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Preparation and Characterization of Cobalt(III) Complexes of Glycine Esters¹

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Complexes of the formulation $cis\text{-}[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{R})\text{Cl}]\text{Cl}_2$, where en is ethylenediamine and R is methyl, ethyl, or isopropyl, were prepared and characterized using elemental analyses, conductivity measurements, paper chromatography, optical resolutions, and visible and infrared spectral data.

Introduction

It has been known for some time that aliphatic amines react with *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride in aqueous medium to yield complexes of the formulation, $[\text{Co}(\text{en})_2(\text{NH}_2\text{R})\text{Cl}]\text{Cl}_2$, where en is ethylenediamine and R an alkyl group.³ In this laboratory we have found that certain esters of glycine (the methyl, ethyl, and isopropyl esters) react with *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ to yield a series of complexes of the analogous formulation, $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{R})\text{Cl}]\text{Cl}_2$.

In recent years there has been interest in metal ion promoted hydrolysis of amino acid esters, amino acid amides, and polypeptides.⁴ The above-mentioned glycine ester containing complexes have proved useful in elucidating the nature of the hydrolytic process, a matter which is presented in a separate paper.⁵ Herein are described the characterization and some unusual physical properties of these complexes.

Experimental Section

Synthesis of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{R})\text{Cl}]\text{Cl}_2$, Where R is CH_3 , C_2H_5 , and $i\text{-C}_3\text{H}_7$.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride (2.85 g, 0.01 mole) was mixed with the glycine ester hydrochloride (0.01 mole) and made into a paste with 2.5 ml of water using a mortar and pestle. With the mixture being ground continuously, 1.0 ml of diethylamine (0.01 mole) was added. The mixture rapidly turned red as a viscous solution was formed. After a few minutes, the mixture coagulated after which it was filtered. The residue, the crude product, was washed successively with methanol, ethanol (absolute), and ether and was then air dried. The crude product was taken up in a minimum of hot water ($\sim 60^\circ$) and recrystallized on cooling after the addition of a few drops of concentrated hydrochloric acid; yield: $\sim 50\%$.

Anal. (Methyl ester complex was dried at 50° overnight *in vacuo* over $\text{Mg}(\text{ClO}_4)_2$.) Calcd for $\text{Co}(\text{C}_7\text{H}_{23}\text{N}_5\text{O}_2\text{Cl}_3)\cdot\text{H}_2\text{O}$: C, 21.38; H, 6.41; N, 17.84; Cl, 27.14. Found: C, 21.33; H, 6.55; N, 17.26; Cl, 27.02. (Ethyl ester complex was dried under the same conditions except at 25° .) Calcd for $\text{Co}(\text{C}_8\text{H}_{25}\text{N}_5\text{O}_2\text{Cl}_3)\cdot\text{H}_2\text{O}$: C, 23.63; H, 6.69; N, 17.23; Cl, 26.16. Found: C, 23.96; H, 7.10; N, 17.30; Cl, 26.16. (Isopropyl ester complex was dried under the same conditions as the methyl ester complex.)

(1) From the Ph.D. thesis of M. D. A., The Ohio State University, Aug. 1964.

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(3) J. Meisenheimer and K. Kiderlen, *Ann.*, **438**, 212 (1924); J. C. Bailar, Jr., and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).

(4) H. Kroll, *ibid.*, **74**, 2036 (1952); L. Meriwether and F. H. Westheimer, *ibid.*, **78**, 5119 (1956); M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957); J. P. Collman and D. Buckingham, *ibid.*, **85**, 3039 (1963).

(5) M. D. Alexander and D. H. Busch, *ibid.*, in press.

Calcd for $\text{Co}(\text{C}_9\text{H}_{27}\text{N}_5\text{O}_2\text{Cl}_3)$: C, 26.80; H, 6.75; N, 17.39; Cl, 26.46. Found: C, 26.73; H, 6.93; N, 17.26; Cl, 27.09.

Analysis reveals that the methyl ester complex is a monohydrate. The water could not be removed by heating without decomposition of the complex. The anhydrous salt was prepared by dissolution of the hydrate in water followed by precipitation with a large excess of isopropyl alcohol. The anhydrous character was verified by a lack of any bands in the OH stretching region of the infrared spectrum of the complex (Figure 1). Also, a comparison of the visible spectra of the monohydrate and the anhydrous salt indicates that the anhydrous formulation is correct. The bromide salt of the methyl ester complex was prepared by dissolution of the chloride in water followed by precipitation with ammonium bromide. The molar extinction coefficients of the bands in the visible spectrum of the bromide, formulated as being anhydrous, are identical with those of the anhydrous chloride.

Conductivity Measurements.—Measurements were made, using an Industrial Instruments conductivity bridge, upon aqueous solutions of the complexes, 0.0015 M.

Visible Absorption Spectra.—Visible spectra were obtained using a Cary Model 14 recording spectrophotometer equipped with matched 1-cm quartz cells. Aqueous solutions of each complex on which measurements were made were of the concentration: 0.0200 ± 0.0002 g of complex per 10.0 ± 0.02 ml of water.

Infrared Spectra.—Infrared spectra were obtained using a Perkin-Elmer Model 337 double-grating infrared spectrophotometer and a Beckman Model IR-8 grating infrared spectrophotometer. Potassium chloride and potassium bromide disks and Nujol and hexachlorobutadiene mulls were used; hexachlorobutadiene was employed for the regions in the infrared where Nujol absorbs. To prepare a pressed disk, a mixture of complex and potassium halide containing approximately 1% complex was subjected to a pressure of about 25,000 psi for a few seconds using a Carver Model B laboratory press.

Paper Chromatography.—Paper chromatograms were obtained according to the method of Stefanovic and Janjic⁶ using 1×7 in. strips of Whatman No. 1 chromatography paper. Eluting solutions were (1) acetone-water-concentrated hydrochloric acid in the volume ratio 80:10:10 and (2) concentrated hydrochloric acid in 1-butanol saturated with water (5 ml of concentrated HCl/100 ml of solution).

Resolution of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{R})\text{Cl}]\text{Cl}_2$, Where R is C_2H_5 and $i\text{-C}_3\text{H}_7$, into Optical Antipodes.—The method employed is a modification of that used by Werner⁷ to resolve *cis*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]\text{Cl}_2$. Two grams of complex was dissolved in 10 ml of hot water ($\sim 70^\circ$). Four grams of silver (+) α -bromocamphor- π -sulfonate was dissolved in 20 ml of hot water, and the solution was filtered while hot. The two solutions were combined, and after 5 min the silver chloride was removed by filtration. After the filtrate had stood for 20 hr at room temperature, large crystals of the α -bromocamphor- π -sulfonate were

(6) G. Stefanovic and T. Janjic, *Anal. Chim. Acta*, **19**, 488 (1958).

(7) A. Werner, *Ber.*, **44**, 1887 (1911).

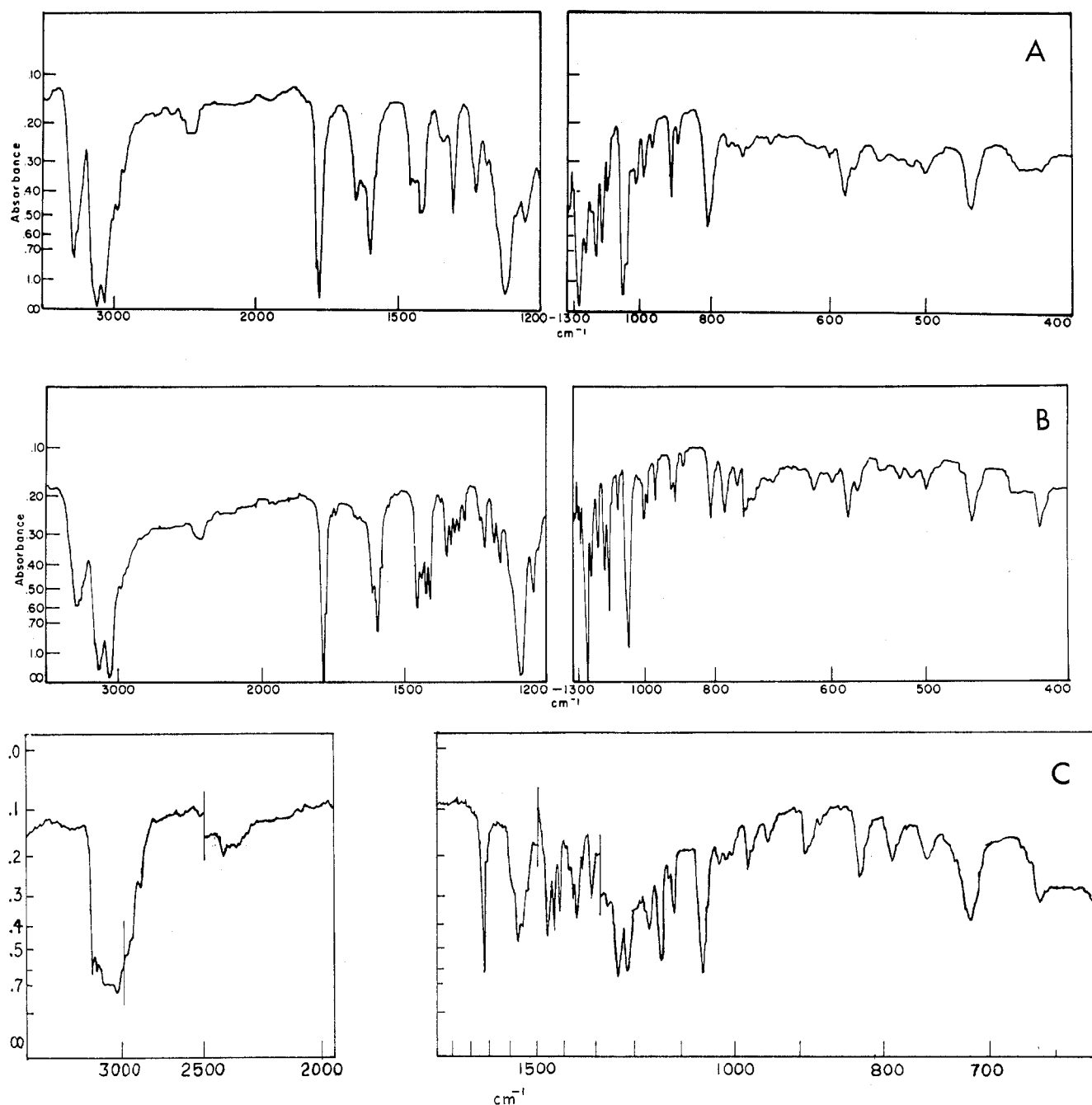


Figure 1.—Infrared spectra of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{CH}_3)\text{Cl}]\text{X}_2 \cdot n\text{H}_2\text{O}$. Spectrum A: $\text{X} = \text{Cl}$; $n = 1$; KCl disk. Spectrum B: $\text{X} = \text{Br}$; $n = 0$; KBr disk. Spectrum C: $\text{X} = \text{Cl}$; $n = 0$; hexachlorobutadiene mull 1300–1500 and 2500–3000 cm^{-1} ; Nujol mull for remainder of spectrum.

filtered off (weight of crystals, 1.0 g). These were dissolved in 15 ml of hot water, and, on standing overnight, crystallization occurred. These crystals were removed by filtration. The α -bromocamphor- π -sulfonate was converted to the chloride by grinding the salt at 0° in ethanol (~ 5 ml) to which concentrated hydrochloric acid (~ 4 ml) had been added. The complex first went into solution and then crystallized as the chloride. Rotations were measured using a Franz Schmidt and Haensch polarimeter upon aqueous solutions of the chlorides (0.026 g/10 ml). Specific rotations: ethyl ester complex, $[\alpha]_{25}^{25}{}_{828.4\text{m}\mu} +75 \pm 5^\circ$; isopropyl ester complex, $[\alpha]_{25}^{25}{}_{828.4\text{m}\mu} +90 \pm 5^\circ$.

Deuteration of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{R})\text{Cl}]\text{Cl}_2$, Where R is C_2H_5 and $i\text{-C}_3\text{H}_7$.—Ten milligrams of complex was dissolved in 0.5 ml of deuterium oxide (the D_2O was previously made basic by adding 1 drop of 0.1 M NaOH solution to 5 ml of D_2O). The solution was allowed to stand for approximately 3 hr and was

then evaporated to dryness over $\text{Mg}(\text{ClO}_4)_2$. The evaporation was complete in 12 hr. The infrared spectrum of the residue revealed exchange of the amino hydrogens by deuterium.

In the isopropyl case, two other deuteration experiments were performed.

(1) In order to exchange the amino hydrogens of the ester before preparation of the complex the following procedure was employed. One-half gram of the ester hydrochloride (0.003 mole) was dissolved in 1 ml of D_2O (0.05 mole). To this was added 0.3 ml of diethylamine (0.003 mole), and the resulting solution was allowed to stand at room temperature for 24 hr. At the end of this period the solution was mixed with 1.0 g of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ to prepare the ester complex. After coagulation, the mixture was filtered; the residue was washed with cold D_2O (0.5 ml) and then dried.

(2) In order to exchange the amino hydrogens of the ethylene-

diamines before preparation of the ester complex, the following procedure was employed. One gram of *trans*-[Co(en)₂Cl₂]Cl was dissolved in 2 ml of D₂O, and to this solution was added 0.3 ml of diethylamine. After standing for 24 hr, 0.5 g of the ester hydrochloride was added to prepare the complex. The coagulant was treated as in the previous experiment. Infrared spectra of the products from the two experiments were essentially indistinguishable.

Results and Discussion

Synthesis.—The method of preparation of the glycine ester containing complexes is identical, with the exception given subsequently, with that used by Bailar and Clapp³ to prepare the unsubstituted amine complexes, [Co(en)₂(NH₂R)Cl]Cl₂. Instead of using the free amine as in Bailar and Clapp's method, the hydrochloride of the ester is employed—the free ester undergoes condensation on standing. The free ester is generated from the hydrochloride *in situ* using the poorly coordinating amine, diethylamine.

Conductivity Studies.—The molar conductance of each of the ester complexes is 220 ± 10 ohm⁻¹ cm.² This is normal for a di-univalent electrolyte (molar conductance of *cis*-[Co(en)₂NH₃Cl]Cl₂ is 230 ohm⁻¹ cm.²). Hence, the conductivity data, together with the elemental analyses given in the Experimental Section, are in accord with the formulation, [Co(en)₂(NH₂-CH₂CO₂R)Cl]Cl₂, for the ester complexes.

Paper Chromatography.—Paper chromatograms were obtained for each of the ester-containing complexes using two eluting solvents: (1) an acetone–water–concentrated hydrochloric acid solution and (2) a 1-butanol–water–concentrated hydrochloric acid mixture. The former has been used to separate *cis*–*trans* isomers of a number of diacidobis(ethylenediamine)-cobalt(III) complexes including the ammine complex, [Co(en)₂NH₃Cl]Cl₂, analogous to the ester complexes.⁶ The latter solution has been employed to separate mixed ethylenediamine–propylenediamine cobalt(III) complexes.⁸ In each case single-spot chromatograms were obtained, which, in considering *cis*–*trans* isomerism, strongly suggest that, for each of the three complexes, the synthetic method employed yields a single isomer.

Visible Absorption Spectra.—Visible spectral data are given in Table I. Included for the purpose of comparison are data for *cis*- and *trans*-[Co(en)₂NH₃Cl]Cl₂ and the analogous methylamine complex, [Co(en)₂(NH₂CH₃)Cl]Cl₂. Two bands are observed in the visible spectrum of each complex. These two bands are assigned to the two spin-allowed d–d transitions commonly observed for octahedral cobalt(III) complexes; *i.e.*, the band at longer wavelength is assigned to the transition, ¹A_{1g} → ¹T_{1g}, and the one at shorter wavelength, ¹A_{1g} → ¹T_{2g}.⁹ From the data of Table I it is seen that the spectra of the three ester complexes are indistinguishable.

A comparison of the spectra of *cis*- and *trans*-[Co(en)₂NH₃Cl]Cl₂ reveals that, although the positions of the

TABLE I
VISIBLE ABSORPTION SPECTRAL DATA FOR [Co(en)₂(NH₂R)Cl]Cl₂

NH ₂ R	λ _{max} ± 2, mμ	ε _{max} ± 1, M ⁻¹ cm ⁻¹
<i>cis</i> -NH ₃	525 ^a	73 ^a
	365	77
<i>trans</i> -NH ₃	525 ^a	47 ^a
	367	53
NH ₂ CH ₃ ^b	526	77
	366	84
NH ₂ CH ₂ CO ₂ CH ₃	525	77
	367	82
NH ₂ CH ₂ CO ₂ C ₂ H ₅	525	77
	367	82
NH ₂ CH ₂ CO ₂ - <i>i</i> -C ₃ H ₇	525	77
	367	82

^a R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

^b Prepared according to the method of Bailar and Clapp.³

bands are essentially the same in both cases, the intensities of the bands in the spectrum of the *trans* isomer are considerably less than in that of the *cis* isomer. On comparing the spectra of these two complexes to those of the ester-containing complexes, it is seen that there is a close resemblance between the spectra of the latter and that of *cis*-[Co(en)₂NH₃Cl]Cl₂. This is a strong indication of the *cis* configuration for each of the ester complexes. The complexes containing the ethyl and isopropyl esters have been resolved into optical antipodes *via* the (+)-α-bromocamphor-π-sulfonate salts, thus proving the presence of the *cis* isomers for these two complexes and supporting the contended *cis* configuration in the methyl case.

Bailar and Clapp³ have presented evidence suggesting that the methylamine complex which they prepared, [Co(en)₂(NH₂CH₃)Cl]Cl₂, has the *cis* configuration. The marked similarity between the spectrum of this complex and those of the ester complexes is in support of their contention.

The formulation of the ester complexes as [Co(en)₂(NH₂CH₂CO₂R)Cl]Cl₂ suggests that the glycine ester is functioning simply as an amine. The similarity between the visible spectra of the ester complexes and that of the methylamine complex clearly supports this notion since the ligand field about the metal ion must be essentially the same in both cases.

Infrared Spectra.—In the infrared spectrum of each of the ester complexes there appears a very sharp and intense band at 1745 ± 5 cm⁻¹ which is attributed to the stretching mode of the carbonyl group of the ester. This is slightly higher in frequency than for the uncoordinated esters but lies within five wavenumbers of the carbonyl stretching band for the ester hydrochloride. The higher frequency in the hydrochloride case has been attributed to the presence of the positive charge on the amino group;¹⁰ and since a similar situation exists for the esters coordinated to cobalt(III), the higher frequency is expected. The position of the carbonyl band is then in accord with the previously mentioned contention that the ester is functioning simply as an amine.

(8) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963).

(9) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 259.

(10) L. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

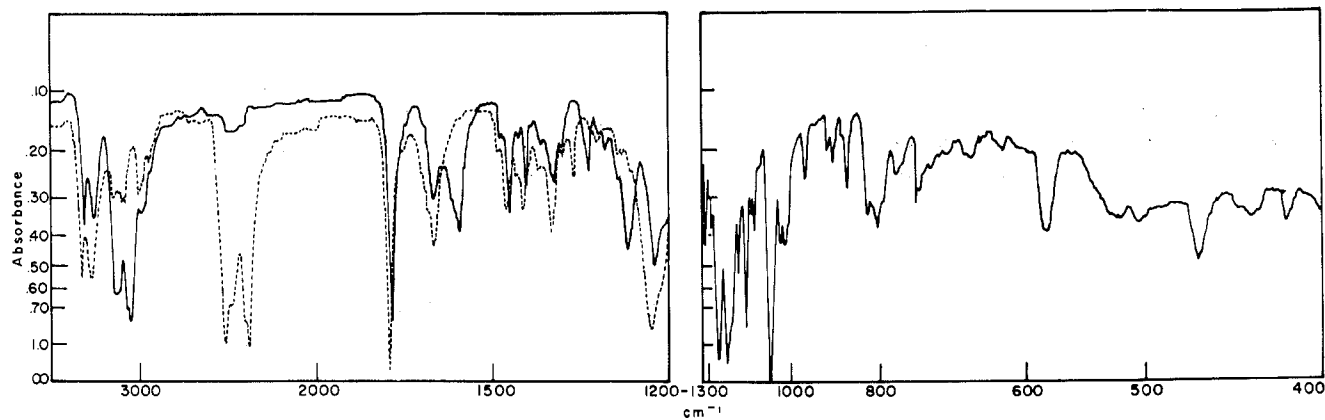


Figure 2.—Infrared spectrum of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5)\text{Cl}]\text{Cl}_2$ (dashed spectrum is that of the deuterated sample).

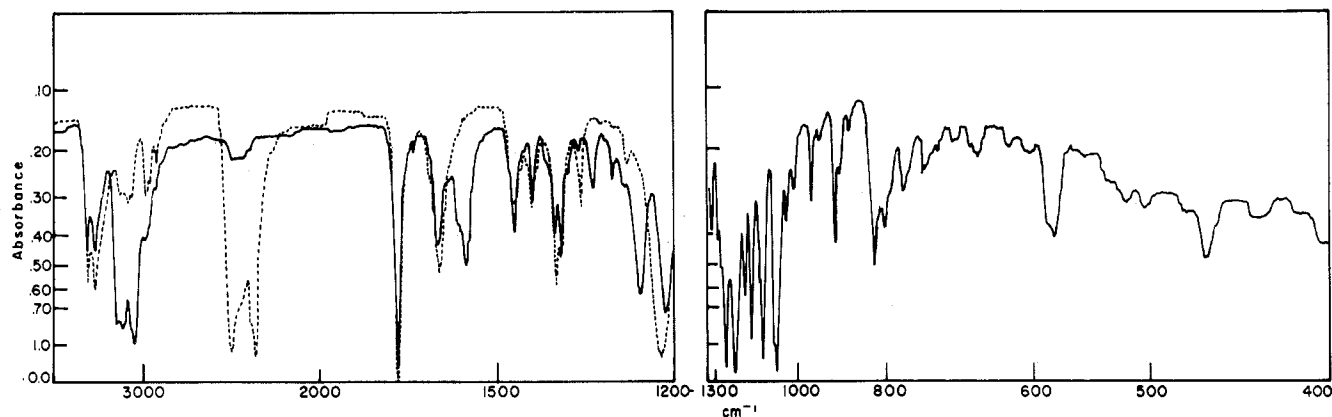


Figure 3.—Infrared spectrum of $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{-}i\text{-C}_3\text{H}_7)\text{Cl}]\text{Cl}_2$ (dashed spectrum is that of the deuterated sample).

For the complex containing the methyl ester of glycine, three different spectra have been obtained; these are shown in Figure 1 and are denoted A, B, and C. Spectrum A, which is that of chloride monohydrate salt, $[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CO}_2\text{CH}_3)\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, in a pressed potassium chloride disk, is indistinguishable from the spectrum of the salt in a Nujol-hexachlorobutadiene mull. However, the spectrum of the chloride monohydrate in a pressed potassium bromide disk is different from A and identical with spectrum B which is that of the bromide salt of the complex in a pressed potassium bromide disk. The spectra of the bromide salt in both a KCl disk and a mull are identical with spectrum B. The mull spectrum of the anhydrous chloride salt of the complex, spectrum C, is identical with the spectrum of the salt in a KCl disk, but the spectrum of the salt in a KBr disk is identical with spectrum B.

Since the spectra of the chloride salts in KCl disks and of the bromide salt in KCl and KBr disks are identical with the spectra of the corresponding mulls, it appears that the disks consist of crystals of the salts dispersed in the potassium halide. However, the data indicate that for the chloride salts in KBr disks this is not the case; the identity of the disk spectra of the chloride salts with the mull spectrum of the bromide salt of the complex suggests that the conditions under which the disks were prepared brings about a reaction of the chlorides with KBr to yield crystals of the bromide dispersed in the KBr. Reactions of salts with

alkali halides similar to this have been observed previously in other systems; *e.g.*, ammonium bromide phases are produced when ammonium halides are pressed into sodium bromide disks.¹¹

In the infrared spectra of the complexes containing the ethyl and isopropyl esters, there are some interesting features which merit attention. The spectra are shown in Figures 2 and 3. The only regions where there are definite differences between the two are 1350–1500 cm^{-1} (CH_2 bending region) and 850–1150 cm^{-1} (CH_2 twisting and rocking region). In the spectra of both, two sharp bands of nearly equal intensity occur at 3400–3600 cm^{-1} . When these two compounds are deuterated, the bands at 3100–3200 cm^{-1} (NH_2 stretching region) decrease very much in intensity as amino hydrogens are replaced by deuterium. However, the bands at 3400–3600 cm^{-1} undergo no change. If the ester group is deuterated before preparation of the complex and the preparation is carried out in D_2O , again the bands at 3100–3200 cm^{-1} become weak, but the bands at 3400–3600 cm^{-1} show no change. Also, if the *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ is deuterated before preparation of the ester complex, the same thing is observed.

In the spectra of both the ethyl and isopropyl ester complexes there exist bands at 1640 and 1570 cm^{-1} . On deuteration, the band at 1640 cm^{-1} remains unchanged, but the band at 1570 cm^{-1} disappears.

In the region, 3400–3600 cm^{-1} , OH stretching modes
(11) W. A. Pleskin and R. P. Eischens, *J. Phys. Chem.*, **59**, 1156 (1955).

are usually found, while the band at 1640 cm^{-1} is in the OH asymmetric deformation region. However, the fact that the bands at $3400\text{--}3600$ and 1640 cm^{-1} are not affected by deuteration indicates that the bands are not due to lattice water. Furthermore, it is possible to remove the lattice water by heating; the spectra of the dehydrated complexes still contain the bands at $3400\text{--}3600$ and 1640 cm^{-1} proving that they do not arise from lattice water vibrations.

The bands could possibly be due to NH_2 stretching and deformation modes even though NH_2 bands are normally found at lower frequencies than these. However, the deuterium-exchange experiments throw considerable doubt on this possibility.

An alternative hypothesis is that the bands arise

from CH_2 vibrations. The bands are much higher in frequency than would be expected for normal CH_2 groups, which necessitates that the methylene groups be in a very unusual environment. If the bands arise from vibrations of the methylene in the glycine residue, then, as a result of the bulkiness of the ester group, the complex might exist in a conformation in the crystal lattice whereby the methylene hydrogens are forced into a very crowded environment about the metal. Such a condition might increase the stretching and deformation frequencies significantly.

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Normal and Mixed-Ligand Chelates of Vanadyl(IV) with Schiff Bases

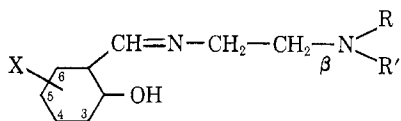
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Vanadyl(IV) chloride reacts with ring-substituted salicylaldehydes and N-substituted ethylenediamines to form two series of compounds, normal or mixed-ligand chelates, according to the nature of substituents at the nitrogen ethylenediamine atom. Visible spectra suggest a five-coordinate structure for normal complexes, resulting from coordination of two Schiff bases acting bidentately around a vanadyl unit, and a hexacoordinate structure for mixed-ligand complexes, resulting from coordination of a salicylaldehyde group and a Schiff base acting tridentately around a vanadyl unit.

Introduction

Previous papers from this laboratory have dealt with the complexing ability of Schiff bases of the general formula



formed from ring-substituted salicylaldehydes and N-substituted ethylenediamines, toward the bivalent metals of the first transition series.¹ With nickel(II) and cobalt(II), ligands of this type behave in a bi- or tridentate manner, according to the nature of substituents R, R', X and the chelated atom, forming planar, octahedral, tetrahedral, or pentacoordinate complexes.

In the present paper we intend to study the behavior of these ligands and of the parent salicylaldehydes with the vanadyl(IV) ion. It has been found that according to the nature of the substituents R and R' two different types of complexes are obtained: (1) complexes with the general formula $[\text{X-SALen-N}(\text{R})\text{R}']_2\text{VO}$, in which the vanadium is linked to two Schiff bases; (2) com-

plexes with the formula $[(\text{X-SAL})(\text{X-SALen-N}(\text{R})\text{R}')\text{VO}]$, in which the vanadium is linked to only one Schiff base and to a salicylaldehyde group. Seventeen compounds of these two series have been prepared and characterized. Their electronic spectra and magnetic susceptibilities have been measured and the results are discussed in order to obtain information on the stereochemistry of the compounds, in the solid state as well as in solution.

Experimental Section

Preparation of the Compounds. Compounds with N- or N,N-Substituted Salicylideneethylenediamines.—These were prepared by the following general method: a syrupy aqueous solution of VOCl_2 (3.6 ml, ca. 0.01 mole) was added to a solution of 0.02 mole of X-salicylaldehyde and 0.02 mole of N- or N,N-substituted ethylenediamine. Sodium acetate (0.02 mole) was then added and the solution was heated under reflux on a water bath for 10 min to 1 hr, depending on the compound. In some cases a product separated immediately from the solution; in other cases, however, a few milliliters of water was added to start the precipitation. The compounds of type 1 can generally be recrystallized without taking particular precaution against oxidation.

In the preparation of complexes with R, R' alkyl groups, except in the cases in which $\text{X} = 5,6\text{-benzo}$, it was necessary to filter the solution of the reagents in order to eliminate a green precipitate which was formed immediately, and then evaporate the filtered solution at moderate temperatures under vacuum. For the compound with $\text{X} = \text{H}$, $-\text{N}(\text{R})\text{R}' = -\text{N}(\text{CH}_2)_3$ (piper-

(1) (a) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965); (b) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965); (c) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965).