoethylamine. For all of the complexes except [Ni(BuL$)_2$], $\bar{\nu}_{NH}$ occurs between 3085 and 3115 cm^{-1} while the brown insoluble powder has its N–H stretching vibration at 3282 cm^{-1}. The N–H stretching frequencies of the free ligands are in the 3300-cm^{-1} region, the normal value for secondary amines. Svatos, Curran, and Quagliano[22] have observed that, when ethylenediamine coordinates, the N–H stretching frequencies drop more than 100 cm^{-1} from their free amine values. This observation is readily interpreted as the result of electron density being drained toward the metal ion leaving the proton on the coordinated amine less tightly bound to the nitrogen. Similar effects with secondary amines have not previously been reported, but clearly the present case provides a good example.

It is concluded, therefore, that the amine nitrogen is not coordinated in [Ni(BuL$)_2$] and that this insoluble brown powder is a polymer which is linked by sulfur bridges (IV). By analogy, a similar structure is assigned to [Ni($Et_2L)_2$] which is also an insoluble brown powder and has a related electronic spectrum. This structure is undoubtedly favored by the bulk of the substituents on the nitrogens. Recall that the N,N-dimethyl- and N-isopropyl-β-mercaptoethylamines give soluble complexes having molecular weights which correspond to the monomeric unit of two ligands and one metal ion. Attempts to change the synthetic conditions in such a way that the monomeric bis complexes of BuL and Et_2L can be formed have failed.

TABLE III
N–H STRETCHING FREQUENCIES OF BIS(N-SUBSTITUTED β-MERCAPTOETHYLAMINE)NICKEL(II) COMPLEXES AND FREE LIGANDS

Complex[a]	$\bar{\nu}_{NH}$, cm^{-1}	Complex[a]	$\bar{\nu}_{NH}$, cm^{-1}
[Ni(BuL$)_2$]	3282	[Ni(DcL$)_2$]	3090
[Ni(*n*-PrL$)_2$]	3115	[Ni(BzL$)_2$]	3105
[Ni(*i*-PrL$)_2$]	3100	[Ni(PeL$)_2$]	3100
[Ni(HxL$)_2$]	3085	OcLH	3300
[Ni(OcL$)_2$]	3086	BzLH	3322

[a] Ligand abbreviations are listed in Table I.



IV

Conversely, polymeric forms of the other complexes have not been observed.

One other feature of the infrared spectrum of [Ni(BuL$)_2$] is its simplicity compared with the spectra of the chelate complexes. This is compatible with the observation that ethylenediamine has a much simpler spectrum than its chelate complexes. The relative complexity of the spectrum of [Ni($Et_2L)_2$] is associated with the ethyl substituents on the nitrogen atom.

The existence of trinuclear complexes is known for β-mercaptoethylamine[1] and 2-(2-mercaptoethyl)pyridine.[5,6] Several complexes of the N-substituted β-mercaptoethylamines have the stoichiometry of three metal ions, four ligand units, and two anions. The complexes can be prepared by the reaction of a bis(mercaptoamine) complex with an excess of nickel ion. Isolation of the solid salt as the chloride is often difficult owing to its high solubility, and addition of a suitable precipitating anion, such as perchlorate or tetraphenylborate, is advantageous. The molar conductivities of $\{$Ni[Ni(*n*-PrL$)_2]_2\}Br_2$ and $\{$Ni[Ni(*i*-PrL$)_2]_2\}Cl_2$ are 207 and 259 ohm^{-1} cm^2, respectively, in water which correspond roughly to those for di-univalent electrolytes. Complexes have been prepared having three nickel(II) ions in their structure with the ligands Me_2L, *n*-PrL, HxL, and OcL. Attempts to form trinuclear complexes with BuL and Et_2L gave either the bis complexes, which have been shown to be bridged polymers, or a dinuclear complex which is discussed below. This result is undoubtedly related to steric considerations and the relative stability of the bis complex. In the trinuclear complex cation, it is necessary that the ligands be arranged in the

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(20) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **225**, 97 (1935).

(21) R. L. Girling and E. L. Amma, *Inorg. Chem.*, **6**, 2009 (1967).

(22) G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).

cis configuration about the outer two metal ions. This geometric condition permits the bridging of the sulfur atoms to the unique central metal ion, an effect which probably lends stability to the *cis* structure. Such an effect is quite important as the steric requirements of the coordinated amines increase. It is interesting that it is possible to prepare and isolate trinuclear complexes even with the two ligands Me_2L and *i*-PrL which are known to give *trans*-bis complexes. $\{Ni[Ni(i\text{-}PrL)_2]_2\}Cl_2$ forms readily in alcoholic solution, but the reaction of $[Ni(Me_2L)_2]$ with excess nickel(II) ions in anhydrous alcohol gives a dark green solution which probably contains the dinuclear complex described below. Upon the addition of sodium tetraphenylborate, a black precipitate forms which, when filtered and dried *in vacuo* over P_4P_{10} for 24 hr with continuous pumping, gives an analysis corresponding to $\{Ni[Ni(Me_2L)_2]_2\}[B(C_6H_5)_4]_2$. This complex, when well dried, has a magnetic moment of 0.80 BM per nickel ion. The steric strain on the nitrogen-bearing edges of the bis complex units is expected to be very great and is indicated by models. This is clearly a case where the insolubility of a sterically unfavorable complex, which is probably present in solution in only small equilibrium amounts, facilitates the winning of the relatively unstable species. This is believed to be the only planar nickel(II) chelate complex in which two dimethylamino groups occupy adjacent coordination sites.

Two examples of heterometallic trinuclear complexes have been synthesized. They are $\{Pd[Ni(n\text{-}PrL)_2]_2\}(ClO_4)_2$ and $\{Pd[Ni(OcL)_2]_2\}[B(C_6H_5)_4]_2$. They are both red diamagnetic solids in which the center metal ion, coordinated by the four bridging mercaptide ions, is palladium(II). These complexes are prepared by reaction of a solution of K_2PdCl_4 with an aqueous suspension of the appropriate bis(N-substituted β-mercaptoethylamine)nickel(II) complex. This heterogeneous reaction usually results in an intractable product which upon treating with ethanol and the appropriate anion forms solid compounds in good physical form.

When the synthesis of $[Ni(Et_2L)_2]$ or the hypothetical $Ni[Ni(Et_2L)_2]_2^{2+}$ is attempted in basic alcoholic solution, a green product is formed which has the stoichiometry $Ni(Et_2L)Cl$. The molecular weight of this complex corresponds to that of the dimer (theory, 453; found, 406), however, and structure II is assigned.[7,8] The conductivity of this compound in methanol is 122 ohm^{-1} cm^2, corresponding to a uni-univalent electrolyte. This result indicates that partial solvolysis occurs

$$[Ni_2(Et_2L)_2Cl_2] + CH_3OH \longrightarrow [Ni_2(Et_2L)_2Cl(CH_3OH)]^+ + Cl^- \quad (2)$$

A similar dark green dinuclear complex has been prepared with Me_2L by a ligand reaction.[23]

The existence of these complexes is interpreted to be a manifestation of the steric requirements of the tertiary amines in these mercaptoamines. Although the presence of an excess of metal ions facilitates the formation of mercaptide bridges, the *cis* structure required for the formation of trinuclear complexes is much less stable than the structure of the dinuclear complexes which allows for maximum separation of the tertiary amines from each other. The effects of such interligand repulsion are well documented for complexes of N-substituted ethylenediamines.[14-17] Me_2L is the only ligand in the series studied which gives both trinuclear and dinuclear complexes. It is believed that the dinuclear complex in this case is more stable owing to the difficulties already mentioned in the formation of the trinuclear salt.

Experimental Section

Materials.—N,N-Dimethylaminoethanethiol hydrochloride in 95.8% purity and N,N-diethylaminoethanethiol hydrochloride in 97.7% purity were purchased from Evans Chemetics, Inc., and used without further purification. N-*n*-Hexyl-β-mercaptoethylamine was prepared by the method of Reynolds, Fields, and Johnson.[24] N-Benzyl-, N-β-phenethyl-, and N-*n*-decyl-β-mercaptoethylamine were purchased from Aldrich Chemical Co., Inc., and used without further purification. The remaining ligands, N-isopropyl-, N-*n*-propyl-, N-*t*-butyl-, and N-*n*-octyl-β-mercaptoethylamine, were supplied by the Walter Reed Institute for Medical Research. Other reagents and solvents used were of reagent grade.

Molecular Weights.—Molecular weights were determined at 37° with a Mechrolab, Inc., vapor phase osmometer, Model 301A, calibrated with benzil. The concentrations of solutions used were 10^{-3} to 10^{-2} *M*.

Infrared Absorption Spectra.—Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Perkin-Elmer Model 337 infrared spectrophotometer. The samples were either pressed in a potassium bromide pellet or run as a Nujol mull. The spectra were calibrated using the polystyrene absorption bands at 1602 and 907 cm^{-1}.

Exact band positions were obtained for several compounds using a Beckman IR-9 spectrophotometer. Samples were mounted in potassium bromide pellets prepared in a vacuum die. Band positions were read directly from the optical disk on the instrument.

Visible and Ultraviolet Absorption Spectra.—Visible and ultraviolet absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. Solution spectra were run by placing the samples in 1-cm Corex or quartz cells. Reflectance spectra were recorded using the diffuse reflectance accessory, Model 1411. For these spectra, the sample was ground in potassium bromide and compressed into a pellet which was placed over the sample port of the integrating sphere. A block of magnesium carbonate was placed behind the pellet to help hold it in place. Another block of magnesium carbonate was placed over the reference port and used as the standard of reflectance.

Transmittance spectra were obtained from solid samples using a Nujol mull technique similar to that reported by Lee, Griswold, and Kleinberg.[25] The mulls were spread on filter paper and clipped to the end of the sample carriage of the Cary 14 near the detector.

Magnetic Measurements.—Magnetic susceptibilities were measured by the Gouy method. Solid samples were ground and packed in a Gouy tube with the aid of a vibrator and frequent tapping on a hard surface. The tube was calibrated with $Hg[Co(SCN)_4]$ before or after each measurement.

Dipole Moment Measurements.—Dipole moment measurements were made at 30° using benzene as solvent. The necessary

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(23) C. A. Root and D. H. Busch, unpublished results.

(24) D. D. Reynolds, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5126 (1961).

(25) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

data were recorded with a General Radio Co. Type 1610A capacitance-measuring assembly, a Bausch and Lomb Abbe-56 refractometer, and a set of calibrated 25-ml pycnometers. Three solutions of varying concentrations were made. The slopes of graphs of dielectric constant, reciprocal density, and refractive index *vs.* weight fraction of solute were determined by a least-squares treatment of the data. From these slopes, the dipole moment was calculated from

$$\mu_D = M^{1/2}(0.00945\alpha + 0.00024\beta - 0.0287\gamma + 0.00028)^{1/2} \quad (3)$$

after the method of Everard, Hill, and Sutton.[26] In eq 3 μ_D is the dipole moment in Debye units; α, β, and γ are the slopes of the graphs of dielectric constant, reciprocal density, or refractive index *vs.* weight fraction, respectively.

Molar Conductance Measurements.—Molar conductances were determined from resistance measurements made on a Model RC-16 conductivity bridge manufactured by Industrial Instruments, Inc. All measurements were made on solutions on the order of 10^{-3} *M* in solute. Solvents used were methanol and water.

Analyses.—All of the carbon, hydrogen, sulfur, and halogen analyses and some of the nitrogen analyses were performed by Galbraith Microanalytical Laboratories. Most of the nitrogen analyses were performed in this laboratory using a Coleman Model 29 nitrogen analyzer by Drs. Weber, Curry, Karn, and Brubaker and Messrs. Warner and Kovi.

Preparation of Bis(N,N-dimethyl-β-mercaptoethylamine)-nickel(II), $\{Ni[(CH_3)_2NCH_2CH_2S]_2\}$.—A 4.75-g sample of 95.8% N,N-dimethyl-β-mercaptoethylamine hydrochloride (0.032 mole) was dissolved in a solution prepared from 25 ml of water and 25 ml of concentrated ammonium hydroxide. To this was added 3.82 g of nickel(II) chloride hexahydrate (0.016 mole) dissolved in 25 ml of water. The deep red solution was stirred for about 15 min before extracting it with about 100 ml of chloroform. The chloroform solution, when taken to dryness on a rotary evaporator, yielded 3.9 g (91%) of crude product. This was recrystallized by dissolving it in 30 ml of 1,2-dichloroethane, filtering by gravity through paper, and adding 30 ml of *n*-hexane to the filtrate. After standing about 8 hr in the refrigerator, the mixture yielded 1.18 g of maroon needles which were isolated by filtration and dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $\{Ni[(CH_3)_2NCH_2CH_2S]_2\}$: C, 35.98; H, 7.55; N, 10.49; S, 24.01. Found: C, 35.78; H, 7.48; N, 10.42; S, 24.31.

Preparation of Bis(N-isopropyl-β-mercaptoethylamine)nickel-(II), $[Ni(i\text{-}C_3H_7NHCH_2CH_2S)_2]$.—A 1.43-g sample of nickel(II) chloride hexahydrate (0.0060 mole) was dissolved in about 40 ml of 7 *N* aqueous ammonia. This solution was gradually added to 40 ml of 7 *N* ammonium hydroxide containing 2.00 g of N-isopropyl-β-mercaptoethylamine hydrochloride (0.013 mole). The reaction mixture turned purple immediately upon addition of the metal ion solution. The reaction was allowed to proceed at about 70° with stirring. The maroon crystalline product started to precipitate from the solution while still hot and the yield was increased by cooling the solution in a refrigerator before filtering. The solid was dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $[Ni(C_3H_7NHCH_2CH_2S)_2]$: C, 40.69; H, 8.20; N, 9.49; S, 21.73. Found: C, 40.42; H, 8.15; N, 9.12; S, 21.98.

Preparation of Bis(N-*n*-propyl-β-mercaptoethylamine)nickel-(II), $[Ni(n\text{-}C_3H_7NHCH_2CH_2S)_2]$.—A 4.39-g sample of nickel(II) chloride hexahydrate (0.018 mole) was dissolved in 50 ml of 7 *N* ammonium hydroxide. This solution was added slowly with stirring to 5.00 g of N-*n*-propyl-β-mercaptoethylamine hydrochloride (0.032 mole) in about 50 ml of 7 *N* ammonium hydroxide. The reaction mixture became purple immediately with the first addition of metal ion solution. As addition continued a green precipitate formed. This was isolated by filtration, washed with water, and dried *in vacuo* over P_4O_{10}; yield, 4.1 g (89.8%). *Anal.* Calcd for $[Ni(C_3H_7NHCH_2CH_2S)_2]$: C, 40.69; H, 8.20; N, 9.49; S, 21.73. Found: C, 40.68; H, 8.25; N, 9.32; S, 21.72.

Preparation of Bis(N-*n*-hexyl-β-mercaptoethylamine)nickel-(II), $[Ni(n\text{-}C_6H_{13}NHCH_2CH_2S)_2]$.—To 2.00 g of N-*n*-hexyl-β-mercaptoethylamine (0.012 mole) in a solution prepared from equal volumes of concentrated ammonium hydroxide and ethanol, 1.43 g of nickel(II) chloride hexahydrate (0.0060 mole) in 7 *N* ammonium hydroxide was added. A green product precipitated from the reaction mixture and was isolated by filtration, then dried *in vacuo* over P_4O_{10}. If the product was contaminated with a brown solid, washing it with benzene removed the brown material. *Anal.* Calcd for $[Ni(C_6H_{13}NHCH_2CH_2S)_2]$: C, 50.66; H, 9.57; N, 7.39; S, 16.91. Found: C, 50.64; H, 9.69; N, 7.32; S, 17.06.

Preparation of Bis(N-*n*-octyl-β-mercaptoethylamine)nickel(II), $[Ni(n\text{-}C_8H_{17}NHCH_2CH_2S)_2]$.—This compound was prepared by the same method as $Ni(n\text{-}PrL)_2$. *Anal.* Calcd for $[Ni(C_8H_{17}NHCH_2CH_2S)_2]$: C, 55.17; H, 10.18; N, 6.43; S, 14.73. Found: C, 55.33; H, 10.20; N, 6.43; S, 14.86.

Preparation of Bis(N-*n*-decyl-β-mercaptoethylamine)nickel(II), $[Ni(n\text{-}C_{10}H_{21}NHCH_2CH_2S)_2]$.—This compound was prepared by the same method as $Ni(n\text{-}PrL)_2$. The reaction mixture was stirred vigorously to disperse the slightly soluble ligand. *Anal.* Calcd for $[Ni(C_{10}H_{21}NHCH_2CH_2S)_2]$: C, 58.64; H, 10.66; N, 5.70; S, 13.05. Found: C, 58.75; H, 10.63; N, 5.60; S, 13.04.

Preparation of Bis(N-benzyl-β-mercaptoethylamine)nickel(II), $[Ni(C_6H_5CH_2NHCH_2CH_2S)_2]$.—This compound was prepared by the same method as $Ni(DcL)_2$. *Anal.* Calcd for $[Ni(C_6H_5CH_2NHCH_2CH_2S)_2]$: C, 55.26; H, 6.18; N, 7.16; S, 16.39. Found: C, 55.50; H, 6.20; N, 7.22; S, 16.48.

Preparation of Bis(N-β-phenethyl-β-mercaptoethylamine)-nickel(II), $[Ni(C_6H_5CH_2CH_2NHCH_2CH_2S)_2]$.—This compound was prepared by the same method as $Ni(DcL)_2$. The product often was brownish, but this did not affect the analysis of the sample. Washing the product with benzene removed the brown material leaving only the green complex. *Anal.* Calcd for $[Ni(C_6H_5CH_2CH_2NHCH_2CH_2S)_2]$: C, 57.29; H, 6.73; N, 6.68; S, 15.29. Found: C, 57.24; H, 6.65; N, 6.80; S, 15.01.

Preparation of Bis(N,N-diethyl-β-mercaptoethylamine)nickel-(II), $\{Ni[(C_2H_5)_2NCH_2CH_2S]_2\}$.—This compound was prepared by the same method as $Ni(n\text{-}PrL)_2$. *Anal.* Calcd for $\{Ni[(C_2H_5)_2NCH_2CH_2S]_2\}\cdot H_2O$: C, 42.24; H, 8.86; N, 8.21; S, 18.79. Found: C, 42.09; H, 8.30; N, 8.44; S, 18.71.

Preparation of Bis(N-*t*-butyl-β-mercaptoethylamine)nickel(II), $[Ni(t\text{-}C_4H_9NHCH_2CH_2S)_2]$.—A 4.04-g sample of nickel(II) chloride hexahydrate (0.017 mole) was dissolved in about 100 ml of 7 *N* ammonium hydroxide. This solution was gradually added to 5.00 g of N-*t*-butyl-β-mercaptoethylamine hydrochloride (0.029 mole) in about 100 ml of 7 *N* ammonium hydroxide. The reaction was not rapid and after 4 hr only 2.2 g (47.2%) of the brown product was isolated by filtration. The solid was dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $[Ni(C_4H_9NHCH_2CH_2S)_2]$: C, 44.59; H, 8.73; N, 8.67; S, 19.84. Found: C, 44.60; H, 8.74; N, 8.50; S, 19.85.

Preparation of Tetrakis(N,N-dimethyl-β-mercaptoethylamine)-trinickel(II) Tetraphenylborate, $\{Ni[Ni((CH_3)_2NCH_2CH_2S)_2]_2\}[B(C_6H_5)_4]_2$.—A 0.50-g sample of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) (0.0019 mole) was dissolved in 50 ml of absolute ethanol. To this was added 50 ml of absolute ethanol containing 0.45 g of nickel(II) chloride hexahydrate (0.0019 mole). The reaction mixture turned deep green and remained clear. An ethanol solution of 1.33 g of sodium tetraphenylborate (0.0037 mole) was added. A precipitate formed on addition of the salt and dissolved with gentle heating and stirring. Upon cooling the reaction mixture, the gray product precipitated and was isolated by filtration and dried *in vacuo* over P_4O_{10}; yield, 0.66 g (57.4%). *Anal.* Calcd for $\{Ni[Ni((CH_3)_2NCH_2CH_2S)_2]_2\}[B(C_6H_5)_4]_2$: C, 62.41; H, 6.55; N, 4.55; S, 10.42. Found: C, 62.23; H, 6.87; N, 4.52; S, 9.82.

Preparation of Tetrakis(N-isopropyl-β-mercaptoethylamine)-trinickel(II) Perchlorate, $\{Ni[Ni(i\text{-}C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$.

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[26] K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

—A 0.50-g sample of bis(N-isopropyl-β-mercaptoethylamine)-nickel(II) (0.0017 mole) and 0.62 g of nickel(II) perchlorate hexahydrate (0.0017 mole) were placed in 150 ml of methanol and stirred at room temperature for 2 hr. Water (15 ml) was added and the reaction was allowed to proceed for an additional 2 hr. Filtration of the reaction mixture yielded 0.58 g of the product (81%). The maroon solid was dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $\{Ni[Ni(C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$: C, 28.33; H, 5.71; N, 6.61; S, 15.31; Cl, 8.36. Found: C, 27.89; H, 5.80; N, 6.98; S, 14.66; Cl, 7.99.

General Preparative Procedure for Tetrakis(N-substituted β-mercaptoethylamine)trinickel(II) Complex Cation.—The synthetic procedures for the preparation of tetrakis(N-isopropyl-β-mercaptoethylamine)trinickel(II) chloride, tetrakis(N-*n*-octyl-β-mercaptoethylamine)trinickel(II) perchlorate, and tetrakis(N-*n*-hexyl-β-mercaptoethylamine)trinickel(II) perchlorate involved the reaction of the bis(N-substituted β-mercaptoethylamine)-nickel(II) complex with twofold excess of nickel(II) salt. The salt may contain a convenient precipitating anion or the anion may be added to the reaction mixture separately as the sodium salt. Perchlorate ion proved to be an excellent choice for obtaining crystalline products. When the ligand has a very bulky amine function, as with N,N-diethyl- and N-*t*-butyl-β-mercaptoethylamine, this procedure will not yield the trinuclear complex.

Preparation of Tetrakis(N-*n*-propyl-β-mercaptoethylamine)dinickel(II)palladium(II) Perchlorate, $\{Pd[Ni(n\text{-}C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$.—A 1.00-g sample of bis(N-*n*-propyl-β-mercaptoethylamine)nickel(II) (0.0034 mole) was suspended in 10 ml of water. To this suspension, 0.537 g of potassium tetrachloropalladate(II) (0.0017 mole) in 10 ml of water was added. The reaction mixture gradually became blood red. After stirring for 90 min at room temperature, the mixture was filtered to remove any undissolved reactant. A solution of 0.98 g of sodium perchlorate monohydrate (0.007 mole) in 15 ml of water was added to the filtrate precipitating the brick red complex salt which was isolated by filtration and dried *in vacuo* over $Mg(ClO_4)_2$; yield, 1.01 g (68.5%). *Anal.* Calcd for $\{Pd[Ni(C_3H_7NHCH_2CH_2S)_2]_2\}(ClO_4)_2$: C, 26.82; H, 5.40; N, 6.26; S, 14.32; Cl, 7.92. Found: C, 27.04; H, 5.19; N, 6.12; S, 14.33; Cl, 7.75.

Acknowledgment.—This investigation was supported by the U. S. Army Research and Development Command.

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Electronic Structure of Tetragonal Nickel(II) Complexes[1a]

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Received October 18, 1967

The electronic spectra of tetragonal nickel(II) complexes have been studied for a variety of axial and equatorial ligands. The spectra contain a large number of bands permitting us to test previously reported approximations that have been used in calculation of the crystal field parameters Ds and Dt. The results show that, contrary to the approach usually made, all off-diagonal matrix elements must be considered when calculating these parameters. Significant errors exist in many literature values. Data are presented to show that for tetragonal nickel(II) complexes, the value Dq^z does not remain constant on going from complex to complex when the in-plane field changes. The values of Dq^z become less as the in-plane field becomes stronger. This is explained on the basis of a ligand inductive effect. Other manifestations of this phenomenon are discussed. The values for the McClure parameter, $\delta\pi$, are interpreted on the basis of two alternative effects: π-electron repulsion (π*-antibonding effects) and metal-to-ligand π bonding.

Introduction

Recently there has been considerable interest[2–9] in the assignment of spectra of tetragonal metal complexes and the interpretations of the ligand field parameters Ds and Dt[3a,4–8] or $\delta\sigma$ and $\delta\pi$.[2] This has been in part stimulated by the pioneering work of Wentworth and Piper.[3] Invariably, the number of bands in the experimental spectra is equal to or less than the number of parameters to be fit (Dq, B, Ds, and Dt). Consequently any reference to configuration interaction (^3F and ^3P interaction) and off-diagonal crystal field matrix elements (interaction of ^3E_g states arising from ^3F) has been ignored or assumed to be small. In the course of our studies on tetragonal nickel(II) complexes,[4,10] we found that the electronic spectra contained a large number of bands. We therefore thought it desirable to examine in detail the method of calculation of the crystal field parameters, for we had enough bands to evaluate the parameters and test the model. We carried out the calculations with the inclusion of all off-diagonal matrix elements and compared these results with those obtained by using the approximations employed by others.[2,3,8] The systems chosen for this work were of the form $Ni(L)_4X_2$ where $(L)_4$ represents four individual ligands, two bidentate

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(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) Abstracted in part from the Ph.D. thesis of D. A. Rowley, University of Illinois, 1968. National Institutes of Health Predoctoral Fellow 1967–1968.

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