hydride catalyzed disproportionation of 1,1-dimethyldisilane were dimethylsilane and a polymer suggests that a hydride transfer occurs with silicon–silicon bond rupture.

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Reactions of Coordinated Ligands. XVI. The Reactions of the Chloroacetate Anion with Mercapto Groups in Nickel(II) Complexes of Mercaptoamines

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Reports of alkylation reactions occurring at the sulfur atoms of coordinated mercaptide groups have appeared in the scientific literature since 1888. However, only recently have the full utility and scope of such reactions been demonstrated.[1,2] The known reactions can be conveniently classified as follows: (1) reactions using monofunctional alkylating agents which simply transform the mercaptide group to a thioether moiety and (2) reactions using difunctional alkylating agents which lead the concomitant formation of two thioether groups and a chelate ring joining them. The reaction of the nickel(II) complex of 2-aminoethanethiol with methyl iodide serves as an example of the first type (Figure 1, reaction 1), whereas the reaction of the same nickel complex with α,α'-dibromo-o-xylene illustrates the second (Figure 1, reaction 2).

We present here an extension of the classes of reactions of coordinated mercaptides to include those in which the alkylating agent contains a functional group which can complex with the nickel ion. The chloroacetate anion meets these requirements and can be employed with nickel(II) complexes of mercaptoamines to generate pseudo-octahedral complexes containing two tridentate ligands each of which possesses three dissimilar donor atoms, nitrogen, sulfur, and oxygen (Figure 1, reaction 3).

The reactions of the $Ni(RR'NCH_2CH_2S)_2$ complexes with the chloroacetate anion proceed smoothly in hot water over a period of 1–5 hr. In the case of the R = R' = H complex, the reaction is performed in boiling water and is characterized by the simultaneous disappearance of the insoluble, green mercaptoamine complex and appearance of a blue solution. Blue crystals are readily obtained by recrystallization from hot water of the solid deposited from the reaction mixture.

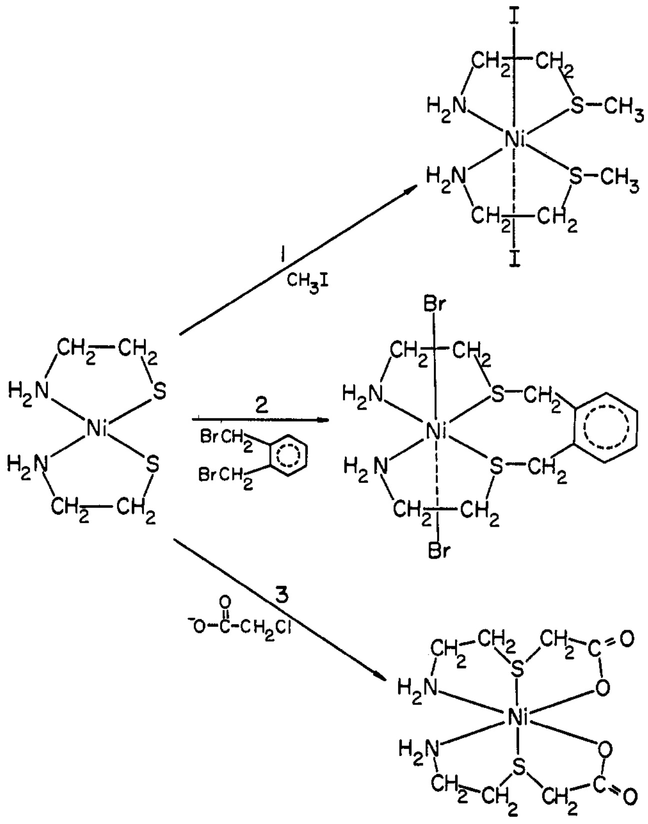

Figure 1. Alkylation reactions of the coordinated mercaptide group. Specific isomers are indicated as products; however, no information is available concerning the isomers of the complexes.

Both the molecular weight and magnetic susceptibility data for the R = R' = H compound support the proposed structure. The molecular weight in water, 300 (theory 327), suggests that the complex exists predominantly as undissociated monomers in this solvent. The six-coordinate nature of the nickel in the crystals is supported by a measured magnetic moment of 3.04 BM, a value similar to six-coordinate amine–thioether complexes previously reported and generally typical of spin-free octahedral nickel(II) complexes.[1,2]

Although it is impossible for the complexes in question to exhibit strictly octahedral symmetry, their electronic spectra can best be interpreted as though the metal ions were in an octahedral site. Apparently the real noncubic field components are small compared with the approximately cubic field because the bands in the electronic spectra can be assigned with the octahedral model as follows: ν_1 to $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$; ν_2 to $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$; ν_3 to $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ (see Table II). In the solid phase the R = R' = H complex shows a split second band which is also common to octahedral complexes of nickel(II) with water and with some amides.[3,4] In each of the aqueous spectra a shoulder at approximately 11,700 cm^{-1} occurs on the high-energy side of the first band. This band may arise from a spin-forbidden triplet to singlet transition.

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TABLE I

INFRARED SPECTRA OF $Ni(RR'NCH_2CH_2SCH_2COO)_2$[a]

R = R' = H, cm^{-1} [b]	R = R' = H, cm^{-1} [c]	R = R' = D, cm^{-1} [c]	Assignment
3267 vi	3270 vi, 3210 m		NH str
3144 m	3170 m, 3150 m		
2949 m			CH str
2923 m			
2873 m			
		2445 i, 2410 m	ND str
		2390 m, 2330 m	
1636 vi	1640 vi	1615 vi	Antisym COO str[d]
1569 vi	1572 vi		NH_2 def[d]
1367 vi	1370 vi	1370 vi	Sym COO str
		1183 m	ND_2 def[d]

[a] vi, very intense; i, intense; m, medium intensity. [b] KBr pellet. [c] Nujol mull. [d] See text for discussion of assignments.

TABLE II

ELECTRONIC SPECTRA OF $Ni(RR'NCH_2CH_2SCH_2COO)_2$

Compound	Solvent	ν_1, cm^{-1} (ϵ_{max})	ν_2, cm^{-1} (ϵ_{max})	ν_3, cm^{-1} (ϵ_{max})
R = R' = H	Nujol mull	10,500	15,300 18,400	27,900
R = R' = H	H_2O	10,380 (11.1)	17,350 (15.6)	27,200 (18.3)
R = R' = CH_3	H_2O	9,780 (12.2)	16,390 (6.4)	25,970 (11.6)
R = H, R' = n-C_3H_7	H_2O	9,990 (11.9)	16,920 (9.4)	26,380 (15.4)

The average ligand fields for the complexes reported here show a recognizable trend as a function of substitution at the amine nitrogen, as well as an expected relationship with other amine–thioether complexes. The *Dq* values for a series of $[Ni(NH_2CH_2CH_2SR)_2X_2]$ complexes are uniformly lower than for any of the products reported here.[1] This fact is consistent with replacing a halide group (X) with a carboxylate function because of the larger contribution to the field strength expected from the latter.[5]

As the degree of substitution of the amine nitrogen increases from primary to secondary to tertiary for the complexes reported here, the *Dq* value drops from 1040 to 999 to 978. A similar reduction of *Dq* as a function of donor atom substitution has been observed for RR'R''M complexes, for ROH complexes, and for $RR'NCH_2CH_2NRR'$ complexes of nickel(II).[6-8] Almost without exception an increase in bulk of the substituted group or an increase in degree of substitution results in a lowering of the *Dq* value. Pavkovic and Meek attribute this diminution to increased steric interactions.[8]

The infrared spectra of the alkylated products provide strong evidence for the proposed structures (Table I). Bands in the 3267 cm^{-1} region are characteristic of the coordinated NH_2 stretching modes whereas the predominant bands at 1640 to 1572 cm^{-1} may be attributed, respectively, to the antisymmetric COO stretch and to the NH_2 deformation.[1,9] However, an unequivocal assignment cannot be made in view of the unusual spectral changes attending deuteration of the complex. The band tentatively assigned to the antisymmetric COO stretch (1640 cm^{-1}) for the protonated species "moves" to 1615 cm^{-1} for the deuterated sample and becomes significantly broader. Furthermore, the very intense 1572 cm^{-1} band for the protonated complex has no counterpart of similar relative intensity for the deuterated species although the corresponding NH and ND stretching vibrations are readily located, have similar relative intensities, and show an appropriate isotopic shift in frequency, NH/ND = 1.33. All these observations are consistent with expectations if the NH_2 deformation and the COO antisymmetric stretch satisfy the conditions for Fermi resonance.[10-12] Nakamoto has indicated the possible similarity of position for the NH_2 deformation and for the COO antisymmetric stretch and the difficulty of assigning them properly.[9] The spectrum from a deuterated sample differs from that of the protonated species because the ND_2 deformation and COO antisymmetric stretch do not have similar energy. The unambiguously assigned COO antisymmetric stretch (1615 cm^{-1}) lies between the positions of the two prominent bands in the protonated spectrum and is broader. In the region where the ND_2 deformations would be expected there are no relatively intense bands. The shifting phenomenon noted here and ascribed to a change in coupling as a function of deuteration has also been observed and similarly explained by Blinc and Hadzi for the CN stretch and OH (or OD) deformation of the nickel(II) dimethylglyoxime complex and of quinone oximes.[13,14]

The infrared spectra of the R = R' = CH_3 and the R = n-C_3H_7, R' = H complexes show intense bands at 1626 and 1621 cm^{-1}, respectively, which are assigned to the COO antisymmetric stretch. The spectrum of the latter complex also shows an intense band at 3174 cm^{-1} which is assigned to the NH stretch.

Experimental Section

Bis(2-aminoethanethiolo)nickel(II) was prepared by the procedure of Jicha and Busch.[15] The other nickel complexes used as starting materials were made by Root's procedure.[16]

Bis(5-amino-3-thiapentanoato)nickel(II).—Bis(2-aminoethanethiolo)nickel(II) (4.22 g, 20 mmoles) was suspended in 150 ml of water containing lithium carbonate (1.48 g, 20 mmoles) and chloroacetic acid (3.78 g, 40 mmoles). The mixture was refluxed for 2 hr and then filtered while hot. The resulting blue solution was reduced to a volume of approximately 50 ml and then cooled to approximately 5° whereupon 5.84 g of blue crystals deposited. The crystals were collected, recrystallized from 70 ml of boiling water, and dried at room temperature for 24 hr over P_4O_{10} at 1 mm pressure; yield 4.6 g (70%). *Anal.*

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(5) We have measured the electronic spectrum of solid $Ni(H_2O)_4(CH_3COO)_2$ and find the bands to be positioned at 8600, 14,390, and 25,300 cm^{-1}. Because water itself has a *Dq* of 860 for nickel(II), we can presume a relatively equivalent position for water and the carboxylate group in the spectrochemical series. This relationship would establish the carboxylate group above the halides in the series.

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Calcd for $Ni(NH_2CH_2CH_2SCH_2COO)_2$: C, 29.38; H, 4.93; N, 8.57; S, 19.61. Found: C, 29.39; H, 5.14; N, 8.46; S, 19.40. The deuterated sample was prepared by recrystallizing an analytical sample of the complex from deuterium oxide and drying as indicated above.

Bis(5-N,N-dimethylamino-3-thiapentanoato)nickel(II).—Chloroacetic acid was added to a mixture of 100 ml of water and sodium hydroxide (20 ml of 0.100 *N*) until the pH was 7.7. To this solution, bis(N,N-dimethyl-2-aminoethanethiolo)nickel(II) (0.27 g, 1 mmole) was added and the resulting reaction mixture was stirred for 5 hr at approximately 60°. The hot mixture was filtered, concentrated to about 2 ml, and cooled. On standing the solution deposited blue crystals which were dried as above; yield 0.13 g (30%). *Anal.* Calcd for $Ni\{(CH_3)_2NCH_2CH_2SCH_2COO\}_2$: C, 37.61; H, 6.31; N, 7.31; S, 16.74. Found: C, 37.09; H, 6.30; N, 7.18; S, 16.19.

Bis(5-N-*n*-propylamino-3-thiapentanoato)nickel(II).—This complex was prepared by the same method as for the dimethyl derivative. An isopropyl alcohol solution of the crude product deposited crystals of the desired composition after addition of chloroform. The sample was dried as above; yield 11%. *Anal.* Calcd for $Ni(C_3H_7NHCH_2CH_2SCH_2COO)_2$: C, 40.89; H, 6.86; N, 6.81; S, 15.60. Found: C, 40.72; H, 6.64; N, 6.72; S, 15.82.

Physical Measurements.—Molecular weights were obtained with a Mechrolab osmometer. Infrared spectra were determined by the KBr pellet technique and in Nujol mulls with a Perkin-Elmer 337 or Beckman IR 9 recording spectrophotometer. A Cary Model 14 spectrophotometer was used for measurements in the ultraviolet, visible, and near-infrared spectral ranges. Magnetic susceptibility data were obtained at room temperature by the Gouy technique.

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Preparation of Lanthanide Chloride Methanolates Using 2,2-Dimethoxypropane

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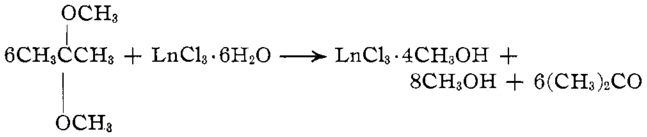
Although the alcoholates of the lanthanide halides have not been studied in detail, it is well known that both the anhydrous and hydrated chlorides are soluble in methyl, ethyl, isopropyl, and *n*-butyl alcohols and in glycerine.[2,3] Few observations have been made on the solid phases obtained from alcoholic solutions of the anhydrous chlorides.

Essentially, the procedures cited in previous studies[4-7] to make the alcoholates have been either (a) direct combination of the anhydrous chlorides with an alcohol, (b) a variation of an azeotropic drying of a hydrated chloride, or (c) an alcohol interchange. In the present investigation, the behavior of several hydrated lanthanide chlorides with easily hydrolyzable compounds was studied to learn whether the water of hydration of the lanthanide chlorides would react with selected reagents to form anhydrous lanthanide chlorides, or hydrates of lower water content, or other complexes.

Several investigators[8-12] have utilized 2,2-dimethoxypropane to obtain dehydrated chlorides, nitrates, and perchlorates in solution, but information about the actual isolation of the dehydrated salts is meager. The dehydrated products were used in solution as intermediates in the preparation of other complexes. 2,2-Dimethoxypropane was selected from among several possible reagents not only because of its strong tendency to react with water but because the reaction products, methanol and acetone, do not enter into bothersome side reactions. However, there is some tendency for polymerization which can be controlled.

2,2-Dimethoxypropane reacts with water in an endothermic reaction to form methanol and acetone. The rate of reaction is proportional to the acidity of the reaction medium, and is impeded by basic conditions.

Experimentally, it was found that a typical reaction with the hydrated lanthanide chlorides was



$$6\mathrm{CH_3}\overset{\mathrm{OCH_3}}{\underset{\mathrm{OCH_3}}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{LnCl_3\cdot 6H_2O} \longrightarrow \mathrm{LnCl_3\cdot 4CH_3OH} + 8\mathrm{CH_3OH} + 6(\mathrm{CH_3})_2\mathrm{CO}$$

Experimental Section

Materials.—2,2-Dimethoxypropane (98%) was used as obtained from The Dow Chemical Co. Infrared analysis showed the absence of water and that it contained methanol and acetone which are the other constituents of the azeotropic mixture. The absolute methyl alcohol was Fisher ACS Reagent Grade. The lanthanide oxides of 99% or better content were used as obtained from the Lindsay Chemical Co. or the Michigan Chemical Corp.

Analytical.—Infrared analyses were made with a Unicam SP-200, using sodium chloride optics. Fluorolube mulls were employed for sample analyses. The 1603 cm^{-1} band of polyethylene standard was used for calibration of the instrument. The presence of water, methanol, acetone, and 2,2-dimethoxypropane was determined by infrared procedures. The lanthanide content was determined by precipitation with oxalic acid and subsequent ignition of the oxalate to the oxide at 800° for 1 hr. The chloride content was determined by precipitation of silver chloride. The precipitated chloride was filtered on an asbestos mat, then dried at 110° for 1 hr.

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