synthetic utility[1,5] of the ligand substitution reactions based on alkylthiolate tetramers.

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Novel Octahedral Complexes of Nickel(II) with Thioether Derivatives of Cysteine Ethyl Ester

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Abstract: The green solid bis complex of cysteine ethyl ester and nickel(II), $Ni(Etc)_2$, has been prepared. Only the primary amine and thio groups appear to be coordinated. The complex is diamagnetic. Its spectrum in chloroform is interpreted to indicate weak thio bridging. The coordinated thio groups in this complex undergo alkylation with benzyl chloride, benzylthiomethyl chloride, and triphenylmethyl chloride. Octahedral nickel(II) complexes of the corresponding thioether derivatives of cysteine ethyl ester, $[NiL_2Cl_2]$, result. The infrared spectrum of the complex containing (*S*)-triphenylmethylcysteine ethyl ester, $[Ni(Ettpmc)_2Cl_2]$, indicates that one coordination position is occupied by the carbonyl oxygen of the ester group from one ligand. This result suggests that rearrangement has taken place, probably due to steric hindrance of triphenylmethyl groups initially in mutually cis positions.

There have been few studies of the solid bis nickel(II) complexes of cysteine methyl or ethyl esters.[2] The behavior of nickel(II) ion and cysteine methyl ester in aqueous solution has been interpreted to indicate coordination of the amine and thio groups.[3,4] There have been numerous reports of bis nickel(II) complexes with ligands containing only amine and thio groups.[5-10] These complexes generally exhibit diamagnetism, indicative of planar coordination.

Solid complexes of nickel(II) with thioether derivatives of cysteine ethyl ester contain three potential donor groups. Coordination of the ester group, if it occurs, is expected to be achieved through the carbonyl oxygen atom. When the carbonyl oxygen atom of a coordinated carboxylic acid group coordinates by bridging to an adjacent metal ion, its donor strength approximates that of a coordinated water molecule.[11] It is reasonable to assume that the carbonyl oxygen of an ester group has a similar, or smaller, donor strength. Hence, the relative donor strengths of the groups are expected to decrease in the order $-NH_2 > SR > -CO_2Et$.[12]

Octahedral nickel(II) complexes of thioether derivatives of cysteine ethyl ester were prepared by alkylation reactions between the appropriate organic chloride and bis(cysteine ethyl ester)nickel(II), $Ni(Etc)_2$. (Abbreviations for the names and formulas of all of the complexes examined in this study are given in Table I.) Similar alkylation reactions have been reported for bis(β-mercaptoethylamine)nickel(II), $Ni(MEA)_2$,[13,14] and other amine-thionickel(II) complexes.[15] There are several reports of the synthesis of similar octahedral nickel(II) complexes directly with the appropriate ligands.[16-19] In these cases, however, there was no ester group in the ligands.

Experimental Section

Preparation. The bis complexes $[Ni(SCH_2CH_2NH_2)_2]$[5] and $[Ni(SCH_2CH(NH_2)CO_2C_2H_5)_2]$ (see below) were made to react with several organic chlorides in an attempt to produce nickel complexes of the type $[NiL_2Cl_2]$. The organic chlorides were benzyl chloride ($PhCH_2Cl$), benzylthiomethyl chloride ($PhCH_2SCH_2Cl$),[20] triphenylmethyl chloride (Ph_3CCl), and diphenylmethyl chloride (Ph_2CHCl). With the exception of benzylthiomethyl chloride, the organic chlorides were used as reagent grade chemicals. Chloroform and DMF were used as solvents. Reagent inorganic salts were used without further purification.

$Ni(SCH_2CH(NH_2)CO_2C_2H_5)_2$. This complex was prepared by a

Table I. Analyses and Properties of Complexes

Compound	Dec pt, °C	C, %		H, %		N, %		Others, %			Mol wt[a]	
		Calcd	Found	Calcd	Found	Calcd	Found		Calcd	Found	Calcd	Found
$Ni(SCH_2CH(NH_2)CO_2C_2H_5)_2$ $Ni(Etc)_2$	195	33.8	33.58	5.67	5.84	7.89	7.74	Ni	16.6	17.10		
$[Ni(PhCH_2SCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$ $[Ni(Etbc)_2Cl_2]$	184–86	47.3	47.39	5.62	5.54	4.61	4.81	Cl	11.6	11.60	608	599
$[Ni(Ph_3CSCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$ $[Ni(Ettpmc)_2Cl_2]$	~100	63.2	63.42	5.53	5.55	3.07	3.11	Cl	7.78	7.26	912	1031 912[b]
$[Ni(PhCH_2SCH_2SCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$ $[Ni(Etbtmc)_2Cl_2]$		44.6	44.22	5.47	5.51	4.00	3.76	Cl	10.1	10.30	700	717
$[Ni_3(SCH_2CH(NH_2)CO_2C_2H_5)_4]Cl_2$ $[Ni_3(Etc)_4]Cl_2$								Cl	8.45	8.84		

[a] In chloroform. [b] In benzene.

method similar to that of Jicha and Busch[5] for the preparation of bis(β-mercaptoethylamine)nickel(II). A solution of 150 ml of water containing cysteine ethyl ester hydrochloride (19.4 g, 0.105 mol) and sodium hydroxide (8.0 g, 0.20 mol) was added slowly with stirring to a warm solution of hexaaquonickel(II) nitrate (14.5 g, 0.05 mol) dissolved in 150 ml of water. As the last few milliliters of ligand solution were added, the deep red solution yielded a green precipitate. The mixture was stirred for several hours and filtered. The precipitate was washed with several portions each of absolute alcohol and water and then dried *in vacuo* over P_4O_{10}, yield 78%.

$[Ni(PhCH_2SCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$. The bis complex described above (0.445 g, 1.25 × 10^{-3} mol) was added to 20 ml of DMF which contained 0.310 ml of benzyl chloride (0.322 g, 2.56 × 10^{-3} mol). After stirring at room temperature for 1 day, the reaction solution was green. Concentration *in vacuo* produced a pale blue solid which was stirred with cold absolute alcohol, filtered, washed with absolute alcohol, and dried *in vacuo* over P_4O_{10}, yield 67%.

$[Ni(Ph_3CSCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$. The cysteine ester complex (1.00 g, 2.82 × 10^{-3} mol) was added to 20–30 ml of chloroform containing triphenylmethyl chloride (1.57 g, 5.64 × 10^{-3} mol). After stirring at room temperature for 1 hour, the color of the reaction solution had changed from red to bright green. Stirring was continued for 1 day. When the chloroform was removed under high vacuum, bright green crystals remained. Elemental analyses indicated the presence of chloroform. The chloroform was removed by heating *in vacuo* at *ca.* 90°. The weight loss (11.3%) corresponded to the removal of 1 mol of chloroform. Because the complex is very soluble in nonpolar solvents, it could not be conveniently recrystallized. However, the infrared spectrum indicates the absence of any significant impurity. When attempts were made to prepare this complex in DMF rather than in chloroform, a green oil was formed. Attempts to crystallize the oil were unsuccessful.

$[Ni(PhCH_2SCH_2SCH_2CH(NH_2)CO_2C_2H_5)_2Cl_2]$. The cysteine ester complex (1.66 g, 4.67 × 10^{-3} mol) was added to a small volume of chloroform containing 1.65 ml of benzylthiomethyl chloride (1.91 g, 1.11 × 10^{-2} mol). An excess of benzylthiomethyl chloride was not necessary, but it reduced the reaction time. Concentration of the chloroform to dryness yielded a light green crystalline solid which was washed with ether and dried *in vacuo* over P_4O_{10}. Additional stirring with absolute alcohol was required to produce a complex with the correct molecular weight.

$[Ni_3(SCH_2CH(NH_2)CO_2C_2H_5)_4]Cl_2$. This complex was prepared according to the procedure given by Jicha and Busch[5] (method 1) for the preparation of the analogous complex with β-mercaptoethylamine. In the present case, a small yield of a red amorphous solid precipitated after the mixture was at 0° for several days. The complex was dried *in vacuo* over P_4O_{10}. It is readily soluble in water from which the green bis complex precipitates upon standing.

Attempted Preparations of Complexes Containing Thioether Ligands. No nickel complexes of the type $[NiL_2Cl_2]$ were isolated from the products of the reaction between $Ni(SCH_2CH_2NH_2)_2$[5] and triphenylmethyl chloride or benzylthiomethyl chloride. When stoichiometric ratios of reactants were used (DMF solvent), the insoluble, dark green, trinuclear complex $[Ni_3(SCH_2CH_2NH_2)_4]Cl_2$[5] was a major product. Concentration of the reaction solutions produced light green oils. Attempts to crystallize these oils were unsuccessful. The elemental analyses of the oils were not consistent with values calculated for the desired complexes. The use of excess chloride prevented the formation of the trinuclear complex but did not lead to the isolation of the desired compounds.

Reaction of diphenylmethyl chloride with $Ni(SCH_2CH(NH_2)CO_2C_2H_5)_2$ in chloroform also failed to produce the desired dichloro complex. After evaporation of the chloroform and the addition of cold absolute alcohol, only an insignificant amount of green solid formed. Neither extending the reaction time, heating, nor using DMF as the solvent produced a significant yield.

Physical Methods. Visible and ultraviolet spectra were recorded using Cary spectrophotometers Models 14 and 14 R.I. For visible solution spectra, the band maxima at one-half peak height are given. The slight asymmetry and broadness of the low energy bands in the spectra of the octahedral nickel complexes limit the accuracy of the measurements of the band maxima to ±5 nm. The concentrations ranged between 3 and 6 × 10^{-2} *M*. Because of the

Table II. Some Infrared Absorptions and Assignments for $Ni(Etc)_2$

Assignment	$Ni(Etc)_2$	Cysteine ethyl ester · HCl
NH_{str}	3270	
	3145	
	3050?	
SH_{str}		2480
$C{=}O_{str}$	1720	1740
Ester I	1235	1230

large variation in the extinction coefficients of the bands in the spectrum of $Ni(Etc)_2$, several different concentrations were used.

A conductivity bridge, Model KCl6B2, made by Industrial Instruments, Inc., was used to measure the conductances. The cell constant of the H-type conductivity cell was calibrated with 0.1 *N* KCl and was found to be 1.11 (5). Reagent grade solvents were used, and measurements were taken at 25°. A Gouy balance was used to measure the magnetic moment of $Ni(Etc)_2$.

Results and Discussion

Neutral Bis Complex $Ni(Etc)_2$. The bis(cysteine ethyl ester)nickel(II) complex, $Ni(Etc)_2$, was found to be diamagnetic, consistent with planar coordination. This result agrees with the diamagnetic nature of solid bis(β-mercaptoethylamine)nickel(II), $Ni(MEA)_2$,[5] and bis(cysteinato)nickel(II), $Ni(cysteine)_2{}^{2-}$, in aqueous solution.[21] That the ester group does not interact with the nickel is confirmed by the infrared spectrum. The infrared absorption bands related to the ester group occur at the same frequencies as those of cysteine ethyl ester hydrochloride. The absence of an S–H stretching vibration in the spectrum of the complex indicates that the thiol group is coordinated and deprotonated.[22] The nitrogen–hydrogen stretching vibrations indicate the presence of coordinated primary amine groups. These results are summarized in Table II.

The visible spectrum of $Ni(Etc)_2$ is also consistent with planar coordination. One, two, or three bands with relatively high intensities are expected.[23] It is particularly significant that the spectrum (Nujol mull) of solid $Ni(Etc)_2$ (λ_{max} 626, 470, 316 nm) is practically identical with that of the complex in pyridine solution (λ_{max} 631, 470, 318 nm; ϵ 35.4, 128, 8.23×10^3). This is visibly indicated by the retention of the green color of the complex in solution. In fact, $Ni(Etc)_2$ gives no evidence of adding pyridine molecules to the coordination sphere upon prolonged treatment with pyridine at elevated temperature. This behavior is in contrast to that of many planar nickel(II) complexes but is in agreement with that of $Ni(MEA)_2$.[5]

The visible spectra of $Ni(Etc)_2$ in various solvents are listed in Table III. $Ni(Etc)_2$ reacts with (the otherwise insoluble) anhydrous nickel chloride in chloroform as well as in DMF to form a species, characterized by an intense absorption at 495 nm. The formation of a trinuclear species in DMF (characterized by a similar absorption at 495 nm) has been suggested as evidence of cis coordination in the case of $Ni(MEA)_2$.[24] In the case of $Ni(Etc)_2$, the formation of the polynuclear species is accompanied by the appearance of an absorption band at 360 nm in the ultraviolet region. This absorption band is also present in the spectrum of $Ni(Etc)_2$ in chloroform. The tailing of this peak increases the intensity of the band at *ca.* 470 nm, effectively obscures any band at *ca.* 600 nm, and imparts a red color to the chloroform solution.

Evaporation of the chloroform from the solution of $Ni(Etc)_2$ yields a glassy solid. The visible spectrum (Nujol mull) of the red solid exhibits shoulders at *ca.* 470 and 350 nm. After drying *in vacuo*, the solid gave elemental analyses in agreement with the formula $Ni(Etc)_2$. The infrared spectrum suggested the presence of a small amount of chloroform. The only detectable effect on other absorptions in the infrared spectrum is a broadening of the C=O stretching vibration. This interaction between chloroform and the ester group may be in part responsible for the solubility of $Ni(Etc)_2$ in chloroform.

Table III. Visible Spectra of $Ni(Etc)_2$ in Various Solvents

Complex	Solvent	λ_1, nm	ϵ_1	λ_2, nm	ϵ_2
$Ni(Etc)_2$	py	630	(35.4)	470	(128)
$Ni(Etc)_2$	DMF	610 sh	(37.1)	477	(159)
$Ni(Etc)_2$	$CHCl_3$			474 sh	(390)
$Ni(Etc)_2$ + $NiCl_2$	$CHCl_3$			495	(1.17×10^3)[a]
$Ni(Etc)_2$ + $NiCl_2$	DMF			496	(9.13×10^2)[a]

[a] Apparent ϵ, assuming that trinuclear complex formation is complete.

Table IV. Conductivities of Octahedral Nickel(II) Complexes in DMF[a]

Complex	M, $ohm^{-1}\ cm^2\ mol^{-1}$	Concn (*M*)
$[Ni(Etbc)_2Cl_2]$	38.8, 45.3[b]	1.15×10^{-3}
$[Ni(Etbtmc)_2Cl_2]$	43.2	7.15×10^{-4}
$[Ni(Ettpmc)_2Cl_2]$	61.8	9.84×10^{-4}

[a] Value for diunivalent electrolyte *ca.* 160 $ohm^{-1}\ cm^2\ mol^{-1}$
[b] Second value measured after 5 hr.

Octahedral Complexes of the Type $[NiL_2Cl_2]$. The octahedral nickel(II) complexes studied here were prepared by the reaction of the appropriate organic chloride with the bis nickel(II) complex, $Ni(Etc)_2$. It is not surprising that triphenylmethyl chloride, Ph_3CCl, and benzylthiomethyl chloride, $PhCH_2SCH_2Cl$, react very readily with $Ni(Etc)_2$. In both cases, nucleophilic substitution of the chlorides is enhanced by resonance stabilization of the carbonium ion intermediates. However, in DMF, these chlorides did not react with bis(β-mercaptoethylamine)nickel(II), $Ni(MEA)_2$, to yield isolatable octahedral complexes. In these cases, the bridged trinuclear complex $[Ni_3(MEA)_4]Cl_2$ was isolated as the only stable reaction product of significant yield. The formation of bridged thio groups in the trinuclear complex tends to increase the resistance toward alkylation.[13] Chlorodiphenylmethane, Ph_2HCCl, did not react with $Ni(Etc)_2$ to a significant extent.

The molecular weights of the octahedral complexes, $[Ni(Etbc)_2Cl_2]$, $[Ni(Etbtmc)_2Cl_2]$, and $[Ni(Ettpmc)_2Cl_2]$, measured by vapor pressure osmometry, indicate that they are monomeric (Table I). Conductivity measurements further substantiate that the chloro groups are coordinated. The complexes $[Ni(Ettpmc)_2Cl_2]$ and $[Ni(Etbtmc)_2Cl_2]$ are nonelectrolytes in nitrobenzene. In the more polar solvent DMF, the conductivities (Table IV) were found to be intermediate between the value expected for a nonelectrolyte and that expected for a uni-univalent electrolyte in this solvent.[25] Busch, *et al.*, have reported that the halo groups of similar complexes are displaced to an intermediate extent by DMF.[13]

The infrared spectra of $[Ni(Etbc)_2Cl_2]$ and $[Ni(Etbtmc)_2Cl_2]$ in chloroform indicate that the primary amine groups are coordinated. Two peaks are present in each spectrum, occurring at 3270 and 3340 cm^{-1} and 3275 and 3340 cm^{-1}, respectively. The carbonyl stretching vibrations of the ester groups in the ligands occur at 1730 cm^{-1}, which shows that the ester groups are not coordinated. The peaks at 1490 and 700 cm^{-1} indicate the presence of phenyl rings.[26]

The infrared spectrum of $[Ni(Ettpmc)_2Cl_2]$ also indicates the presence of phenyl rings and coordinated amine

Table V. Visible Spectra of Octahedral Nickel(II) Complexes[a]

Complex	λ_1, nm	ϵ	λ_2, nm	ϵ	λ_3, nm	ϵ
$[Ni(Etbc)_2Cl_2]$	1106	(6.8)	634	(9.7)	392	(20)
$[Ni(Etbtmc)_2Cl_2]$	1105	(7.5)	627	(11.0)	386	(36)
$[Ni(Ettpmc)_2Cl_2]$	1135	(6.7)	675	(11.5)	390 sh	(50)

[a] In chloroform.

groups. However, two absorptions are present in the carbonyl stretching region. One occurs at 1735 cm^{-1}, indicating the presence of an uncoordinated ester group. The other occurs at 1680 cm^{-1}, indicating the presence of a coordinated ester group.[27] In chloroform, the peaks occur at these same positions and their intensities are very nearly equal.

The results indicate that in $[Ni(Ettpmc)_2Cl_2]$, the chloro groups, the primary amine groups, and one ester group are coordinated to the nickel ion. The visible spectrum of this complex in chloroform contains three peaks (Table V) which are typical of octahedrally coordinated nickel(II).[13,23] Since the infrared spectrum indicates the presence of an uncoordinated ester group, the sixth coordination position must be occupied by one of the thioether groups.

It is suggested that steric hindrance between the bulky triphenylmethyl groups prevents the thioether groups from assuming mutually cis positions in the octahedral complex. Extensive rearrangement of the donor groups in chloroform is unlikely. Therefore, these results suggest that the cis-planar arrangement of the nitrogen and sulfur donors is maintained in the alkylated octahedral nickel(II) complexes. Only if the coordinated thio groups of the complex, $Ni(Etc)_2$, react with triphenylmethyl chloride in initially mutually cis positions, will the steric hindrance of the triphenylmethyl groups induce rearrangement. This proposal is in agreement with the reactions of $Ni(MEA)_2$ with α-diketones and α,α'-dibromo-*o*-xylene to form complexes with tetradentate macrocyclic ligands.[28-30]

Complexes of the type $[Ni(N\text{-}SR)_2Cl_2]$ which have been previously reported all exhibit very little (if any) solubility in noncoordinating solvents.[13,17-19,31] The octahedral complexes reported in this paper are readily soluble in chloroform. Their solution spectra are listed in Table V. The three absorption peaks in each spectrum indicate a rather symmetric octahedral field.[23] The low energy band is broad, but all the bands are quite symmetrical. The energy of the first band represents the average ligand field strength.[23] These values (both *ca.* 9050 cm^{-1}), for the first two complexes, are greater than that (8600 cm^{-1}) for $[Ni(BAA)_2Br_2]$[13] (BAA = benzyl 2-aminoethylsulfide). This result is consistent with the greater donor strength of Cl^- as compared to that of Br^-. The reflectance spectrum of $[Ni(mta)_2Cl_2]$ (mta $\equiv$ *o*-methylthioaniline) has been reported to contain a band at 9850 cm^{-1}.[18] In the case of $[Ni(Ettpmc)_2Cl_2]$, the energy of this first band (8850 cm^{-1}) is significantly lower, which is consistent with the presence of a weaker ester carbonyl donor. The visible spectra of the solid complexes $[Ni(Etbc)_2Cl_2]$ and $[Ni(Etbtmc)_2Cl_2]$ are essentially identical with the solution spectra. However, in both cases, the lowest energy band gives evidence of being composed of more than a single band.

To further ensure that the desired neutral ligand was formed *in situ* during the preparation of $[Ni(Ettpmc)_2Cl_2]$, ligand recovery was attempted by a replacement reaction. Ethylenediamine was added to a suspension of the nickel complex in ether. The infrared spectrum and elemental analyses of the pink solid which formed are in agreement with its formulation as $[Ni(en)_3]Cl_2 \cdot 2H_2O$. Addition of ether saturated with HCl gas to the ether filtrate produced a white crystalline solid. Its infrared spectrum is consistent with that expected for (*S*)-triphenylmethylcysteine ethyl ester hydrochloride. Elemental analyses indicated a small amount of impurity. In view of the instability of the carbon-sulfur bond toward HCl in chloroform,[32] the presence of this impurity is not surprising.

The recovery of the neutral ligand from the complex $[Ni(Etbtmc)_2Cl_2]$ was attempted by the same procedure. The white crystalline solid which was isolated melts at 137-138°. Its infrared spectrum and elemental analyses confirm that it is (*S*)-benzylthiomethylcysteine ethyl ester hydrochloride. The proton nmr spectrum in $CDCl_3$ contains the following peaks (ppm): −1.30, triplet, (CH_3); −3.46, doublet, $(\text{-}S\mathit{CH}_2CH(NH_2)\text{-})$; −3.68, $(\text{-}S\mathit{CH}_2S\text{-})$; −3.85, $(Ph\mathit{CH}_2S\text{-})$; −7.30, (Ph-). The relative intensities of these peaks are consistent with the assignments which were made. In addition, a broad peak centered at −4.4 ppm with relative intensity of three protons is seen.

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