a large number of bond properties for polyatomic molecules. With due consideration to its limitations, its use as a tool for elucidating other problems seems justified.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY]

The Properties and Infrared Absorption Spectra of Complexes of Cobalt(III) with Pentadentate Ethylenediaminetetraacetic Acid and Hydroxyethylethylenediaminetriacetic acid

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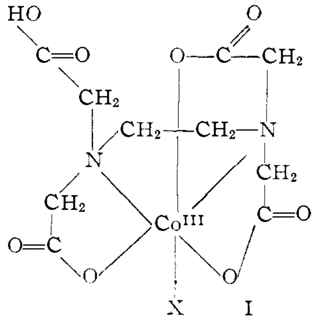
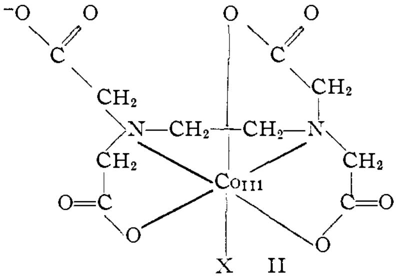
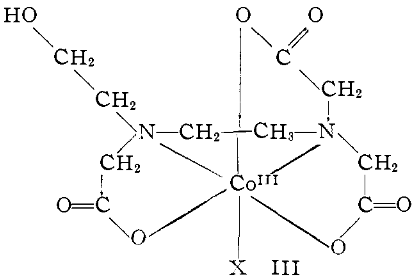
A series of complex compounds containing pentadentate ethylenediaminetetraacetic acid and pentadentate hydroxyethylethylenediaminetriacetic acid have been prepared and characterized. These compounds have the general formulas Na[Co(HY)X] and Na[Co(YOH)X], respectively, where Y represents the tetranegative anion of the first-named ligand, YOH represents the trinegative anion of the second ligand, and X is Cl^-, Br^- or NO_2^-. In addition to the acid salts of the complexes of ethylenediaminetetraacetic acid, the neutral salts, $Na_2[Co(Y)X]$, have been prepared. The infrared spectra of the complexes have been measured and interpreted in considerable detail. The structures of the complexes as inferred from their chemistries have been found to be compatible with the spectral data. It has also been shown that the study of infrared spectra should generally make possible the identification of complexed carboxyl groups and carboxylic acid groups in the presence of each other, while the distinction between complexed carboxyl groups and free carboxylate ions may be definitive only when the metal ion has a great tendency to form covalent bonds.

Cobalt(III) complexes of pentadentate ethylenediaminetetraacetic acid were first prepared by Schwarzenbach.[1] He reported a number of compounds of the general formula $M^I[Co(HY)X]$, where M^I is an alkali metal ion, Y is the tetranegative anion of ethylenediaminetetraacetic acid, and X is Br^- or NO_2^-. The conclusion that the polyfunctional ligand is pentadentate in these compounds was based on chemical studies. His conclusion was substantiated by the study of the C=O stretching vibrations in the infrared spectra of the compounds by Busch and Bailar.[2] The structure of this type of anion is shown below (I).


I

The corresponding compound in which the monodentate group is chloride ion has now been prepared, and, in addition, the "neutral" salts (structure II), $Na_2[Co(Y)X]$, have been prepared for the same series of monodentate groups X. A third related series of compounds involving hydroxyethylethylenediaminetriacetic acid also has been prepared. These may be represented by the general formula Na[Co(YOH)X], where YOH is the trinegative anion of hydroxyethylethylenediaminetriacetic acid and the remaining symbols have the same meaning as given above (structure III).


II


III

In structures I, II and III, the two nitrogen atoms and three carboxyl groups are coördinated to the cobalt(III) ion and the sixth functional group of the hexafunctional organic molecule is free. The only variation indicated by these three structures is in the nature of the unattached group.

In recent years, infrared spectroscopy has received considerable attention as a tool in the determination of the structures of complex inorganic compounds. Because of experimental difficulties, the application has been restricted, for the most part, to the study of organic functional groups and the effect which complex formation has on these groups. The carboxyl group has been the subject of several studies of this kind. The first work along this line was carried out by Douville, Duval and Lecompte[3] on the oxalato complexes of several

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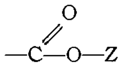
[1] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

[2] D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953).

[3] F. Douville, C. Duval and J. Lecompte, *Compt. rend.*, **212**, 697 (1941).

metal ions. The study of the complexes formed by the oxalate ion has been extended recently by Sen.[4] As a result of the investigation of the metal complexes of glycine, Sen, *et al.*,[5] concluded that the link between the carboxylate group and a metal ion is largely ionic. A somewhat different view has been expressed by other investigators.[2,6,7] According to this point of view, it is supposed that, if a carboxyl group is linked to some group Z (structure IV)


IV

the carboxylate resonance will increase as the ionic character of the O–Z link increases. Since an increase in carboxylate resonance imparts enhanced single-bond character to the carbonyl group, it also causes a lowering of the frequency of the C=O stretching vibration. In consequence, the C=O stretching frequency provides some information relating to the ionic character of the bond. On this basis, it has been possible to distinguish between a carboxyl group bound to a proton and a carboxyl group bound to a metal ion.[2,6] This application is re-ëxamined and improved in the discussion to follow. As is shown in structure II, a carboxyl group might also be present as an uncomplexed carboxylate ion. It has recently been suggested that uncomplexed carboxylate groups may be distinguished from complexed carboxyl groups on the basis of the sharpness of the carbonyl absorption band.[7] The studies summarized below demonstrate the applicability of infrared spectral correlations to this problem and point out certain limitations which are inherent in this technique. The infrared absorption bands of the coördinated nitro group, as reported in previous investigations, are also verified by the spectra of the compounds under consideration.

Experimental

Infrared Spectra.—The infrared spectra were obtained on solid samples of the compounds in potassium bromide discs.[8] The measurements were made with a Perkin–Elmer Model 21 Recording Spectrophotometer equipped with a sodium chloride prism.

Preparation of Sodium Hydrogen Chloro-(ethylenediaminetetraacetato)-cobaltate (III) 1/2-Hydrate.—Ten grams of disodium dihydrogen ethylenediaminetetraacetate was dissolved in 75 ml. of distilled water. To this solution 2.15 g. of sodium hydroxide, 6.37 g. of cobalt(II) chloride 6-hydrate and 12 ml. of glacial acetic acid were added. The solution was cooled to 0°, chlorine was passed through it for approximately six hours, and it was allowed to stand overnight. Upon filtering, a blue crystalline product was obtained. It was recrystallized from water, washed several times with absolute ethanol, and dried *in vacuo* at 50°.

Anal. Calcd. for $Na[Co(C_{10}H_{13}O_8N_2)Cl]\cdot{}^1/_2H_2O$: C, 28.90; H, 3.40; N, 6.74. Found: C, 29.02; H, 3.64; N, 6.90.

Preparation of Sodium Chloro-(hydroxyethylethylenediaminetriacetato)-cobaltate (III) 1.5 Hydrate.—Twelve grams of cobalt(II) chloride 6-hydrate and 17.2 g. of trisodium hydroxyethylethylenediaminetriacetate were dissolved in 75 ml. of distilled water and the solution was cooled to 0°. Chlorine was passed into the solution for approximately ten hours and the solution was allowed to stand overnight. A finely divided purple product was obtained by the addition of absolute ethanol. Since this product tends to convert into a tar upon standing in the air, it was immediately placed in a desiccator. After drying, the product was washed several times with absolute ethanol and redried *in vacuo* over P_2O_5.

Anal. Calcd. for $Na[Co(C_{10}H_{15}O_7N_2)Cl]\cdot 1.5H_2O$: C, 28.62; N, 6.68; H, 4.34. Found: C, 28.84; N, 6.64; H, 4.44.

Preparation of Sodium Nitro-(ethylenediaminetetraacetato)-cobaltate(III) 1-Hydrate.—This compound was prepared by the method of Schwarzenbach.[1] The analysis for the sample used here was reported in reference 2.

Preparation of Sodium Nitro-(hydroxyethylethylenediaminetriacetato)-cobaltate(III).—This substance was prepared by a method similar to that given by Schwarzenbach[1] for the compound above. Twenty-four grams of cobalt(II) chloride 6-hydrate in 100 ml. of distilled water was mixed with a solution of 34.7 g. of trisodium hydroxyethylethylenediaminetriacetate. Fifteen grams of sodium nitrite and, after cooling to 0°, 70 ml. of glacial acetic acid were added. The solution was allowed to stand overnight, whereupon crystallization took place. The brick-red product was purified by recrystallization from water and dried at 150°.

Anal. Calcd. for $Na[Co(C_{10}H_{15}O_7N_2)NO_2]$: N, 10.42; H, 3.75; C, 29.79. Found: N, 10.32; H, 3.84; C, 29.77.

Preparation of Sodium Bromo-(hydroxyethylethylenediaminetriacetato)-cobaltate(III) 1-Hydrate.—Seventeen and two-tenths grams of trisodium hydroxyethylethylenediaminetriacetate and 12 g. of cobalt(II) chloride 6-hydrate were dissolved in 75 ml. of distilled water and the solution was cooled to 5°. A solution of 4 ml. of bromine in 10 ml. of glacial acetic acid was added and the resulting solution was stirred for approximately 12 hours. The bright violet color gradually changed to blue and a bluish green precipitate formed. This product was isolated by filtration and purified by dissolving in water and precipitating with ethanol. The precipitate was filtered, washed with absolute ethanol until the washings were colorless, and dried *in vacuo* at 80° over P_2O_5. *Anal.* Calcd. for $Na[Co(C_{10}H_{15}O_7N_2)Br]\cdot H_2O$: C, 26.39; H, 3.77; N, 6.16. Found: C, 26.88; H, 3.41; N, 6.12.

Preparation of Disodium Nitro-(ethylenediaminetetraacetato)-cobaltate(III) 1-Hydrate and Disodium Chloro-(ethylenediaminetetraacetato) - cobaltate(III).—One and twenty two hundredths grams of sodium hydrogen nitro-(ethylenediaminetetraacetato)-cobaltate(III) 1-hydrate was dissolved in 50 ml. of distilled water and 27.1 ml. of 0.1 *N* sodium hydroxide was added while the solution was stirred. Immediately after the addition of the sodium hydroxide, absolute ethanol was added in order to precipitate the product. After filtering, the product was washed with absolute ethanol and anhydrous ether, and dried *in vacuo* over P_2O_5. (The chloro compound was prepared in the same manner beginning with the corresponding chloro complex.)

Anal. Calcd. for $Na_2[Co(C_{10}H_{12}N_2O_8)NO_2]\cdot H_2O$: C, 26.27; H, 3.09; N, 9.19. Found: C, 26.54; H, 3.12; N, 9.25. Calcd. for $Na_2[Co(C_{10}H_{12}N_2O_3)Cl]$: C, 28.02; H, 2.82; N, 6.54. Found: C, 27.94; H, 3.15; N, 6.50.

Results and Discussion

Chemical Properties of the Complex Compounds.—The colors of the complex salts are dependent in all cases on the nature of the monodentate group X. They are NO_2^-, brick-red; Br^-, blue-green; and Cl^-, blue. The colors of the complex anions are not altered by removal of the proton from the uncomplexed carboxyl group to form the neutral salts in the case of the complexes with ethylenediaminetetraacetic acid, *i.e.*, the salts Na $[Co(HY)NO_2]$ and $Na_2[Co(Y)NO_2]$ are identical in color. This observation extends to the complexes of the second ligand, hydroxyethylethylenediaminetriacetic acid, which coördinates through the same set of donor atoms as are used by pentadentate ethylenediaminetetraacetic acid; however, in this case an uncoördinated hydroxy ethyl group re-

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(4) D. N. Sen, thesis, Notre Dame University, 1953.

(5) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

(6) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 716 (1956).

(7) S. Kirschner, *ibid.*, **78**, 2372 (1956).

(8) M. M. Stimson and M. J. O'Donnell, *ibid.*, **74**, 1805 (1952).

TABLE I

INFRARED ABSORPTION OF COBALT(III) COMPLEXES CONTAINING PENTADENTATE LIGANDS[a]

	Compound	(H_2O or ROH)	–CH	Carboxyl group 1 (–OH)	 2 (–COOH)	 3 (COO–M)	 4 (COO^-)	 5 (COOH)	NO_2 group 1	 2	 3	–CH_2–OH
1	$Na[Co(HY)NO_2]\cdot H_2O$	3540	3040(W)	2600–2800 (vW)	1745(M)	1650(S)	......	1228(M)	1415(M)	1343(M)	833(W)	..
2	$Na_2[Co(Y)NO_2]\cdot H_2O$	3580	3040(W)	....	......	1650(S)	1604(M)	......	1408(M)	1343(M)	833(W)	..
3	$Na[Co(HY)Cl]\cdot{}^1/_2H_2O$	3540	3080(W)	2500–2700 (vW)	1750(M)	1650(S)	......	1228(M)	......	......	.....	..
4	$Na_2[Co(Y)Cl]$	3580	3040(vW)	....	......	1648(S)	1600 (M,sh)	......	......	......	.....	..
5	$Na[Co(YOH)NO_2]$	3610	3040	....	......	1652(S)	......	......	1408(M)	1342(M)	833(W)	1080
6	$Na[Co(YOH)Cl]\cdot 1^1/_2 H_2O$	3580	3080(W)	....	......	1658(S)	......	......	......	......	.....	1030 1070
7	$Na[Co(YOH)Br]\cdot H_2O$	3640 3560	3040(W)	....	......	1654(S)	......	......	......	......	.....	1032 1070

[a] Explaining the abbreviations used in the table: Y, ethylenediaminetetraacetate anion; YOH, hydroxyethylethylenediaminetriacetate anion; v, very; W, weak; M, moderate; S, strong; sh, shoulder.

mains rather than the free carboxyl group. Thus, the salts Na[Co(YOH)X] have the same colors as the corresponding Na[Co(HY)X] salts.

The solubilities of the complex salts are profoundly affected by the nature of the free group. The salts containing a free carboxylic acid group are relatively simple to crystallize and may generally be caused to crystallize by the addition of a strong acid to their solutions. In contrast, the salts having a free hydroxyethyl group are very soluble and, in the case of the chloro complex, may be obtained in the solid form only by the use of mixed solvents or by evaporating to dryness. The latter procedure is often complicated by the deposition of the complex as a tar-like film. The effect of the monodentate anion X also appears very distinctly in the solubilities, especially in the case of the compounds of the formula Na[Co(YOH)X]. Whereas the chloro complex presents considerable difficulty in its crystallization, the corresponding bromo complex has a solubility low enough to permit its isolation from concentrated aqueous solution in crystalline form. The related nitro complex exhibits a convenient solubility in water, undergoing crystallization without difficulty.

The stabilities of the complex anions toward displacement of the group X are functions of both the nature of X and the nature of the uncomplexed functional group of the pentadentate ligand. The largest single factor affecting this stability appears to be the nature of the monodentate group. The nitro complexes may be kept in solution for weeks with no chemical evidence of such reactions occurring while the chloro and bromo complexes undergo change, either to aquo or hydroxo complexes containing the pentadentate ligand or to the complex containing the ligand as a hexadentate chelating agent. The nature of the free functional group of the pentadentate ligand appears to affect the stability toward these substitution reactions since the reactions of the complexes $[Co(Y)Br]^=$ and $[Co(Y)Cl]^=$ appear to be faster than those of $[Co(YOH)Br]^-$ and $[Co(YOH)Cl]^-$. It should be noted that this is probably related to the coördinating ability of the uncomplexed functional group.

Infrared Spectral Studies.—In Table I, assignments are given for eleven absorption bands which are of diagnostic value in the study of the structures of these and similar compounds. The bands of primary concern are those associated with the carboxyl group. Five absorptions are considered in this connection, and three of these appear only in the case of the *carboxylic acid* group. These are the bands of 2600–2800 cm.$^{-1}$ (–OH stretch), 1700–1750 cm.$^{-1}$ (C=O stretch), and 1228 cm.$^{-1}$. The first band (2600–2800 cm.$^{-1}$) is very weak and therefore more limited in usefulness than the other two bands. The C=O stretching vibration is, of course, present in the spectrum of the carboxyl group regardless of the manner in which it may be bonded, and it is this same vibration which gives rise to two of the regions of absorption not associated with the carboxylic acid group. The third band (1228 cm.$^{-1}$) appears to be unambiguously associated with the carboxylic acid group, as is witnessed by its presence in both complexes which contain the functional group and its absence from the other spectra. From Table I, it is seen that the compounds formulated as Na[Co(HY)X] both show these three bands, thus demonstrating the presence of the free carboxylic acid group.[2]

The two remaining bands associated with the carboxyl group are both manifestations of the C=O stretching vibration. The first of these (1648–1658 cm.$^{-1}$) arises from the complexed carboxyl group as is indicated by its presence in the spectra of all of the complexes reported. This band shows little variation in its frequency in this series of cobalt(III) complexes.

The preceding correlations have been discussed, in part, previously[2,6]; however, the fifth region of absorption has not been considered in connection with complex compounds of cobalt(III) with ligands of this kind. This band is associated with the C=O stretching vibration of the uncomplexed carboxylate ion. The structures of the compounds having this group (lines 2 and 4, Tables I and structure II) are inferred from the known structures of the starting materials from which they are prepared, from the simple reactions leading to their formation and from their properties as described above.

$$[Co(HY)X]^- + OH^- \longrightarrow [Co(Y)X]^= + H_2O$$

On the basis of correlations appearing in the literature,[9] the carboxylate ion is expected to absorb in the region from 1550 to 1600 cm.$^{-1}$. The compounds of general formula $Na_2[Co(Y)X]$ would, therefore, be expected to exhibit two ab-

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[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 6.

sorption bands, one in the region around 1650 cm.$^{-1}$ corresponding to the complexed carboxyl group and a second in the region from 1550 to 1600 cm.$^{-1}$ arising from the free carboxylate ion. Furthermore, if the inferred structures of these compounds are correct, there should be three complexed carboxyl groups and one free carboxylate group so that the 1650 cm.$^{-1}$ band should be much more intense than the band in the range 1550 to 1600 cm.$^{-1}$.

In Table I, two such bands are reported for the compound $Na_2[Co(Y)NO_2]$, and the relative intensities vary in the manner expected. This compound therefore provides an ideal demonstration of the identification of a free, ionic carboxylate group in a compound which contains complexed carboxyl groups. The certainty of this conclusion is enhanced by the assignment of all the bands not found in most of the other complex compounds listed in Table I to the nitro group, in accord with previous reports[10,11] on the positions of the bands of complexed nitro groups and with the spectra of the other nitrite-containing complexes reported here (compare lines 1, 2 and 5 of Table I). Along with the appearance of the moderately strong 1604 cm.$^{-1}$ band, the three bands associated with the carboxylic acid group vanish (compare lines 1 and 2 of Table I), thus further confirming the conclusion.

The second compound studied in connection with the uncomplexed carboxylate ion is $Na_2[Co(Y)Cl]$. In this case, it is also obvious that no carboxylic acid group is present since the three bands identifying the group in $Na[Co(HY)Cl]$ do not appear in the spectrum of the neutral salt. However, the C=O stretching vibrations are not split distinctly into two bands. Instead, a single strong band appears at 1648 cm.$^{-1}$, and this band has a rather well developed shoulder of moderate intensity at 1600 cm.$^{-1}$. In light of the absence of ambiguity in the preceding case, it is quite logical to assign these bands to the C=O of the three complexed carbonyl groups and the C=O of a single carboxylate ion, respectively.

The spectra of the cobalt(III) complexes of hydroxyethylethylenediaminetriacetic acid provide further substantiation for the interpretations set forth above. These compounds, which are of the general formula $Na[Co(YOH)X]$, presumably have the structure shown in III above. This structure involves three complexed carboxyl groups but neither free carboxylic acid nor uncomplexed carboxylate ion. The data given in Table I reveal that only one of the absorption bands derived from carboxyl groups appears in their spectra, and this is the band at approximately 1650 cm.$^{-1}$ which arises from the complexed carboxyl group. The band is sharp and symmetrical. The absorptions of the nitro group in $Na[Co(YOH)NO_2]$ are also reported in Table I, and bands in the range from 1030 to 1085 cm.$^{-1}$ have been assigned to the $-CH_2OH$ group.[9]

In the discussion immediately preceding, positive evidence has been given to show the feasibility of detecting complexed carboxyl groups and uncomplexed carboxylate ions in the presence of each other. It has been shown that separations as great as 46 cm.$^{-1}$ may exist between the C=O stretching vibrations of a free carboxylate ion and a carboxyl group bonded to a cobalt(III) ion. In other cases where a separation of this magnitude can be anticipated, it would seem reasonable to consider the presence or absence of a band in the 1550 to 1600 cm.$^{-1}$ range as evidence of the state of bonding of a carboxyl group which might otherwise remain in question. The second example given above leads to two limitations which are significant in this respect. The frequency of the complexed carboxyl group will differ from compound to compound even with the same metal ion, and more markedly in going from one metal ion to another. Similarly, variations in the frequency of the carboxylate anion may complicate the matter. In addition, the bands may vary in breadth. In the compound $Na_2[Co(Y)Cl]$, the separation between the shoulder (1600 cm.$^{-1}$) and the band of the complexed carboxyl group (1648 cm.$^{-1}$) is 48 cm.$^{-1}$, an increase of 2 cm.$^{-1}$ over that mentioned for the nitro complex; however, an accompanying increase in breadth is sufficient to merge the two bands into a single band with a shoulder. It might be expected that a decrease in this interval by 10 to 15 cm.$^{-1}$ would cause the complete disappearance of the shoulder, leaving only a single sharp band which might be only very slightly unsymmetrical. From this it is concluded that the resolution of the average infrared spectrophotometer may not be adequate to guarantee that a distinction can be made between a complexed carboxyl group and a free carboxylate ion. Whether or not such a distinction can be made would seem to depend largely on the nature of the central metal ion in the complex, since it has been shown that the C=O frequency of the complexed carboxyl group depends on the metal ion,[4,5,11] while the free carboxylate ion should be relatively independent of the nature of the metal ion.[5] A separate band for free carboxylate ion should therefore appear in the infrared spectrum on any complex of this type having no interfering complexed carboxyl group which absorbs below 1650 cm.$^{-1}$. Since the higher frequencies are expected to occur as the covalent character of the bond between the carboxyl group and the metal ion increases,[4,5,11] this technique should be most useful among complexes of metals having at least as great a tendency to form covalent bonds as has cobalt(III).

Acknowledgment.—The authors are indebted to Mr. O. E. Schupp and Mr. S. Lambert for their assistance in the spectral measurements.

COLUMBUS, OHIO

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[10] J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

[11] D. H. Busch, thesis, University of Illinois, 1954.