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Cobalt(III) Complexes of Cysteine and Cysteine Derivatives[1]

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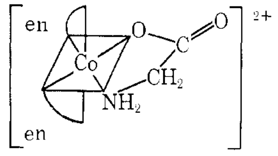
Received June 5, 1969

A series of new cobalt(III) complexes of the formulation $Co(en)_2AA^{n+}$, where en is ethylenediamine and AA is $^-SCH_2CH(NH_2)COO^-$ (Cy); $^-SCH_2CH(NH_2)COOH$ (HCy); $^-SCH_2CH(NH_2)COOC_2H_5$ (OECy), and $CH_3SCH_2CH(NH_2)COO^-$ (SMCy), has been prepared and the compounds have been characterized using elemental analyses, conductivity and molecular weight measurements, visible and infrared spectral data, and nmr studies. The coordination of cysteine in $Co(en)_2Cy^+$ is through amino and mercaptide groups. The carboxylate group of cysteine in this complex is not coordinated; it is protonated upon treatment with acid. Ethyl cysteinate is coordinated through the amino and mercaptide groups in $Co(en)_2OECy^{2+}$ whereas S-methyl-L-cysteine is coordinated through amino and carboxylate groups in $Co(en)_2SMCy^{2+}$. Methylation of the mercaptide in $Co(en)_2(Cy)^+$ results in a novel rearrangement from N and S chelation to N and O chelation.

Introduction

The cobalt(III) complexes of the type $Co(en)_2AA^{2+}$ containing an amino acid anion were first prepared by the reaction of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride with amino acids such as glycine and sarcosine in aqueous solution.[2] Subsequently a variety of aminoacidobis(ethylenediamine)cobalt(II) complexes have been prepared and studied.[3-6] Mathieu,[7] Shimura,[8] and Liu and Douglas[9] reported the absorption spectral, ORD, and CD curves for compounds of this class. Matsuoka, *et al.*,[3] studied the stereochemistry of mixed amino acid complexes of cobalt(III) and Alexander and Busch[10,11] prepared and characterized cobalt(III) complexes containing monodentate glycine and glycine esters. The earlier studies were concerned with amino acids having nitrogen- and oxygen-containing functional groups. It has long been recognized that in complexes of the type $Co(en)_2amac^{2+}$ (amac is an amino acid anion) (I), all three ligands are chelated in a bidentate manner.



I

Cysteine is of particular interest in compounds of this composition because of the presence in its structure of three functional groups, only two of which can bind to the cobalt(III) in a given derivative. The mode of chelation of this potentially flexidentate[12,13] ligand is explored in the discussion to follow.

Experimental Section

The reactions of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride with L-cysteine, S-methyl-L-cysteine, and L-cysteine ethyl ester were carried out by mixing them along with base in stoichiometric amounts. Tris(ethylenediamine)cobalt(III) was removed by adding sodium iodide and filtering. Subsequently, the product was recrystallized as the iodide. The reaction conditions were somewhat different for each reaction. The preparation of these new complexes, their characterization, and various properties are described herein.

Materials.—L-Cysteine (General Biochemicals), S-methyl-L-cysteine, and L-cysteine ethyl ester hydrochloride (Aldrich) were used without further purification. *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by the standard procedure.[14] All other chemicals were reagent grade.

Preparation of Cysteinatobis(ethylenediamine)cobalt(III) Iodide.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride (1.42 g, 0.005 mol), L-cysteine (0.61 g, 0.005 mol), and sodium hydroxide (0.40 g, 0.01 mol) were dissolved in 20 ml of water and the solution was maintained at 60° for 40 min on a stirring hot plate. To the warm solution was then added 2.00 g of sodium iodide, and the tris(ethylenediamine)cobalt(III) iodide which precipitated upon cooling was removed by filtration. The filtrate was again filtered after standing at room temperature for 15 min, and 1.00 g of sodium iodide was added to the resulting filtrate. After the alkali iodide had dissolved, the mixture was allowed to stand at room temperature for 1 day. The dark brown crystals that settled to the bottom of beaker were filtered and washed with a little methanol. The product was recrystallized by dissolving in a minimum amount of boiling water and adding sodium iodide to the filtered solution. The recrystallized product was filtered, washed with 25 ml of methanol, and dried *in vacuo* over silica gel; yield, 0.95 g (43%). *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2\{SCH_2CH(NH_2)COO\}]I\cdot H_2O$: C, 18.97; H, 5.23; N, 15.80; S, 7.24; I, 28.64. Found: C, 19.10; H, 5.15; N, 15.72; S, 7.35; I, 28.85. The dark brown compound was moderately soluble in water but insoluble in organic solvents. The compound reacted with dilute hydrochloric acid resulting in protonation of the carboxyl group (infrared spectrum). After removal of excess hydrochloric acid by evaporation, the compound was dried *in vacuo* over silica gel at 70°. *Anal.* Calcd for $[Co(en)_2\{SCH_2CH(NH_2)COOH\}]ICl\cdot H_2O$: C, 17.52; H, 4.62; N, 14.60; Cl, 7.39; I, 26.46. Found: C, 17.32; H, 4.73; N, 14.68; Cl, 7.40; I, 26.38.

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[1] From the Ph.D. Dissertation of V. M. Kothari, The Ohio State University, 1966.

[2] J. Meisenheimer, *Ann.*, **438**, 217 (1924).

[3] N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **39**, 1257 (1966).

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[9] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[10] M. D. Alexander and D. H. Busch, *ibid.*, **5**, 602 (1966).

[11] M. D. Alexander and D. H. Busch, *ibid.*, **5**, 1590 (1966).

[12] The term *flexidentate* indicates that the ligand is capable of chelating in more than one way; *e.g.*, tridentate, three bidentate forms and three monodentate modes.

[13] *Cf.* W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, **80**, 3191 (1958).

[14] J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

Preparation of Ethyl-L-cysteinatobis(ethylenediamine)cobalt(III) Iodide.—The procedure employed for this preparation was analogous to the previous one. The dark brown solution containing 1.42 g (0.005 mol) of *trans*-$[Co(en)_2Cl_2]Cl$, 0.93 g (0.005 mol) of ethyl-L-cysteine hydrochloride, and 0.40 g (0.01 mol) of sodium hydroxide was maintained at 50° for 30 min. Sodium iodide, 1.50 g, was added and $Co(en)_3^{3+}$, which precipitated upon cooling, was removed by filtration. Addition of 2.00 g of sodium iodide to the filtrate caused the precipitation of the purple-brown crystalline product, which was filtered and washed with a little water and ethanol. The product was recrystallized by dissolving in the minimum amount of hot 1:1 water–ethanol, followed by the addition of 2.00 g of sodium iodide. After washing with ethanol, the purple-brown crystalline complex was dried *in vacuo* over silica gel; yield, 1.44 g (48%). *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2\{SCH_2CH(NH_2)COOC_2H_5\}]I_2 \cdot H_2O$: C, 18.04; H, 4.71; N, 11.69; S, 5.35; I, 42.36. Found: C, 18.29; H, 4.86; N, 11.49; S, 5.39; I, 42.56.

Preparation of S-Methyl-L-cysteinatobis(ethylenediamine)cobalt(III) Iodide.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride (2.84 g, 0.01 mol) was added to a warm solution of S-methyl-L-cysteine (1.35 g, 0.01 mol) and sodium hydroxide (0.40 g, 0.01 mol) in 20 ml of water. The deep purple solution was maintained at 50° for about 30 min; during this time it became reddish brown. Sodium iodide, 2.50 g, was added to the solution and $Co(en)_3^{3+}$ was removed from solution as described previously. After dissolving an additional 2.50 g of sodium iodide in the solution and allowing it to stand at room temperature for 4 hr a deep red tar settled to the bottom of the beaker. The mother liquor was decanted and allowed to stand. A crystalline product was observed in the decanted liquor. This crystalline precipitate and the tar were purified separately by stirring for about 1 hr in hot ethanol and then filtering and washing with absolute ethanol. The infrared spectra of the two materials are identical. These two materials are combined and recrystallized from 1:1 water–ethanol, followed by the addition of sodium iodide. The recrystallized product was filtered and washed with absolute ethanol and dried *in vacuo* over silica gel; total yield before recrystallization, 3.17 g (56%). *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2\{H_3CSCH_2CH(NH_2)COO\}]I_2$: C, 16.94; H, 4.27; N, 12.35; S, 5.65; I, 44.75. Found: C, 17.41; H, 4.58; N, 12.36; S, 5.35; I, 44.37. The brick red product is soluble in water, dimethyl sufoxide, and N,N-dimethylformamide.

Reaction of Cysteinatobis(ethylenediamine)cobalt(III) Iodide with Methyl Iodide.—$[Co(en)_2\{SCH_2CH(NH_2)COO\}]I \cdot H_2O$ (0.20 g) was suspended in 15 ml of a 2:1 mixture of methanol and water, and excess methyl iodide was added with stirring. Stirring was continued for about 10 hr and the reddish orange solution was evaporated to dryness. The tarlike material remaining was stirred in 20 ml of warm absolute ethanol for 2 hr to give the red-orange product. The product was filtered, washed with absolute ethanol, and dried *in vacuo* over silica gel; yield, 0.25 g (95%). *Anal.* Calcd for $[Co(NH_2CH_2CH_2NH_2)_2\{CH_3SCH_2CH(NH_2)COO\}]I_2 \cdot H_2O$: C, 16.52; H, 4.47; N, 11.96; I, 43.38. Found: C, 16.84; H, 4.50; N, 11.84; I, 42.71.

Physical Measurements.—In order to determine the acid strength of $[Co(en)_2\{SCH_2CH(NH_2)COOH\}]ICl$, a potentiometric titration at 25° was performed and the pK_a value of this acid complex was calculated from the plot of milliliters of base *vs.* pH. Assuming activity coefficients of unity, the approximate pK_a value was found to be 3.7.

Molecular weights were determined in water with a Mechrolab vapor-pressure osmometer. The instrument was calibrated with solutions of sucrose, and sample concentrations between 10^{-2} and 10^{-3} *M* were employed.

Molar conductances in water were obtained with an Industrial Instruments, Inc., Model RC 16 conductivity bridge. Measurements were made at 25° and the concentrations of solutions were approximately 10^{-3} *M*.

The infrared absorption spectra from 4000 to 400 cm^{-1} were obtained employing the potassium bromide pellet technique on a Perkin-Elmer Model 337 recording spectrophotometer. The polystyrene spectrum was used for calibration.

Visible spectra were obtained on solutions with a Cary Model 14 recording spectrophotometer equipped with Beckman cortex or quartz cells.

Proton magnetic resonance spectra were obtained with a Varian Model A-60 nuclear magnetic resonance spectrometer.

Deuteration experiments were carried out by dissolving samples of complex in D_2O and subsequently isolating them.

All analyses except those for nitrogen were performed by Galbraith Laboratories, Inc. Most of the nitrogen analyses were performed in our laboratories with a Coleman Model 29 nitrogen analyzer.

Results and Discussion

Previous investigators have reported the isolation and detailed study of cobalt(III) complexes having the formulation $Co(en)_2(\text{amino acid})^{2+}$, in which amino acids such as glycine act as bidentate chelating ligands, coordinating through amino and carboxylate groups. Relatively little has been done with similar derivatives of tridentate ligands even though they offer the additional interesting question of which functional groups are utilized in chelation.

The reactions of *trans*-$[Co(en)_2Cl_2]Cl$ with L-cysteine, S-methyl-L-cysteine, and L-cysteine ethyl ester in aqueous media have resulted in the isolation of the new compounds $[Co(en)_2\{Cy\}]I$, $[Co(en)_2\{SMCy\}]I_2$, and $[Co(en)_2\{OECy\}]I_2$, respectively. The reaction of $[Co(en)_2\{Cy\}]I_2$ with methyl iodide was found to result in the formation of a product closely similar to that obtained from the reaction of *trans*-$[Co(en)_2Cl_2]Cl$ with S-methyl-L-cysteine.

The molecular weight and molar conductance data (Table I) suggest that $[Co(en)_2\{Cy\}]I$ is a uni-univalent electrolyte and $[Co(en)_2\{SMCy\}]I_2$ and $[Co(en)_2\{OECy\}]I_2$ are di-univalent electrolytes. Hence, the molecular weight and conductivity data together with the elemental analyses given in the Experimental Section confirm their formulations.

TABLE I

MOLECULAR WEIGHTS AND MOLAR CONDUCTANCES OF THE COMPLEXES (H_2O, 25°)

Compound	Mol wt		Λ_M, ohm^{-1}	Electrolyte type
	Theory	Found[b]		
$[Co(en)_2\{Cy\}]I \cdot H_2O$	443	439	95	MX
$[Co(en)_2\{HCy\}]ICl \cdot H_2O$	...	...	553	MHX_2
$[Co(en)_2\{OECy\}]I_2 \cdot H_2O$	567	549	209	MX_2
$[Co(en)_2\{SMCy\}]I_2$	585	574	227	MX_2
$[Co(en)_2\{SMCy\}]I_2 \cdot H_2O$[a]	...	...	248	MX_2

[a] Prepared from the reaction of $[Co(en)\{Cy\}]I \cdot H_2O$ with CH_3I. [b] Obtained as a value per ion and multiplied by the number of ions.

Antisymmetric COO stretching frequencies for these cobalt(III) complexes are given in Table II. The infrared spectra provide conclusive evidence as to which groups of the cysteine are coordinated in $[Co(en)_2\{Cy\}]I$. There is no band observed in the 2500-cm^{-1} region (S–H stretching mode) suggesting that the mercaptide group is definitely coordinated at one of two sites. The other site may be occupied by the amino or

TABLE II

ANTISYMMETRIC COO STRETCHING FREQUENCIES (cm^{-1})

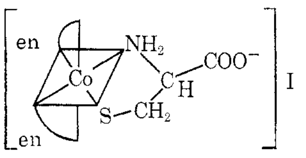
Compound	ν, cm^{-1}	Group
$[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$	1616	$-\text{CO}_2^-$
$[\text{Co(en)}_2\{\text{HCy}\}]\text{ICl}$	1721	$-\text{CO}_2\text{H}$
$[\text{Co(en)}_2\{\text{OECy}\}]\text{I}_2$	1706	$-\text{CO}_2\text{C}_2\text{H}_5$
$[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$	1656	$-\text{CO}_2\text{Co}$
$[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2{}^b$	1652	$-\text{CO}_2\text{Co}$
$[\text{Co(en)}_2\{\text{NH}_2\text{CH}_2\text{CO}_2\}]\text{Cl}_2$	1640^a	$-\text{CO}_2\text{Co}$
cis-$[\text{Co(en)}_2\{\text{NH}_2\text{CH}_2\text{CO}_2\}\text{Cl}]\text{Cl}$	1600^a	$-\text{CO}_2^-$
cis-$\text{Co(en)}_2\{\text{NH}_2\text{CH}_2\text{COOH}\}\text{Cl}^{2+}$	1735^a	$-\text{CO}_2\text{H}$

[a] Reference 13. [b] Prepared from the reaction of $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ with CH_3I.

the carboxylate group. An intense C=O stretching band occurs at 1616 cm^{-1} in the infrared spectrum of $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$. This value is consistent with the presence of free carboxylate ions. For $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ the C=O stretching band occurs at 1656 cm^{-1}, as is typical of coordinated carboxylate groups. The higher frequency for coordinated carboxylate groups is well established.[15-17]

Alexander and Busch[10,11] observed the C=O stretching band at 1640 cm^{-1} in the infrared spectrum of chelated $[\text{Co(en)}_2\text{NH}_2\text{CH}_2\text{COO}]\text{Cl}_2$ complex, and for the monodentate complex *cis*-$[\text{Co(en)}_2\{\text{NH}_2\text{CH}_2\text{COO}\}\text{Cl}]\text{Cl}$, in which an uncoordinated carboxylate group is present, the C=O stretching band was found at 1600 cm^{-1}. Strongly acidic solutions of the complex containing monodentate glycine show a sharp intense band at 1735 cm^{-1}. This is associated with a free carboxylic acid group.

The C=O band in $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ is distinguished from the adjacent NH_2 mode because it is unchanged upon equilibration with deuterium oxide. If $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ is dissolved in acidic solution, a new complex can be obtained. In the infrared spectrum of this complex, a sharp intense band occurs at 1721 cm^{-1}. Since this is the region where C=O stretching bands are observed for cysteine hydrochloride (1742 cm^{-1}) and other α-amino acid hydrochlorides,[18] the presence of the carboxylic acid function is indicated, and structures II and III are assigned for $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ and its hydrochloride $[\text{Co(en)}_2\{\text{HCy}\}]\text{ICl}$, respectively.



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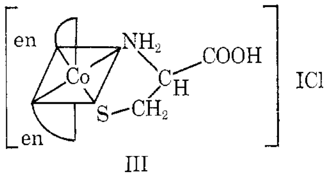


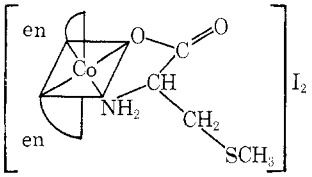
III

The pK_a of the carboxylic function in $[\text{Co(en)}_2\{\text{HCy}\}]\text{ICl}$ is found to be 3.7, indicating it to be a fairly strong acid. Although this pK_a value is in the vicinity of those of some amino acid hydrochlorides, it is not as low as that of cysteine hydrochloride (pK_a = 1.96).[19] This implies that the binding of the mercaptide ion and amino group to cobalt(III) is not as effective at generating acidity in the carboxylic function as is protonation of each group.

The molar conductance of the acid complex is 553 ohm^{-1} (Table I). This is much too high for a di-univalent electrolyte (normal range for 0.001 M solution, 225–270 ohm^{-1})[20] but is not inconsistent with the proposed structure. Since the acid function at 0.001 M concentration is highly dissociated, much of the conductance is due to the proton. (The molar conductance of 0.001 M HCl is 423 $\text{ohm}^{-1}\ \text{cm}^{-1}$.) These observations further confirm the assigned structures for $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ and $[\text{Co(en)}_2\{\text{HCy}\}]\text{ICl}$.

The sharp C=O stretching band at 1656 cm^{-1} in the infrared spectrum of $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ indicates that the carboxylate group is coordinated.[15-18] The carbonyl band is not affected upon deuteration of the amino groups of the complex and, if the complex is isolated from the acidic solution, the CO band is changed very little, <10 cm^{-1}. This further substantiates that the carboxylate group is coordinated in $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$.

The N–H stretching frequencies in $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$, $[\text{Co(en}_2)\{\text{HCy}\}]\text{ICl}$, and $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ are about 100–200 cm^{-1} lower than those for primary amines.[18] Two bands occur at 3100–3200 cm^{-1} (NH_2 stretching region) indicating that the amino groups in these complexes are coordinated. When these compounds are equilibrated with D_2O, the bands at 3100–3200 cm^{-1} are decreased very much in intensity as the amino hydrogens are replaced by deuterium. On deuteration, the NH_2 bending modes which occur at 1555 cm^{-1} in $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ and at 1562 cm^{-1} in $[\text{Co(en)}_2\{\text{Cy}\}]\text{I}$ also disappear. These observations suggest that the amino and carboxylate groups of S-methyl-L-cysteine are coordinated in $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ (IV).



IV

The proton magnetic resonance spectrum of $[\text{Co(en)}_2\{\text{SMCy}\}]\text{I}_2$ (Figure 1) shows two peaks of very similar intensity centered at 143 cps upfield from the water peak. These bands are assigned to the hydrogens of the methyl groups that are bound to sulfur atoms. The occurrence of two bands is probably due to the presence of diastereoisomers. The optical activity of the complex combined with the dissymmetry of natural

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(15) K. Swaminathan and D. H. Busch, *J. Inorg. Nucl. Chem.*, **20**, 159 (1961).

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(18) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 242, 249.

(19) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943.

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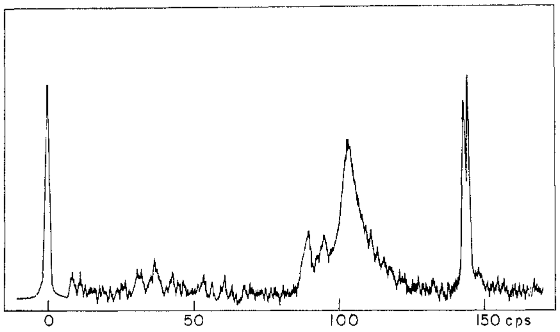


Figure 1.—Pmr spectrum of $[Co(en)_2\{CH_3SCH_2CH(NH_2)COO\}]I_2$ in D_2O.

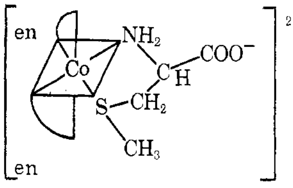
cysteine is responsible for this diastereoisomerism. No attempt has been made to separate these isomers.

The two β-methylene hydrogens of the S-methyl-L-cysteine ring exhibit a doublet in the 85–93-cps region. The single hydrogen on the α-carbon atom shows a multiplet structure (poorly defined) about 53–65 cps upfield from water. The complexity results from the interaction with protons of the β-carbon atom and of the nitrogen. The other peaks in the 25–50-cps region upfield from water are perhaps due to the hydrogens of nitrogen that have not completely exchanged with deuterium. The protons attached to the carbon atoms of the ethylenediamine rings produce a broad resonance at 110 cps upfield from the water resonance. Broad resonance of this nature has been observed for other *cis*- and *trans*-bis(ethylenediamine) complexes of cobalt(III) by Clifton and Pratt[21] and, later, by many other investigations.

$[Co(en)_2\{SMCy\}]I_2$ is also obtained from the reaction of $[Co(en)_2\{Cy\}]I$ with methyl iodide

$$[Co(en)_2\{Cy\}]I \xrightarrow[CH_3OH \atop H_2O]{CH_3I} [Co(en)_2\{SMCy\}]I_2$$

The analytical data confirm the formulation of $[Co(en)_2\{SMCy\}]I_2$, but a slight color difference and small variations in other properties (Tables I–III) suggest a slight contamination or a different isomer distribution. It should be noted that the transformation given in the equation above requires a change in the mode of chelation of the cysteine moiety as a result of the ligand reaction. The bound sulfur atom of the N- and S-chelated $Co(en)_2(Cy)^+$ (II) presumably first acts as a nucleophile to form N- and S-bonded S-methylcysteine (V). This is followed by an isomerization reaction in which the free carboxyl group displaces the thioether from the coordination sphere. This yields the product $Co(en)_2(SMCy)^{2+}$ in its usual structural form (IV).



V

TABLE III
VISIBLE SPECTRAL DATA

Compound	λ_{max}, mμ	$\bar{\nu}$, cm^{-1}	$\epsilon_{0,max}$, M^{-1} cm^{-1}
$[Co(en)_2\{Cy\}]I \cdot H_2O$	600 sh	16,670	43
	490	20,410	128
$[Co(en)_2\{HCy\}]ICl \cdot H_2O$	593 sh	16,860	38
	475	21,050	116
$[Co(en)_2\{OECy\}]I_2 \cdot H_2O$	590 sh	16,950	54
	484	20,660	150
cis-$[Co(en)_2\{NH_2CH_2CO_2\}Cl]Cl$[a]	525	19,050	80
	365	27,400	83
$[Co(en)_2\{SMCy\}]I_2 \cdot H_2O$	483	20,700	101
	345	28,980	162
$[Co(en)_2\{SMCy\}]I_2$[b]	465	21,500	97
	350 sh	28,570	195
$[Co(en)_2NH_2CH_2CO_2]Cl_2$	487	20,530	98
	346	28,900	107

[a] Reference 13. [b] Prepared from the reaction of $[Co(en)_2\{Cy\}]I \cdot H_2O$ with CH_3I.

The reaction of ethyl-L-cysteine with *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride was carried out in the presence of sodium hydroxide. Attempts to carry out the reaction using a weaker base, such as diethylamine (in order to avoid the possible hydrolysis of the ester), were not successful. The formulation and isolation of the complex indicates that the ester group was not removed by the strong base.

In the infrared spectrum of $[Co(en)_2\{OECy\}]I_2$, two bands occur at 3100–3200 cm^{-1}. When the compound is deuterated, these bands decrease in intensity as amino hydrogens are replaced by deuterium. This confirms coordination of the NH_2 group. The band at 1567 cm^{-1} (NH_2 bending mode) also disappears upon deuteration. A sharp intense band also occurs at 1706 cm^{-1} in the infrared spectrum of this complex. This band is assigned to the stretching mode of the carbonyl group of the ester. This is much lower in frequency than that for cysteine ethyl ester hydrochloride (1742 cm^{-1} in our work) and ester complexes of cobalt(III) of the type $Co(en)_2\{NH_2CH_2COOR\}Cl^{2+}$.[10,11]

The proton magnetic resonance spectrum (Figure 2) of $[Co(en)_2\{OECy\}]I_2$ is quite similar to that of $[Co(en)_2(NH_2CH_2CO_2C_2H_5)Cl](NO_3)_2$.[22] The resonance due to the methyl group of the ethyl ester is split by the hydrogens of the adjacent methylene group and produces a triplet at about 200 cps upfield from the water peak. The ethyl methylene group resonance appears as a quartet at about 125 cps upfield from water. This pattern overlaps the broad resonance due to the hydrogens of the ethylenediamine groups. The hydrogens on the methylene group adjacent to the sulfur atom produce a doublet in the 95–110-cps region due to the splitting by the single hydrogen on the carbon adjacent to the nitrogen atom. The strong band at about 45 cps upfield is a spinning side band from the water peak. The single hydrogen on the carbon atom adjacent to the nitrogen atom shows a poorly defined multiplet at 50–58 cps upfield from the water peak. The unex-

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[21] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

[22] D. H. Williams, Ph.D. Dissertation, The Ohio State University, 1964.

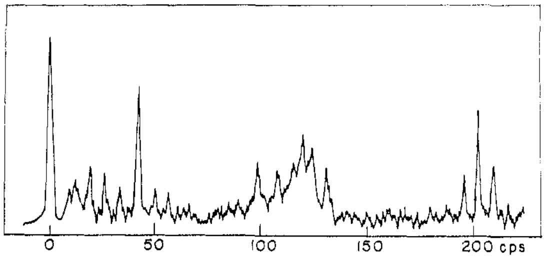
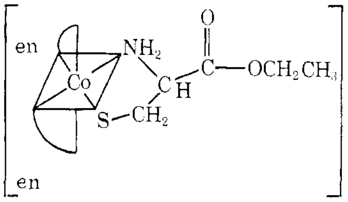


Figure 2.—Pmr (60-Mc) spectrum of $[Co(en)_2\{SCH_2CH_2(NH_2)COOC_2H_5\}]I_2 \cdot H_2O$ in D_2O.

changed amine hydrogens produce a complex resonance pattern in the 0–40-cps region. $[Co(en)_2\{OECy\}]I_2$ is assigned structure VI.



VI

The electronic spectra of these cobalt(III) complexes are also consistent with the structures assigned. Two bands assignable as d–d transitions have been observed for each complex. For the complex which contains a nitrogen–oxygen coordinated cysteine residue, $Co(en)_2\{SMCy\}^{2+}$, the spectrum is typical of those usually found for octahedral coordination, with only a slight dissymmetry to the long-wavelength band. The band at longer wavelength is assigned to the transition $^1A_{1g} \rightarrow {}^1T_{1g}$, and the one at shorter wavelength to $^1A_{1g} \rightarrow {}^1T_{2g}$.[23] The visible spectrum of $[Co(en)_2\{SMCy\}]I_2$ (Table III) is very similar to that of $[Co(en)_2\{NH_2CH_2COO\}]Cl_2$[10,11] which contains glycinate chelated through the amino and carboxylate groups. This supports the conclusion that in $[Co(en)_2\{SMCy\}]I_2$ the coordination of S-methyl-L-cysteine takes place through the amino and carboxylate groups.

The spectra of the complexes $[Co(en)_2\{CY\}]I$, $[Co(en)_2\{HCy\}]ICl$, and $[Co(en)_2\{OECy\}]I_2$ are remarkably similar in band maxima and extinction coefficients (Table III) and in each of these complexes the coordination takes place through the amino and mercaptide groups. The positions of the two d–d transitions reported in Table III are consistent with assignments based on the C_{4v} symmetry approximated by the donor atoms (five nitrogens and one sulfur arrayed octahedrally,) rather than true O_h symmetry.[23,24] The low-energy band (16,600–17,000 cm^{-1}) is assigned to the transition $^1A_{1g} \rightarrow {}^1E_g$, while the band at higher energy is assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$.

In the visible spectrum of $[Co(en)_2\{SMCy\}]I_2$, the d–d transitions occur at 483 and 383 mμ. The bands are higher in frequency than two bands in the visible spectra of *cis*-$[Co(en)_2\{NH_2CH_2COO\}Cl]Cl$, $[Co(en)_2\{Cy\}]ICl$, and $[Co(en)_2\{OECy\}]I_2$ (Table III). This reflects the relative positions of the groups in the spectrochemical series, $-S^- < Cl^- < -CO_2^-$.[25]

The *Dq* values for the mercaptide group in $[Co(en)_2\{Cy\}]I$, $[Co(en)_2\{HCy\}]ICl$, and $[Co(en)_2\{OECy\}]I_2$ and the carboxylate group in $[Co(en)_2\{SMCy\}]I_2$ are calculated assuming C_{4v} symmetry and applying the equations reported by Wentworth and Piper.[24] *Dq* for the carboxylate group was calculated using the value of 20,700 cm^{-1} (unresolved band, Table III) from the spectrum of $[Co(en)_2\{SMCy\}]I_2$, which was resolved into two bands: $\nu_1 = 19{,}930\ cm^{-1}$; $\nu_2 = 21{,}470\ cm^{-1}$. The *Dq* value of 1914 cm^{-1} obtained from calculations for the carboxylate group in $Co(en)_2\{SMCy\}^{2+}$ compares well with the value of 1904 cm^{-1} for the carboxylate group of propionate ion in the $Co(NH_3)_4\{OOCC_2H_5\}_2^{2+}$complex and 2021 cm^{-1} for the carboxylate group of propionate ion in $Co(NH_3)_5\{OOCC_2H_5\}^{2+}$. This indicates that the COO^- group lies between NCS and H_2O in the spectrochemical series.[24] A value of 980 cm^{-1} for the *Dq* of the mercaptide ion in $Co(en)_2\{Cy\}^+$, $Co(en)_2\{HCy\}^{2+}$, and $Co(en)_2\{OEC\}^{2+}$ complexes was calculated using the mean value of 20,707 cm^{-1} for ν_2 and 16,827 cm^{-1} for ν_1. The *Dq* of the mercaptide ion calculated above indicates that the ligand field strength of this function is quite low and that it falls close to iodide in the spectrochemical series. In spite of the low position of mercaptide ion in the spectrochemical series for Co(III), it coordinates strongly.[26] In other cobalt(III) complexes of cysteine,[27] the mercaptide ion is always coordinated and there is a competition between the amine and the carboxylate groups for the other coordination positions.

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